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SULFUR OXYGENATION OF RUTHENIUM-DITHIOLATE NITRILE HYDRATASE
MIMIC ENHANCES LIGAND LABILITY AND HYDROLYSIS ACTIVITY

By

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B.S., Universidad Peruana Cayetano Heredia, 2000
M.S., University of Louisville, 2010

A Thesis
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College of Arts and Sciences of the University of Louisville
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Doctor in Philosophy

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University of Louisville
Louisville, Kentucky

May 2012

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A Thesis Approved on

March 27, 2012

By the following Thesis Committee:

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Dr. Robert M. Buchanan

Dr. Mark E. Noble

Dr. Christopher T. Burns

Dr. Moises A Carreon

DEDICATION

This dissertation is dedicated to my parents

Mrs. Beatriz Castillo Rojas

and

Mr. Ernesto Masitas Carmelo

to all my brothers

Flavio, my twin Rafael, Gustavo and Alejandro

and to all my friends and family around the world.

Spiritus ubi vult spirat

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ABSTRACT

SULFUR OXYGENATION OF RUTHENIUM-DITHIOLATE NITRILE HYDRATASE MIMIC ENHANCES LIGAND LABILITY AND HYDROLYSIS ACTIVITY

Mr. César Antonio Masitas Castillo, M.S., University of Louisville.

March 27, 2012

Nitrile hydratase (NHase) is a metalloenzyme that contains a non-heme iron (III) or non-corin cobalt (III) in a non-redox active role. NHase is used as biocatalyst in the industry for the hydrolysis of nitriles to amides. The trivalent metal ions are six-coordinate with the ligand sphere made up of three cysteines, two amide nitrogens, and a water/hydroxide or nitrile substrate. Interestingly, the N_2S_3 active site contains two post-translationally modified cysteine residues, resulting in an unusual thiolato (RS^-), sulfenate ($RS(O)^-$), sulfinato ($RS(O)_2^-$) donor set. Synthetic work to mimic the unusual donor set by direct oxygenation of a metallodithiolate precursor with dioxygen has been reported by our research group. In this research we have investigated the N_2S_3 ligand 4,7-bis-methylmercaptopropyl-1-thia-4,7-diazacyclononane ($bmmp-TASN$)²⁻ to systematically probe the metal's influence on sulfur reactivity. As result of this research the ruthenium complex ($bmmp-TASN$)RuPPh₃ (**1**) reacts with dioxygen to yield ($bmmp-O_2-TASN$)RuPPh₃ (**2**), ($bmmp-O_3-TASN$)RuPPh₃ (**3**) and ($bmmp-O_4-TASN$)RuPPh₃ (**4**). By careful control and optimization of the reaction conditions, high yields and functional synthetic models are obtained. Catalytic activity is reported in **1**, **2** and **3** with 85 ± 11 turnover in 18 hours for the formation of benzamide for compound **3**.

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CHAPTER I

INTRODUCTION

Nitrile hydratase (NHase) is a crucial enzyme of the nitrile metabolism in several microorganisms that catalyzes the hydration of nitriles to their corresponding higher value amides at ambient pressure, temperature and at physiological pH, Figure 1.¹⁻⁵ Microbial NHases have great potential as biocatalysts for organic chemical processing because these enzymes can convert nitriles to amides in a chemo-, regio-, and/or enantioselective manner.⁴ One of the most attractive features of nitrile metabolizing enzymes is their ability to selectively hydrolyze one cyano group of a dinitrile to its corresponding amide, something that is not possible using conventional chemical methods.⁶⁻¹⁰ However, NHase enzymes are under continuous enzymological investigation to magnify its potential for the synthesis of different amides. Several of the disadvantages of NHases involve their limited substrate acceptability, low enantioselectivity and thermostability. As a consequence of these disadvantages, it is required to study and improve the design of better catalysts for the hydrolysis of a wide range of organic nitriles at the industrial and environmental level.¹¹

Figure 1. Nitrile hydratase hydrolysis reaction.

Biological and chemical hydrolysis

Nitrile hydratase has captured substantial interest as a catalyst for commercial bioprocesses in industry. The bioprocess includes a large-scale production of acrylamide,¹² nicotinamide¹³ and 5-cyanovaleramide.¹³ The bio-hydrolysis process has a gain over traditional chemical nitrile hydrolysis routes. The advantages of the bio-process are the synthesis of a metallo-enzyme catalyst through active expression of the NHase. Other advantage is the use of a water matrix using physiological buffer of neutral to slightly basic pH. The most remarkable property is the low or mild temperature < 30°C operation of the catalyst that allow the hydrolysis of acrylonitrile. The hydrolysis process use a narrow range of nitrile substrate that can be applied in the chemo-, stereo-, and region- selective amide synthesis. The process requires a simple organic-phase extraction after a complete and high yield conversion of substrate and not by product formation.

In contrast, the chemical hydrolysis process is performed under acid or base conditions in a water media at 200 - 300 °C. The chemical process requires high pressure but it can be applied to a broad-range of nitriles without chemo-stereo or region-selectivity specificity. The one cost efficient step in the hydrolysis process is the recycling of the metallic copper or copper chromite catalyst, that is only possible in a heterogeneous reaction matrix using a transition metal catalysis. The extraction and purification of the product is performed through organic-phase extraction and multi-step purification of product with the objective to remove trace of sub product such as organic acid and by product like carbon monoxide and HCN with a low yield of amide.¹¹

Biologically speaking, nitriles are starting materials and intermediates in the metabolism of several microorganisms, plants and animals. Hydrolysis of nitrile to

carboxylic acid and amine is an important reaction in organic synthesis and in nature. At industrial level, there are two approaches to face the hydrolysis of nitriles; chemical hydrolysis and enzymatic hydrolysis by nitrile hydratase enzyme. The enzyme was discovered in the bacterium *Arthrobacter* sp. J-1 and studied by Asano *et al.* in the Department of Agricultural Chemistry at University of Kyoto Japan.¹⁴ Further studies in the year 2000 by Kato *et al* identified the *Arthrobacter* sp. J-1 as *Rhodococcus rhodochrous* J1.¹⁵ The early work of Asano *et al* in acrylonitrile conversion to acrylamide had a great impact in academia and industry as an efficient process for the hydrolysis of nitriles. As a result of this work, the industrial and big scale process of hydrolysis conversion moved from a chemical synthesis process to a biochemical enzymatic process.

In the nitrile metabolism pathway, the nitrile compounds follows two different route to produce carboxylic acids.¹⁶ In the first pathway, nitriles undergo a direct transformation to corresponding carboxylic acids and ammonia by the activity of the nitrilase enzyme. In the second pathway, the nitriles are first hydrolyzed by NHase to amide, and later to carboxylic acid and ammonia by the activity of the amidase enzyme, both pathways are illustrated in the Figure 2.

1) Nitrilases

2) Nitrile Hydratases

Figure 2. Nitrile metabolic pathways.

Nitrile hydratase in biological systems

Typically, a nitrile metabolizing microorganism has either a nitrilase or NHase and amidase system for the hydrolysis of nitriles. Nevertheless, some microbes such as *R. rhodochrous* J1, *R. rhodochrous* LL 100-21, *R. rhodochrous* PA-34 and *N. globerula* NHB-2 have both nitrilase and NHase-amidase hydrolysis systems.¹¹ A big number of microorganism, belonging to various species of following diverse genera of Proteobacteria such as *Acidovorax*, *Agrobacterium*, *Bacillus*, *Bradyrhizobium*, *Burkholderia*, *Comamonas*, *Klebsiella*, *Mezorhizobium*, *Moraxella*, *Pantoea*, *Pseudomonas*, *Rhizobium*, *Rhodopseudomonas*, *Serratia*, *Actinobacteria* such as *Amycolaptosis*, *Arthrobacter*, *Brevibacterium*, *Corynebacterium*, *Microbacterium*, *Micrococcus*, *Nocardia*, *Pseudonocardia*, *Rhodococcus* have been described to display NHase activity, and their role in the synthesis of amides or bioremediation of nitriles have been very well documented, showing the maximum hydrolysis activity.¹¹

Evolutionary development studies show that the NHases are entirely bacterial enzymes and have an enormous presence in a large number of the genera of phyla Proteobacteria, *Actionobacteria*, *Cyanobacteria* and *Firmicutes*. Phylogenetic systematic studies provides the molecular evidence of NHase gene in genera such as *Azorhizobium*, *Methyalocella*, *Acidiphilium*, *Rhodomicrobium*, *Roseovarius*, *Roseobacter*, *Rhodobacterales*, *Thalassiobium*, *Octadecabacter*, *Dinoroseobacter*, *Methylobacterium*, *Legionella*, *Variovorax*, *Acinetocacter*, *Bordetella*, *Silicibacter*, *Phaeobacter*, *Ruegeria*, *Oceanibulbus*, *Sinorhizobium*, *Hoeflea*, *Sulfitobacter*, *Oceanicola* and *Labrenzia* of phylum - Proteobacteria; *Mycobacterium*, *Rhodobacteraceae*, *Streptomyces*, *Geodermatophilus* and *Rubrobacter* of phylum - Actinobacteria; and *Acaryochloris* and *Synechococcus* of phylum - Cyanobacteria, nevertheless NHase enzymatic activity is still not stated in them. Remarkably, phylogenetic studies of NHases confirm the absence of molecular proof of NHase gene in yeasts and molds. There is no evidence of NHase activity in plants; nevertheless, phylogenetic studies indicate the molecular proof of the existence of NHase gene in *Ricinus communis*.

The hydrolysis activity of the nitrile hydratase has been attributed to the asymmetric configuration of its active site, Figure 3. As mention before the first industrial scale organic biotransformation was the NHase-mediated hydrolysis of acrylonitrile, which also signifies the first biotechnology application in the petroleum industry.¹⁷ Annual NHase catalyzed acrylamide production has reached 95 Kiloton (25% of worldwide output) and 3500 tons of nicotinamide are produced annually with biocatalysts.¹⁸ At least 10 amides have been produced on batch scales or larger.^{11,19-26} All of these make attractive the study and improvement of this catalyst.

Figure 3. Post-translational NHase active site.

While the NHase biocatalysis has been pioneering the production, its volumes of production fail to meet commercial demands. Also, the biocatalysts process is subject to enzyme inactivation by the substrate or product during turnover. In addition, substantial waste is generated as compared to known chemical methods. Nevertheless NHase continues to attract attention on the industrial scale. Additional uses of the NHase include bioremediation of toxic nitriles^{11,27,28} such as those in pharmaceutical waste-water,²⁹ shale oil,³⁰ and herbicide³¹ and contaminated soil.³²

The related Co-containing thiocyanate hydrolase (SCNase) shares a similar active site NHase.^{33,34} Biologically, SCNase catalyzes thiocyanate degradation to carbonyl sulfides, ammonia and hydroxide ($\text{SCN}^- + 2\text{H}_2\text{O} \rightarrow \text{COS} + \text{NH}_3 + \text{OH}^-$).³³ Thiocyanate is a natural product of cyanide detoxification by the ubiquitous enzyme thiosulfate transferase (rhodanase).³⁵ SCNase is found in CN^- containing waste water sludge from coal gasification factories.³⁴

Nitrile hydratase is present in gram-positive bacteria, which have a strong cell wall. One of the key steps to increase the recovery of the NHase is the fracturing of this cellular wall. Ultra sonication, French press and bead-beater process have been used as

protocols to break the cell wall. These protocols can be used at the same time with hydrolytic enzymes to improve the recovery of NHase. The final purification is carry out in the cell fill extract using ammonium sulfate extraction and column chromatography. The purified NHase extract have molecular mass from 54kDa to 530KDa. The NHase are composed of two different subunits α and β , each of these sub units have a molecular weight between 22 KDa to 29KDa.¹¹

Nitrile hydratase molecular structure

Nitrile hydratase contains a non-heme iron (III) or non-corrin cobalt (III) both of which are non-redox active. In addition to these two metals, a recent publication by Okamoto and Eltis have identified one cobalt, two copper and one zinc per functional NHase enzyme; however the configuration of these metals in the holoenzyme have not yet been determined.³⁶ The optimal conditions for catalysis of the NHase enzyme are physiological pH that can varied between 6.5 to 8.5 and temperature between 20 to 35 °C. In a few NHases maxima activity at 60 °C has been reported. The effect of pH on the enzyme is observed at low pH where the enzyme suffers of denaturalization and subunit dissociation. Another effect of the low pH is the ionization of some relevant residues.³⁷

The NHase families have several amino acid sequences in the α - and β -subunit. However, the structural studies on the NHases enzymes indicate that the region of α -subunit VC(T/S)LCSC(Y/T) is highly conserved. The cobalt-type NHase have threonine (T) and tyrosine (Y) as third and eighth amino acid residues of metal binding first coordination sphere, which are replaced by serine (S) and threonine (T), respectively, in iron-containing NHase.³⁸ The catalytic center of the NHase is buried in the interior of the protein, therefore the substrate and the product have to immerse and ascend from the

hydrolysis pocket. The distance between the metal center in Co-type NHase and the protein surface is 15 Å.³⁹ The transport of the substrate and product is accomplished through an interface channel between the subunits α and β .⁴⁰ It has been postulated that the specificity of the NHase is due to the stereospecificity and substrate affinity profile of the channel.⁴⁰ This statement is in concordance with the limited substrate acceptance and low enantioselectivity of the NHase.

In the active site of the NHase enzyme the trivalent metal ion is six-coordinate in a low-spin coordination environment with the ligand sphere consisting of three cysteines, two amide nitrogens, (N_2S_3 coordination sphere) and a water/hydroxide or NO in the sixth coordination site.^{1,41,42} Some Fe-type NHases show photoreactivity and bind nitric oxide (NO), whereas Co-type NHase not.⁴³⁻⁴⁵

Interestingly, the N_2S_3 active site contains two post-translationally modified cysteine residues. A sulfenate/sulfenic acid ($RSO^-/RSOH$) and a sulfinato (RSO_2^-) donor are found in the positions cis to the suggested substrate binding site, while the trans position contain an unmodified thiolate (RS^-). NHase cultured under anaerobic conditions lacks S-oxygenation and is catalytically inactive until exposed to O_2 , which initiates S-oxygenation and instills activity.⁴⁶ This asymmetric S-oxygenated environment is also observed in thiocyanate hydrolase⁴⁷ (SCNase), a related enzyme with different substrate preferences that could result from changes in charge distribution and/or substrate accessibility.

Mechanism insight based on structural information in the enzyme

The crystal structures of Fe- and Co-NHases have been reported^{48,49} at resolutions of 2.65 Å in the Fe active form, and in the NO-bound inactive state, at 1.7 Å. Using time-

resolved X-ray crystallography with Fe-NHase and t-butylisonitrile as a surrogate substrate, Odaka and co-workers observed analogues of coordinated nitrile substrates and amide product complexes strongly suggesting a nitrile-bound pathway.⁵⁰ An alternate mechanism proposed by Holtz based on through kinetic investigations prefers a conserved serine residue to the sulfenate donor as the proximal base.^{51,52}

Very recent NHase mutants reported by Odaka confirm serine's importance, but call its role as base into question as it is not required for the hydrolysis.⁵³ Further, Odaka prepared inactive mutants with "over-oxygenation" of sulfenate to the less basic sulfinic acid. Deactivation of NHase by oxidants has been noted elsewhere,⁵⁴ but a novel Fe-NHase recently characterized by high-resolution X-ray crystallography displays bis-sulfinate coordination, no activity has been described.⁵⁵ Fewer studies are reported for SCNase, but over-oxygenation also inactivates that enzyme, which is presumed to follow a similar mechanism as NHase.⁵⁶

From the point of view of the catalytic properties, Fe- and Co-NHase are very similar although Fe preferentially hydrates small aliphatic nitriles,⁵⁷ whereas Co exhibits a high affinity for aromatic nitriles^{58,59}. Recent studies indicate that post-translational modification of cysteine-112 and 114 to sulfinic acid and sulfenate derivatives is essential for catalytic activity and the photo-dissociation of NO. The probable functions of the S-oxygenated cysteines include modulation of the Lewis acidity of the metal center,⁶⁰ promotion of NO binding/photo-regulation,^{45,50,61-65} utilization as a proximal base to activate H₂O,^{50,64,65} or modification of substrate/product binding affinity.⁶⁶

Although the catalytic mechanism of hydrolysis remains unclear, there are few mechanisms proposed. Initially, three mechanisms of hydrolysis were suggested:⁴⁸ (I) an

inner mechanism, (II) an outer-sphere mechanism and (III) a second outer-sphere mechanism. Over the last 10 years, there has been continuing interest in unraveling the NHase mechanism from biochemical, bioinorganic, and computational perspectives. Recently, based on analyses of the protein structure of *Pseudonocardia thermophila* JCM 3095 *Pt*NHase, an inner mechanism has been proposed.⁵² This mechanism involves a catalytic chord formed between Trp72, Tyr68, and RSer112, Scheme 1. In this mechanism, Tyr68 is deprotonated at pH 7.6 and forms a hydrogen bond with Trp 72. This interaction stabilizes the charge associated with a deprotonated tyrosine residue and Tyr68 functions as the active site general base. Displacement of the metal-bound water molecule by a nitrile activates the CN bond toward nucleophilic attack and places the water molecule in the proper orientation to facilitate proton transfer from water molecule to the nitrile N atom. The second transfer occurs between the active site water molecule and Try68.⁵² Once proton transfer occurs, the resulting imidate can tautomerize to form an amide with a subsequent proton transfer from RSer116, which functions to shuttle protons from Tyr68. Finally, the amide product is displaced by a water molecule providing the regenerated catalyst. No matter the rationality of the last approach, it lacks a dynamic approach and spectroscopic analysis, for this reason it is necessary to more accurately study this enzyme and its properties from the perspective of bioinorganic modeling.

Scheme 1. Inner mechanism proposed for the *P1*NHase, active site of NHase enzyme with function nucleotide assignment.

The design of nitrile hydratase synthetic models using metals like platinum (II),⁶⁷ ruthenium (II),⁶⁸⁻⁷¹ cobalt (III)⁷² and nickel (0)^{73,74} support that displacement of hydroxide by nitrile and undergoes hydrolysis of the metal bound nitrile by a water molecule. This generates a metal- bound iminol that rearranges to release the amide product. Of all these catalysts, the Co(III) model studied by Mascharak *et al.* is the only one that pursued the biomimetic design of the nitrile hydratase with the use of the compound $[\text{Co}(\text{PyPS})(\text{CN})]^{2-}$, Figure 4, in 5 ml of Tris buffer (10 mM, pH 9.5) and 1.5 mL of acetonitrile at 50 °C with the generation of 0.56 mmol (18 turnovers after 4 hours).

Figure 4. $[\text{Co}(\text{PyPS})(\text{CN})]^{2-}$ NHase synthetic model.

In the outer-sphere hydrolysis mechanism (II), the coordinated hydroxide perform a nucleophilic attack into the nitrile and subsequently the iminolate species generated rearrange to amide keeping the coordination through the oxygen. In the third mechanism or second-outer sphere, the hydroxide coordinated to the metal center extract a proton of a nearby water molecule. The hydroxide performs a nucleophilic attack in the nitrile near to the active site.

Recent studies based on DFT calculations proposed two new mechanisms called first shell and second shell mechanism.^{64,75} The second shell mechanism involves the formation of a metal-bound hydroxide (nucleophile) that attacks the electron deficient carbon of the nitrile. Subsequent rearrangement of the metal-bound iminol intermediate yields an oxygen-bound amide that exchange with water to reset the process. In the first shell mechanism, Scheme 2, the attack of a metal-coordinated nitrile (A) by water activated through interaction with the sulfonate yields a metal-coordinated imidate

intermediate and a metal-coordinated sulfenic acid (B). Deprotonation of the acid by the imidate provides the iminol complex (C), which tautomerizes to the amide product (D)

Scheme 2. NHase proposed mechanism, nitrile bind the metal center and sulfenate acts as near base.

The approach adopted by inorganic groups involves the study of the NHase enzyme based on the design of small molecular complexes. These models reproduce structural, electronic, and functional properties of the enzyme's active site. The systematic modification of the structural frame in these models provides insight regarding complex properties, such as ligand affinity, Lewis acidity, oxidation/reduction properties and spectroscopic characteristics. However, model studies based on the Fe-NHase enzyme are complicated by several factors. First, there are inherent synthetic difficulties associated with iron-thiolate chemistry^{76,77} including undesired metal and ligand-centered reactivity as well as internal redox processes. These challenges commonly results in isolation of iron-oxo clusters and/or ligand disulfide. Nevertheless, iron-thiolates can

react with oxygen in a spin-state dependent process to yield various sulfur-oxygenated derivatives.⁷⁸ As such, the spin-state plays an important role in synthetic design.

Syntheses of NHase mimics compounds

The syntheses and studies of NHase model complexes with N_2S_2 , N_3S_2 , and N_2S_3 donor frameworks have been fruitful to address structural changes and correlate them with the NHases properties. In this research area over the last 10 years the work of the Artaud, Grapperhaus, Kovacs and Mascharak groups are most notable. Nevertheless, the NHase mechanism remains elusive and studies of O_2 reactivity that reproduce the post-translational modifications are limited. While it is well known that O_2 reacts with some metal-thiolates to yield sulfinates (SO_2R)⁷⁹, additional products including sulfonates (SO_3R) or intractable products such as disulfides or oxoclusters are obtained. Additionally, O-atom transfer reagents remain the best candidate to prepare sulfenates ($S(O)R$), however this approach to generate sulfur oxygen derivatives is restricted by the reactivity of the compounds produced and isolation problems. Sulfenate synthesis is limited by the potential for sulfenate disproportionation to sulfinate and thiolate. As such, metal-coordinated sulfenates have been reported in few cases and usually with the use of O-atom reagents. For example *tert*-butyl *N*-sulfonyloxaziridine⁸⁰ was used to isolate mono iron-sulfenate/thiolate models, while H_2O_2 was employed for a mixed sulfenate/sulfinate⁷⁹ nickel complex, a vanadium(V)- η^2, η^2 side-on disulfenate complex,⁸¹ and cobalt η^{2-} sulfenate,⁸² and finally $H_2O_2 \cdot \text{urea}$ ^{83,84} was used for a cobalt disulfenate.

Julie Kovacs' group at the University of Washington focused on imine nitrogen donors (neutral, strong sigma donors) and amide nitrogen donors with thiolates in her NHase models, such as the complex $[Fe^{III}(((\text{tame-N}_2\text{S})S_2\text{Me}_2))]^{2-}$ (Figure 5 compound C).

The anionic bis- carboxamide, tris-thiolate N_2S_3 coordination sphere is potentially similar to the unmodified form of NHase. Studies of complexes such as $[Fe^{III}((tame-N_3)S_2Me_2)]^+$ (A), $[Fe^{III}(Et-N_2S_2Me_2)(py)]^-$ (B), and $[Fe^{III}((tame-N_2S)S_2Me_2)]^{2-}$ (C) reveal how anionic charge build up (from cationic A to anionic B and dianionic C) and Fe spin-state influence apical ligand affinity, Figure 5.

Figure 5. NHase models that modulate charge and affect the affinity of the apical position.

The strong N_2S_2 basal plane ligand field and anionic charge of equatorial carboxamides in the thiolate-ligated complexes results in a weakened apical ligand interaction even with strong donors. The substitution of apical nitrogen by a thiolate pulls the Fe^{3+} from the square planar plane N_2S_2 . This structural rearrangement is associated with the better affinity of the iron for the thiolate. The spin state $S = 3/2$ and its half d_z^2 occupied orbital are considered the cause of the low affinity for apical substrates. This low affinity for substrates diverges from affinity of the sulfur oxygenated NHase active site. The active site has a low-spin configuration, an empty apical site orbital and at the same time higher affinity for apical ligands such NO. The thiolates compounds in Figure

5 have a $S = 3/2$ spin state. They require the pairing of electrons to accomplish a $S = 1/2$ configuration and in this way coordinate a substrate in the apical position. This configuration will generate a barrier for ligand binding formation in these penta-coordinated complexes. These results strongly suggest the need of a post-translational sulfur oxygenation of the square plane NHase cysteinates to coordinate substrates. This oxygenation is essential in order to weaken the equatorial ligand field and increase the Lewis acidity of the d_z^2 orbital pointing toward the vacant apical site. In this way the affinity for substrates is increases and the reactivity of H_2O or nitriles for the hydrolysis mechanism is possible. The series of complexes synthesized by the Kovacs group support the nitrile bound mechanism, The penta-coordinate complexes A, B, and C bind NO , SCN^- and N_3^- at room temperature and $[Fe^{III}(Pr,Pr)S_2^{Me_2}]^+$ (Pr, Pr) and $[Fe^{III}(Et,Pr)S_2^{Me_2}]^+$ (Et,Pr) bind nitriles at low temperature.⁸⁵ Water binding affinity could not be evaluated as the complexes are readily decomposed.

In a recent study, the Kovacs' group supports the proposed role of sulfenate as a proximal base in the nitrile bound mechanism. They trapped and structurally characterized a Co- iminol species similar to the representation in the Scheme 3 and a Co-amidate by using alkoxide and amine donors in place of the difficult to synthesize sulfenate.⁶⁵ In addition, they have also reported one of the only three structurally characterized sulfenate/sulfinate complexes.⁸² Other highlights include Co(III) complexes with relatively fast exchange kinetics due to trans-thiolates and collaborative XAS studies to elucidate the protonation state of the sulfenate donor in NHase.⁸⁶

Scheme 3: Co-nitrile and Co-amide structures isolated in a NHase model by Kovacs.

Pradip Mascarak's group at University of California Santa Cruz has focused on the simultaneous coordination of deprotonated amides and thiolates using ligands N₃S₂ coordination system such as PyPSH₂ in Figure 6. The Fe complexes are low-spin and the +3 oxidation state is stabilized by the strong σ -donating ability and anionic charge. The electronic absorption spectra of these complexes are similar to those of Fe-NHase suggesting the green color of the enzyme arises from a thiolate-to metal charge-transfer band. These Fe(III) complexes are stable in aqueous solution and do not undergo hydrolytic decomposition. The Co(III) derivatives are capable of hydrolyzing nitriles to amides with modest catalytic activity (~17 turnovers, pH 9, 50 °C) in aqueous buffer.⁷² The cobalt derivative of PyPSH readily binds water lowering its pK_a to 8.3. The mono-sulfinate derivative of this complex has a lower pK_a for the bound water of 7.2. These findings led to the hypothesis that the modified thiolates in NHase modulates the pK_a of the bound water in order to facilitate the hydrolysis reaction under physiological conditions.⁸⁷ The proper disposition of donor groups, especially the trans thiolate-S donor, allows for rapid lability of the sixth site in these Co(III) complexes. In addition to water this model PyPsX can bind X= CH₃OH, pyridine, and CN⁻, but show no interaction with nitriles in solution. The work provides support for both the inner-sphere and outer-

sphere mechanisms of hydrolysis involving bound water. More recently, Mascharak has neatly shown that S-oxygenation facilitates photolability in Fe-NO complexes.⁸⁸

The crystal structure of the Fe NHase inactive form at 1.7 Å has an NO as ligand

Figure 6. PyPSH model of NHase that bind H_2O .

substrate. The NO inactivates the catalytic activity of the enzyme. However upon exposure to light the NO is released and the enzyme regains activity. This experiment suggests that the catalytic activity of the NHase is photo-regulated by NO. Masharack *et al.* synthesized a NHase analogue with the NO motif. The complex $[(\text{Cl}_2\text{Ph-PepS})\text{Fe}(\text{NO})(\text{DMAP})]^-$ in Figure 7 has a NO reactivity that shows lability in coordinating solvents such as MeCN, THF or DMF at room temperature and at 40 °C. In non-coordinating solvents the NO complex is stable at room temperature and do not show photolability. The synthesis of sulfur oxygenated derivatives, characterized by FT-IR and EPR spectroscopy suggests the NO release upon photolysis of $[(\text{Cl}_2\text{Ph-PepSO}_4)\text{Fe}(\text{NO})(\text{DMAP})]^-$. This research implies an important role for the sulfur oxygenation in controlling NO photorelease from Fe-NHase.⁸⁸

Figure 7. Thiolate sulfur oxygenation controls nitric oxide photolability.

Research work performed by Isabell Artaud and Jean Claude Chottard at the Université René Descartes (Paris, France) has also focused on deprotonated carboxamides and thiolates. The model complex $[\text{Co}^{\text{III}}(\text{L-N}_2\text{SOSO})(t\text{BuNC})_2]^-$ has a tetradentate diamide-dithiolate in the equatorial plane and non-labile tert-butylnitriles in the axial positions as show in Figure 8. Although the metal center is coordinatively saturated, the complex catalytically hydrolyzes nitriles (50 turnovers, 4° C, pH 4.8). When isotopically labled H_2^{18}O was introduced into the solution,⁸⁹ the labeled oxygen atoms were incorporated into the sulfenate moieties, suggesting the S-oxygenate is the oxygen source for the hydration of nitriles. This study reinforce the recent result of Masafumi Odaka of the Tokio University of Agriculture and Technology that address the sulfenate important role on the catalytic activity of the NHase enzyme.⁵⁶

Figure 8. Synthesis scheme for the complex $[\text{CoIII}(\text{L-N}_2\text{SOSO})(\text{tBuNC})_2]^-$ and $[\text{CoIII}(\text{L-N}_2\text{SO}_2\text{SO}_2)(\text{tBuNC})_2]^-$.

After all these years of NHase research only three NHase models with hydrolytic activity have been reported. Maschack's proposed H_2O -bound mechanism with 17 turnovers,^{60,72} Sherear suggests a nitrile-coordinated intermediate for his Co-metallopeptide mimics N_2S_3 , which include a spectroscopically detected sulfenate/sulfinate donor set using electrospray ionization-mass spectrometry (ESI-MS), gel-permeation chromatography (GPC), Co K-edge X-ray absorption spectroscopy, vibrational, and optical spectroscopies.⁹⁰ Its mixed S-oxygenation allows up to 58 turnovers at $\text{pH} = 8.0$, but like NHase is inactive in the mono- or bis-sulfinate form. Finally, a ligand-centered pathway is proposed by Chottard for his coordinatively saturated bis-sulfenate Co-complex with axial isonitrile donors, which functions best (50 turnovers) under a pH of 4.8.⁹¹ The bis-sulfinate derivative is inactive. Similar complexes are reported by Yano, although hydrolytic was not noted. The related bis-sulfinate of

Artuad is active (14 turnover, pH = 7), but only after substitution of isonitriles with CN^- and H_2O .⁹²

Although several NHase mechanisms including water-bound and outer-sphere pathways have been proposed using a bioinorganic and biochemistry approach, the most supported mechanism involves a nitrile-bound pathway. Attack of a metal-coordinated nitrile (I) by water activates with the sulfenate yields a metal-coordinated imidate intermediate and a metal-coordinated sulfenic acid (II). Deprotonation of the acid by the imidate provides the iminol complex (III) with structural rearrangements ends in an amide product (IV), Scheme 2.

The Grapperhaus' group at University of Louisville has focused on complexes with the ligand **L** (4,7-bis-(2'-methyl-2'-mercaptopropyl)-1-thia-4,7-diazacyclononane, bmmp-TASN) that have a N_2S_3 environment, Figure 9. The bmmp-TASN ligand has a facial N_2S donor with unreactive sulfur donor and reactive cis sulfur site in the active center of the enzyme in addition of the exchangeable 6th coordination position, as observed in the Figure 9.

Figure 9. Comparison of NHase active site and bmmp-TASN model.

The objective of this model is to systematically probe the metal's influence on sulfur reactivity and give insight about the role of the sulfur oxygenated thiolates. Previously, the synthesis of $\text{LFeCl } \mathbf{1'}$ was reported from H_2L , NEt_3 , and $[\text{NBu}_4][\text{FeCl}_4]$ in ethanol.⁹³ The oxygen sensitivity of $\mathbf{1'}$ and a related iron(III) dithiolate complex $\text{LFeCN } \mathbf{2'}$ was reported. Oxygen exposure of the high-spin complex $\mathbf{1'}$ results in disulfide formation and decomplexation of the metal with subsequent iron-oxo cluster formation.⁹⁴ Oxygen exposure of the low-spin complex $\mathbf{2'}$ yields the disulfonate complex $(\text{bmmp-O}_6\text{-TASN})\text{FeCN } \mathbf{4'}$, Figure 10. The corresponding nickel dithiolate, $\text{LNiCN } \mathbf{5'}$, yields the related disulfonate derivative, $(\text{bmmp-O}_6\text{-TASN})\text{NiCN } \mathbf{6'}$ upon addition of H_2O_2 . Further evaluation of $\mathbf{1'}$ and $\mathbf{2'}$ using density functional theory calculations indicate that the low-spin complex $\mathbf{2'}$ contains $\text{Fe-S}_{\text{thiolate}}$ bonds with calculated covalencies of 75% and 86%, while the high-spin complex $\mathbf{1'}$ contains $\text{Fe-S}_{\text{thiolate}}$ bonds with calculated covalencies of 11% and 40%. These results suggest that spin-state and Fe-S bond covalency play major roles in determining the reaction pathway associated with oxygen exposure.⁷⁸ Based on the sulfur-oxygenation low-spin $\mathbf{2'}$ results, we synthesized the low spin Ru derivative $\text{LRuPPh}_3 \mathbf{1}$ to evaluate its oxygen sensitivity and resulting sulfur oxygen derivatives.

high-spin

low-spin

Low spin Ni derivative
(bmmp-O₆-TASN)Ni

Figure 10. Spin state of iron influences Fe-SR reactivity with O₂.

CHAPTER II

EXPERIMENTAL METHODS

Materials

All chemicals were obtained from commercially available sources and were used as received unless otherwise noted. All glassware was flame-dried under vacuum three times prior to use and refilled with argon. All solvents were dried and freshly distilled using conventional techniques under a nitrogen atmosphere before degassing using freeze-pump-thaw techniques or purging with argon for 15 minutes. Standard Schlenk techniques under an argon atmosphere or an argon-filled glovebox were utilized for the manipulation of all compounds in this study. Oxygen addition was accomplished with the use of a 23 ml gas transfer bulb (fabricated by Wilmad-LabGlass) connected to a Schlenk line.

1-Thia-4,7-diazacyclononane (TASN) was prepared according to the method of Hoffmann *et al.*⁹⁵ The ligand H₂(bmmp-TASN) was prepared as previously reported and stored as oil under argon in the glovebox.^{93,96} RuCl₂(PPh₃)₃ was prepared according to literature methods.⁹⁷ Oxygen (99.8%) was obtained from Welder's Supply, Louisville, KY. Reactions were carried out under argon atmosphere at room temperature, unless otherwise specified.

Physical methods

Elemental analyses were obtained from Midwest Microlab (Indianapolis, IN). Infrared spectra were recorded as KBr pellets using a Thermo Nicolet Avatar 360 spectrometer at 4 cm^{-1} resolution. The infrared spectra was analyzed in the OMNIC 6.0a Thermo Nicolet Corporation Copyright 1992-2001 and in the KnowItAll[®] Informatic System 8.2 Copyright 2001-2010. ^1H , ^{13}C and ^{31}P NMR spectra were obtained on a Varian Inova 500 MHz spectrometer and the analysis of the data was performed in MestReNova Version 7.0.2-8636 © 2011 Mestrelab Research S.R.L. NMR measurements were carried out under argon atmosphere in J-Young NMR tubes at 25°C , unless otherwise specified. Electrospray Ionization mass spectrometry (+ESI-MS) was performed by the Laboratory for Biological Mass Spectrometry at Texas A&M University.

Cyclic voltammetry (CV) was performed using a EG&G Princeton Applied Research potentiostat/galvanostat model 273 potentiostat with a three electrode cell (glassy carbon working electrode, platinum wire counter electrode, and Ag pseudo reference electrode) at room temperature in an argon filled glovebox. All potentials were scaled to a ferrocene standard used as internal reference. The cyclic voltammetry and square wave were set up in the Model 270/250 research electrochemistry software 4.40 copyright 1996 EG&G instruments INC. The analysis and plot of electrochemistry data was performed in SigmaPlot for Windows Version 11.0 Copyright© 2008.

Electronic absorption spectra were recorded with an Agilent 8453 diode array spectrometer with an air free 1 cm path length quartz cell or an air free 0.5 cm path length quartz cell with a condenser for temperature dependence experiments in the hydrolysis

assays with ester substrates. Analysis and process of data were performed in UV-Visible ChemStation copyright © Agilent Technologies 95-00.

Crystallographic studies

Crystals were mounted on a glass fiber for collection of x-ray data on a Bruker SMART APEX CCD diffractometer. The SMART⁹⁸ software package (v 5.632) was used to acquire thirty-second frame ω -scan exposures of data at 100K to a 2θ max = 56.22° using monochromated MoK α radiation (0.71073 Å) from a sealed tube and a monocapillary. Frame data were processed using SAINT⁹⁹ (v 6.45) to determine final unit cell parameters. The structure was solved by Patterson methods using SHELXS-90¹⁰⁰ and refined by least squares methods on F^2 using SHELXL-97¹⁰¹ incorporated into the SHELXTL¹⁰² (v 6.14) suite of programs. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed in their geometrically generated positions and refined as a riding model. Crystallographic parameters for **1**, **2** and **3** are published.^{129,141} The **8**, **9**, **10** and **11** crystal structure are presented in this thesis, crystallography parameter are included in the appendix. The crystallographic data was collected and processed by Dr. Mark Mashuta.

Synthesis-Chapter III

(4,7-bis-(2'-methyl-2'-mercaptopropyl)-1-thia-4,7-

diazacyclononane)(triphenylphosphine) ruthenium (II) (bmmp-TASN)RuPPh₃ (1**)**

A suspension of 650 mg (2.51 mmol) of H₂(bmmp-TASN) in dry-degassed 20 mL of THF was cooled to -78°C in a liquid nitrogen - acetone bath and 1.20 mL (12.7 mmol) of *n*-butyl lithium (2M in hexane) was added using a glass syringe (Precaution; *n*-butyl

lithium reacts violently with water). The solution was allowed to slowly warm to room temperature and then transferred via cannula to a Schlenk flask containing 1.50 g (5.72 mmol) of $\text{RuCl}_2(\text{PPh}_3)_3$. The resulting solution was stirred for 12 hours and then refluxed for 15 minutes. An orange solid is observed on the walls of Schlenk flask 30 minutes after the beginning of the reaction. The resulting orange solid was isolated by filtration due to its low solubility in THF and washed with diethyl ether under air free conditions. The orange solid was then washed with 100 ml of H_2O and 3 portions of 20 ml of diethyl ether. This final washing step does not required air – free methods. The complex is stable in the solid state, but readily reacts with dioxygen in solution. Yield: 344 mg (0.503 mmol, 20 %). Electronic absorption (acetonitrile (22 °C)): λ_{max} (ϵ) 438 (883). IR (KBr pellet), cm^{-1} : 2902 (br), 1483 (m), 1457 (m), 1431 (m), 1133 (m), 1085 (m), 1066 (m), 1030 (m), 1014 (m), 751 (s), 701 (m), 696 (m) 592 (m), 516 (m). $E_{1/2} = -851$ mV, (+)ESI-MS, m/z calcd. For $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3$, $[\text{M}^+]$ 684.14 found, 684.11. Anal Calcd for $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3$: C: 56.20%, H: 6.34%, N: 4.10%. found C: 55.13%, H: 6.52%, N:3.92%. ^{31}P NMR 43.37 ppm in CD_3OD referenced to PPh_3 -6.23 ppm at 25°C. X-ray quality crystals of **1** were obtained by slow evaporation of a methanolic solution under air-free conditions.

(bmmp-O₂-TASN)RuPPh₃ (2)

A suspension of **1** (128 mg, 0.18 mmol) was stirred in 50 mL of dry, degassed MeOH in a 250 mL Schlenk flask with a connected gas sample bulb with a volume of 23 mL charged with O_2 (0.94 mmol) at a pressure of 1 atm. The flask containing **1** was evacuated just to the point of solvent boiling at which time the valve to the gas sample bulb was opened introducing the O_2 . The solution was stirred for 5 min after which the

solution was filtered to remove any trace solids followed by evacuation of the solvent. The crude product was dissolved in degassed methanol. Slow evaporation of the solvent under air-free conditions in the glovebox yielded pure **2** as orange crystals. Yield: 93 mg (0.13 mmol, 72%). Electronic absorption (acetonitrile (22 °C)): λ_{max} (ϵ) 338 (1200), 385 (764). IR (KBr pellet), cm^{-1} : 3058 (m), 2981 (br), 2961 (br), 2918 (br), 1948 (br), 1635(m), 1580 (s), 1489 (s), 1477 (s), 1458 (s), 1432 (s), 1139 (s), 1020 (s), 916 (s), 870 (s), 751 (s), 703 (s), 696 (s). $E_{1/2}$ = -393 mV, (+)ESI-MS, m/z calcd for $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3\text{O}_2$, $[\text{M}]^+$ 716.1268 found, 715.6971 Anal. Calcd for $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3\text{O}_2$: C: 53.69%, H: 6.05%, N: 3.91% found C: 52.90%, H: 6.17%, N: 3.99%. ^{31}P NMR 34.34 ppm in CD_3OD referenced to PPh_3 -6.23 ppm at 25°C.

(bmmp-O₃-TASN)RuPPh₃ (3)

To a suspension of 204 mg (0.298 mmol) of **1** in 75 mL dry, degassed MeOH was added 23 ml (0.94) mmol of O_2 . The addition of O_2 was performed under atmospheric pressure. The solution was stirred for 12 hours after which the solvent was removed under vacuum. The yellow crude product was dissolved in degassed water and filtrated. The yellow solution was concentrated and dissolved in methanol. Slow evaporation of the solvent under air-free conditions yielded pure **3** as yellow plates. Yield: 179 mg (0.245 mmol, 82%) Electronic absorption (acetonitrile (22 °C)): λ_{max} (ϵ) 336 (1486). IR (KBr pellet), cm^{-1} : 2925 (br), 1482 (m), 1461 (m), 1432 (m), 1402 (m), 1137 (s), 1086 (s), 1020 (s), 923 (m), 914 (m), 750 (s), 695 (s), 595 (s) 526 (m), 515 (m). $E_{1/2}$ = -263 mV, (+)ESI-MS, m/z calcd for $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3\text{O}_3$, $[\text{M}^+]$ 732.1217 found, 731.1147 Anal Calcd for $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3\text{O}_3$: C: 52.51%, H: 5.92%, N: 3.83% found C: 51.36%, H: 6.06%, N: 3.89%. ^{31}P NMR 33.68 ppm in CD_3OD referenced to PPh_3 -6.23 ppm at 25°C.

Alternative protocol for synthesis of compound 3 starting from compound 2

To a suspension of 200 mg (0.279 mmol) of **2** in 75 mL dry, degassed MeOH was added 23 ml (0.94 mmol) of O₂. The addition of O₂ was performed under atmospheric pressure. The solution was stirred for 12 hours after which the solvent was removed under vacuum. The yellow crude product was dissolved in degassed water and filtrated to obtain purified compound **3**. The yellow solution was concentrated and dissolved in methanol. Slow evaporation of the solvent under air-free conditions yielded pure **3** as yellow plates, the product was characterized by electrochemistry with an E_{1/2} = -263 mV [M+H]⁺ 733.12 found, 733.13. Yield: 120 mg (0.164 mmol).

(bmmp-O₄-TASN)RuPPh₃ (4**)**

A suspension of 50 mg (0.066 mmol) of **1** in 50 mL of dry, degassed MeOH was gently purged with O₂ for 2 h. The system was closed under an O₂ atmosphere and stirred for 120 h after which the solvent was removed under vacuum. The crude product was dissolved in water and filtered to remove insoluble products. Evaporation of the filtrate yields **4**. Yield: 15 mg (0.020 mmol, 30%). Electronic absorption IR (KBr pellet), cm⁻¹: 2970 (br), 2918 (br), 1948 (br), 1668 (s), 1580 (s), 1462 (s), 1437 (s), 1136(s), 1120 (s), 1029 (s), 1015 (s), 921 (s), 874 (s), 754 (s), 721 (s), 697 (s). (+)ESI-MS, *m/z* calcd for C₃₂H₄₃N₂PRuS₃O₄, [M]⁺ 748.12 found, 748.12. Three attempts to obtain elemental analyses consistent with the ESI-MS were unsuccessful. This is ascribed to the partial degradation of **4** in water during isolation. The “best” analysis assumed Anal. Calcd For C₃₂H₄₃N₂PRuS₃O₄·0.5PPh₃: C: 56.02%, H: 5.79%, N: 3.19% found C: 52.41%, H: 6.10%, N: 3.09%.

(bmmp-TASN)RuPPh₃ + excess O₂

A suspension of 296 mg (0.433 mmol) of **1** in dry degassed 150 ml of MeOH was purged with O₂ for 15 minutes and then stirred under an O₂ atmosphere saturation for 96 hours. The solution was solvent removed under vacuum yielding a brown, intractable solid. IR (KBr pellet) cm⁻¹: 2920 (br), 1440 (m), 1431 (m), 1267 (s), 1123 (s), 1091 (s), 1017 (s), 924 (s), 869 (s), 799 (s), 747 (s), 699 (s), 593 (s) 523 (m).

Isotopic Labeling Studies (bmmp-¹⁸O₂-TASN)RuPPh₃ (5**)**

The ¹⁸O isotopically labeled derivative of **2** was obtained via direct oxygenation of **1** with ¹⁸O₂. A suspension of **1** (128 mg, 0.187 mmol) was stirred in 50 mL of dry, degassed MeOH in a 250 mL Schlenk flask with a connected gas sample bulb with a volume of 23 mL charged with O₂ (0.94 mmol) at a pressure of 1 atm. The flask containing **1** was evacuated just to the point of solvent boiling at which time the valve to the gas sample bulb was opened introducing the O₂. The solution was stirred for 5 min after which the solution was filtered to remove any trace solids followed by evacuation of the solvent. The crude product was dissolved in degassed methanol. Slow evaporation of the solvent under air-free conditions in the glovebox yielded pure **5** as orange crystals. Yield: 93 mg (0.13 mmol, 72%). (+)ESI-MS, *m/z* calcd for C₃₂H₄₃N₂PRuS₃¹⁸O₂, [M]⁺ 719.93 found, 720.13. IR (KBr pellet) cm⁻¹: 2962 (br) 2921 (br), 1435 (s), 1104 (s), 1082 (s), 751 (s), 696 (s), 530 (s).

(bmmp-¹⁸O₃-TASN)RuPPh₃ (6**)**

The ¹⁸O isotopically labeled derivative of **3** was obtained via direct oxygenation of **1** with ¹⁸O₂. To a suspension of **1** (20.0 mg, 0.03 mmol) in dry degassed MeOH (10 mL) was added 0.14 mmol of ¹⁸O₂. The reaction was stirred for 12 hours at room

temperature after which the solvent was removed under vacuum. The crude product was dissolved in methanol. Slow evaporation of the solvent under air-free conditions yielded isotopically labeled **6**. Yield: 18 mg (0.03 mmol, 82 %). IR (KBr pellet), cm^{-1} : 2925(br), 1683 (m), 1462 (m), 1437 (m), 1402 (m), 1119 (s), 1092 (s), 1020 (s), 998(s), 980(m) 900 (s), 877 (m), 751 (s), 696 (s), 589 (s) 526 (m), 517 (m). +ESI-MS, m/z calcd for $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3^{18}\text{O}_3$, $[\text{M}^+]$ 731.93 found, 737.12. IR (KBr pellet) 2925(br), 1683 (m), 1462 (m), 1437 (m), 1402 (m), 1119 (s), 1092 (s), 1020 (s), 998(s), 980(m) 900 (s), 877 (m), 751 (s), 696 (s), 589 (s) 526 (m), 517 (m).

Synthesis-Chapter IV

(bmmp-TASN)Ru(PMePh₂) (**7**)

A solution of **1** (21.5 mg, 0.0314 mmol) was stirred in 22 mL of dry, degassed chlorobenzene in a 250 mL Schlenk flask. 29 μl (31.20 mg 0.16 mmol) of methyldiphenylphosphine was transfer to the solution in the glovebox using a Eppendorf Research[®] adjustable volume pipette of 1000 μl . The flask containing **1** and methyldiphenylphosphine was heated at 100 °C for 36 hours using and oil bath. The solution was concentrated under air free conditions at room temperature using the Schlenk line. The yellow solid was transfer to the glovebox inside the Schlenk flask. Yield 3.5 mg (0.0056 mol, 20%) ³¹P NMR 34.64 ppm in CD₃OD referenced to PPh₃ - 6.23 ppm at 25°C.

(bmmp-O₂-TASN)Ru(PMePh₂) (**8**)

A solution of **2** (11 mg, 0.015 mmol) was stirred in 5 mL of dry, degassed MeOH in a 50 mL Schlenk flask. 20.2 mg (0.10 mmol) of methyldiphenylphosphine was added

to the solution inside the glovebox. The flask containing the solution was heated at 62 °C for 36 hours. The solvent was evacuated under air free conditions at room temperature and the crude was dissolved in degassed MeOH under air-free condition for crystallization using solvent evaporation technique in a test tube inside the glovebox. After two days the solution was filtered using a cotton pipette setup and crystals were collected from the walls of the tube at the fifth day from the setup of the crystallization. Yield: 9.0 mg (0.013 mmol, 92%). (+)ESI-MS, m/z calcd for $C_{27}H_{41}N_2O_2PRuS_3$, $[M+Na]^+$ 676.1009 found, 677.1144 ^{31}P NMR 25.49 ppm in CD_3OD referenced to PPh_3 - 6.23 ppm at 25°C. X-ray quality crystals of **8** were obtained by slow evaporation of a methanolic solution under air-free conditions.

(bmmp-O₃-TASN)Ru(PMePh₂) (9)

A solution of **3** (12 mg, 0.016 mmol) was stirred in 5 mL of dry, degassed MeOH in a 50 mL Schlenk flask. 15.0 mg (0.075 mmol) of methyldiphenylphosphine was added to the solution inside the glovebox. The flask containing the solution was heated at 62 °C for 36 hours. The solvent was evacuated under air free conditions at room temperature and the crude was dissolved in degassed MeOH under air-free condition for crystallization using solvent evaporation technique. After two days the solution was filtered using a cotton pipette setup and crystals were collected from the walls of the tube at the fifth day from the setup of the crystallization. Yield: 10 mg (0.015 mmol, 94%). (+)ESI-MS, m/z calcd for $C_{27}H_{41}N_2O_3PRuS_3$, $[M+Na]^+$ 693.0958 found, 693.1192 ^{31}P NMR 22.54 ppm in CD_3OD referenced to PPh_3 -6.23 ppm at 25°C. X-ray quality crystals of **9** were obtained by slow evaporation of a methanolic solution under air-free conditions.

[(bmmp-TASN)Ru]₂ (10)

A suspension of 650 mg (2.51 mmol) of H₂(bmmp-TASN) in dry-degassed 20 mL of THF was cooled to -78 °C in an acetone bath and 1.20 mL (12.7 mmol) of *n*-butyl lithium (2M in hexane) was added using a glass syringe (Precaution; *n*-butyl lithium reacts violently with water). The solution was allowed to slowly warm to room temperature and transfer via cannula to a Schlenk flask containing 1.50 g (5.72 mmol) of RuCl₂(PPh₃)₃. The resulting solution was stirred for 12 hours and then refluxed for 15 minutes. Orange solid is observed in the wall of Schlenk flask 30 minutes after the beginning of the reaction. The resulting orange solid was isolated by filtration due to its low solubility in THF and washed with diethyl ether under air free conditions. The orange solid was then washed with 100 ml of H₂O and 3 portions of 20 ml of diethyl ether. The solid was dissolved in methanol for crystallization by ether diffusion. After one month, the crystals of the bimetallic compound were recovered from the walls of the air free reaction tube. Three attempts to reproduce the bimetallic product were unsuccessful. X-ray quality crystals of **10** were obtained by solvent diffusion methanol-ether under air-free conditions. In each attempt **1** was isolated as a metal powder containing product.

(bmmp-TASN)RuCO (11)

A suspension of **1** (50 mg, 0.073 mmol) was stirred in 25 mL of dry, degassed MeOH in a 50 mL Schlenk flask. The flask was connected to a CO gas line, the sample was bubbled for 20 minutes and the solution was stirred for 20 hours at 70 °C followed by evacuation of the solvent. The yellow crude product was dissolved in methanol. Slow evaporation of the solvent under air-free conditions yielded pure **9** as yellow crystals.

Yield: 25 mg (0.055 mmol, 75%). Electronic absorption (methanol (22 °C)): λ_{max} (ϵ) 331 (956). IR (KBr pellet), cm^{-1} : 2887 (br), 1889(s), 1358(s), 1084(s), 1049(s), 880 (s), (+)ESI-MS, m/z calcd. For $\text{C}_{15}\text{H}_{28}\text{ON}_2\text{RuS}_3$ [M^+] 450 found, 453 and Anal Calcd for $\text{C}_{32}\text{H}_{43}\text{N}_2\text{PRuS}_3$: C: 40.07%, H: 6.28%, N: 6.23%. found C:39.79%, H:6.13%, N:5.98%. X-ray quality crystals of **11** were obtained by slow evaporation of a methanolic solution under air-free conditions in the glovebox.

Computational methodology

Geometry optimization and subsequent molecular orbital (MO) analysis of complexes **1-4** were performed using the Gaussian 03 suite of programs. Density functional theory (DFT) calculations employed the BP86^{66,86} and B3LYP^{64,75,103,104} functionals based on its fruitful estimation of geometries for numerous transition metal complexes. For these calculations, the LANL2DZ basis set was used for the Ru atom while the 6-31G(d) basis set was applied for all other atoms. Input coordinates for compounds **1-4** were taken from the crystallographic coordinates of **3** with the addition or abstraction of oxygen atoms as needed to complete the family of derivatives. Optimized coordinates are listed in Tables A1-A4 of the Appendix. Similar results were obtained with the BP86 and B3LYP functionals. The former provided a slightly better correlation with experimental bond distances and angles and was used for analyses of the frontier orbitals. Molecular orbitals were visualized from cube files using ChemBio3D Ultra 12.0 and the VMD software package.¹⁰⁵

Hydrolysis of acetonitrile

Attempts to hydrolyze acetonitrile with **3** were performed following the protocol described by Chottard *et al.*⁸⁹ A mixture of **3** (5 mg, 0.007 mmol) and 1,4-

dimethoxybenzene (7 mg, 0.050 mmol) in CH₃CN (0.5 mL) and a HOAc/NaOAc buffer (1 M, pH = 4.8, 0.5 mL) was stirred at room temperature for 5 days under an argon atmosphere. The solvent was removed under reduced pressure to yield a yellow residue that was extracted with chloroform. The organic extract was dried under reduced pressure and the solid residue dissolved in CD₃OD. Analysis by ¹H and ¹³C NMR failed to yield the expected resonances for acetamide in a trail at 4 °C. Attempts at 4 °C with **1** and **2** also show no evidence of nitrile hydrolysis.

Solutions of **1**, **2** and **3** in 1:1:1 mixture of acetonitrile, methanol, and PIPES buffer (pH = 7.0) were tested for 5 days at 25 °C. The mixture was composed of **1** (5mg, 7μmol) in CH₃CN (0.5 ml), methanol (0.5 ml) and PIPES (1 M, pH = 7.0, 0.5 ml). The identity of the acetamide was confirmed by ¹H NMR and ¹³C NMR and It was quantified using 1,4-dimethoxybenzene (7 mg, 0.050 mmol) as an internal standard.

Acetonitrile experiment using compounds **1**, **2** and **3** were performed in a NMR J-young tube in a mixture of 500 μl of MeOH deuterated and 200 μl D₂O. For compound **3**, It was used 2.2 mg (3.0 μmol) of compound and 2.2 mg (6.7 μmol) of (C₄H₉)₄N⁺BF₄⁻ as reference. It was used 5 μL (94.6 μmol) of acetonitrile as substrate. The mixture MeoH and D₂O was used to help to solubilize the compound **3**. The reference (C₄H₉)₄N⁺BF₄⁻ was integrated in the region 0.94 ppm to 1.01 for the equivalent of 3 protons. The experiment was performed for 11 day in an oil bath. The sample was only removed from the bath for ¹H NMR determinations of 20 minutes. The ¹H NMR was performed with a relax delay 1.0 sec, 256 repetitions with a total time of 15 minutes, at 25 °C in a 400 MHz instrument. Similar experiments were performed in compound **1** and **2**.

Hydrolysis of 4-nitrophenyl acetate

A mixture of **1** (5 mg, 7 μ mol) and 4-nitrophenyl acetate (16 mg, 0.088 mmol) in MeOH/H₂O (8.2 mL/8.2 mL) and citrate buffer (1 M, pH=4.8, 1.8 mL) was stirred at room temperature or 4 °C for 5 days. The reaction was monitored by UV-visible spectroscopy, and results were compared to a control sample with no added metal complex. The same method was applied to solutions containing **2** and **3**. Hydrolysis of CH₃CN: A mixture of **1** (5 mg, 7 μ mol) and 1,4-dimethoxybenzene (7 mg, 0.050 mmol) in CH₃CN (0.5 mL) and an HOAc/NaOAc (1 M, pH = 4.8, 0.5 mL) or PIPES (1 M, pH = 7.0, 0.5 mL) buffer was stirred at room temperature and at 4 °C for 5 days. After chloroform extraction, the organic soluble residue was dissolved in CD₃OD for ¹H and ¹³C NMR analysis. The same procedure was applied to **2** and **3**.

Hydrolysis of acrylonitrile

200 μ l (11.11 mmol) of water deuterated was added to a solution of acrylonitrile 5 μ l, (0.08 mmol), 2.2 mg (3.01×10^{-3} mmol) of **3**, 3.7 mg (0.01 mmol) of (C₄H₉)₄N⁺BF₄⁻ and 500 μ l of CD₃OD using a Eppendorf Research[®], adjustable-volume pipette of 1000 μ l in a NMR J-young tube in the glovebox. The solution was heated to 70 °C for 20 days. The ¹H NMR resonances (D₂O) of the solution before heating were at δ 6.29 (dd, J = 18.0 Hz, 2H, $H_2=CHCN$) and 5.82 (q, J = 12.0 Hz, 1H, $H_2C=CHCN$). During heating, these resonances decreased and the resonances for acrylamide appeared: δ 6.24 (t, J = 1.5 Hz, 1H, $H_2C=CHCONH_2$) and 5.83 (t, J = 3.0 Hz, 2H, $H_2C=CHCONH_2$).

Hydrolysis of benzonitrile

1500 μ l (83.30 mmol) of water deuterated was added to a solution of benzonitrile 500 μ l, (4.85 mmol) and 500 μ l of stock solution of 5.4×10^{-4} M (2.70×10^{-7} mmol) of

complex **1-3** using a micropipette into an air free reaction tube in the glovebox. The solution turned yellow in the aqueous phase. The benzonitrile formed a clear layer on the top of the solution due to its poor solubility in the aqueous layer. The sample was heated at 124 °C in an oil bath for 18 hours in an oil bath. A white precipitate formed when the solution is cooled down to room temperature after the trial is completed. The solvent was removed under reduced pressure to yield a yellow residue that was extracted with ether. The organic extract was passed through a silica gel column. Analysis by ^1H and ^{13}C NMR yield the expected resonances for benzamide. These results were complemented and verified with FT-IR analysis. Yield: 85 ± 11 turnovers based in mols of catalyst. IR (KBr pellet), cm^{-1} : 3390 (s) 2930 (br) 1670 (s) 1580 (s) 1470 (br) 1415 (br) 1120 (s). Additional hydrolysis studies with complexes **1** and **2** were conducted according to the protocol listed above. The reaction yields 65 ± 1 turnovers for compound **1** and 86 ± 9 turnovers for compound **2**. The analysis of the blank following the same conditions with exception of the catalyst gave 7 ± 2 turnovers.

CHAPTER III

CONTROLLED SULFUR-OXYGENATION OF A RUTHENIUM(II)- DITHIOLATE

Background

The hydrolytic metalloenzymes nitrile hydratase (NHase) and thiocyanate hydrolase (SCNase) share an infrequent post-translational modification.^{42,45-47,56,106} Metal-coordinated thiolates in these enzymes react with dioxygen to yield sulfur-oxygenated derivatives as a requirement for catalytic activity. The active site of NHase contains a low-spin Fe(III) or Co(III) in an N_2S_3 donor set composed of two carboxamido nitrogen donors and three cysteine derived sulfurs, Figure 11.

Figure 11. Active site of NO-inactivated Fe-containing NHase.

The active sites of nitrile hydratase (NHase)^{106,107} and thiocyanate hydrolase (SCNase)⁴⁷ share common asymmetric thiolate (RS⁻), sulfenate (RSO⁻)/sulfinate (RSO₂⁻) donor set that results from the post-translational modification of two cysteines via sulfur oxygenation of metal-coordinated cysteine under aerobic conditions. The synthesis and studies of small-molecule provide numerous examples of metal sulfinates prepared upon O₂ oxidation, but metal sulfenates are rare because they tend to oxidize further to sulfinates or sulfonates (RSO₃⁻) or disproportionate into disulfides. Consequently, only three mixed sulfenate/sulfinate complexes have been structurally reported.^{79,82,108} Of these, the only one isolated from aerobic oxidation is a sulfenic acid (RSOH)/sulfinate derivative of [Ru(DPPBT)₃]⁻ (DPPBT=2diphenylphosphinobenzenethiolate) for which no yield is reported.¹⁰⁸ A more biologically relevant (N₃S₂)Co, Figure 12, example reported by Kovacs *et al.* is readily isolated by H₂O₂ oxidation of the sulfinate precursor due to η^2 -coordination of the sulfenate, which prevents further reactivity but does not mimic coordination of the active sites.⁸²

Figure 12. Representation of [Co(III)((η^2 -SO)(SO₂)N₃(Pr,Pr))]⁺.

In the apo- and native SCNase enzyme, the structure of the side chains as well as the main chain in the first coordination sphere are well preserved with those in Co and Fe types NHase.⁴⁷ Like NHase two of the three cysteine thiolates of the SCNase have been post-translationally oxygenated resulting in the thiolate (RS⁻), sulfenate (RSO⁻), sulfinato (RSO₂⁻) donor combination.^{42,47,106} A number of small molecule active site mimics have been prepared to help delineate these proposed roles and the sulfur-oxygenation pathway.^{3,78,80,82,87-89,93,96,109-112}

The oxygen reactivity of thiolates has been explored in the last 30 years due to its implications in degradation of enzymatic and catalytic sites, disulfide formation, demetallation and oxo-cluster formation. In this area, it has been reported oxygen uptake by metal-sulfur complexes. This modification results in a positive shift in the redox potential and structural rearrangement such as the metal bond distances in the complexes. Initial studies for sulfenate complex synthesis were performed using Co(III) complex by Deutsch *et al.*¹¹³ These studies of thiolate reactivity were following up with H₂O₂ kinetic studies for the oxidation of the thiolate to sulfenate and the subsequent oxidation to sulfinato.¹¹⁴ In addition, it has been performed studies of the reactivity of sulfur bonded Co(III) complexes.¹¹⁵

Studies by Schrauzer, Maroney and Darensbourg were focus in the synthesis and characterization of nickel dithiolate complexes. The Darensbourg group focused in the complex [1,5-bis(2-mercaptoethyl)-1,5-diazacyclooctanato]nickel(II) dithiolate complex and its sterically hindered derivatives. A family of oxygen derivatives were generated upon reaction with ³Σ O₂, ¹Δ O₂, or H₂O₂ with a yield that range from 18 % to 85 % as we can observe in the Figure 13.^{116,117}

Figure 13. Synthesis and characterization of nickel sulfur oxygen derivatives.

The typical approach to prepare sulfur-oxygenated mimics of NHase or SCNase involves the reaction of metal-thiolate precursors with O-atom transfer agents such as H_2O_2 , *N*-sulfonyloxaziridine, (1*S*)-(+)-(10-camphorsulfonyl)oxaziridine, or urea hydrogen peroxide.^{80,82,88,89,112,118} These efforts have been successful for the isolation of

sulfenate,^{80,89,112,118} sulfinate,^{88,89} and a mixed sulfenate/sulfinate complex with η^2 -sulfenate coordination.⁸² A major advantage of O-atom transfer agents is the ability to quantitatively add oxidizing equivalents at controlled rates. Less well developed are reactions employing dioxygen, which is the proposed reagent in the enzymatic systems.^{42,46,56} While several sulfinate complexes have been reported upon O₂ exposure of thiolate precursors,^{82,116,119-127} isolation of sulfenate^{120,128} or mixed sulfenate/sulfinate complexes from O₂ are rare due to the reactivity of the sulfenate.^{79,108,129}

As noted in chapter 1, the Grapperhaus laboratory has focused on NHase model complexes based on the penta coordinate N₂S₃ chelate 4,7-bis-(2'-methyl-2'-mercaptopropyl)-1-thia-4,7-diazacyclononane (bmmp-TASN).^{78,93,96,109} With this ligand, a series of iron complexes was synthesized and their oxygen sensitivity was investigated.⁹³ Oxygen exposure of the high-spin complex (bmmp-TASN)FeCl yields ligand disulfide with decomplexation of the metal and subsequent iron-oxo cluster formation.⁹⁴ In contrast, O₂ addition to the low-spin complex (bmmp-TASN)FeCN generates the bis-sulfonate (2RSO³⁻) complex (bmmp-O₆-TASN)FeCN.⁷⁸ While the low-spin complex promoted sulfur oxygenation, the reaction proceeded beyond the oxygenation level (sulfenate/sulfinate) observed in NHase and SCNase. As proof of concept the low-spin ruthenium(II) complex (bmmp-TASN)RuPPh₃ (**1**) was synthesized and its O₂ reactivity under limited O₂ conditions explored to yield a family of ruthenium sulfur oxygen derivatives as it is observed in Scheme 4.

Scheme 4. Oxygenation pathway of **1**.

Synthesis and characterization of **1**

Complex **1** is isolated from the metal precursor $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{H}_2(\text{bmmp-TASN})$ upon deprotonation of the ligand with *n*-butyl lithium in tetrahydrofuran as an air- and water-stable orange solid. The complex contains a Ru(II) ion with a dithiolate pentacoordinate ligand in an octahedral configuration. The reaction is performed overnight but the formation of the product begins after 20 minutes. The protocol of isolation involves the air free filtration of the product and washing the product with ether to remove unreactive material. Further work up involves water washing under aerobic condition to remove phosphine oxide. In an O_2 -saturated methanol solution, **1** reacts over 96 hours to yield an intractable brown product with an FT-IR spectrum (Figure A1 in the Supporting Information) reminiscent of our previously reported iron disulfonate derivative.⁷⁸

Initial studies of sulfur oxygenation in compound **1** with oxygen transfer reagent such as H_2O_2 and thiourea peroxide generate a mixture of sulfur oxygen derivatives. The sulfur oxygenated derivatives are not isolable by column chromatography or thin layer chromatography (TLC) preparative. All the products of oxygenation are air sensitive in solution. Repeated attempts to isolate analytically pure samples from this product mixture were unsuccessful. The formation of a family of sulfur oxygen derivatives can be avoided by limiting the quantity of O_2 and the reaction time as it is observed in Scheme 5.

Scheme 5. Synthesis and reactivity of **1**.

Oxygenation studies followed by TLC

Oxygenation studies of the complex **1** were monitored by TLC. These studies were achieved with the isolation of complexes and subsequent TLC studies under air free conditions in the glovebox. Methanol solution saturated with potassium chloride allows

the separation between the **1-4** complexes. The initial reactivity studies were performed with FT-IR and TLC in parallel to determinate the time frame of the reaction. The formation of the intense bands at 1139 and 1020 cm^{-1} attributed to the asymmetric and symmetric S=O stretches of the sulfinato donor after 5 minutes of the reaction set up the first reaction time of this study. Monitoring the reaction by silica gel thin layer chromatography (TLC) revealed additional products. As outlined in Scheme 4, the oxygenation of **1** proceeds in a series of steps with distinct time frames. Immediately following O_2 exposure, the thiolate/sulfinato complex (bmmp- O_2 -TASN)RuPPh₃ **2** is observed, $R_f = 0.56$, along with the thiolate precursor **1**, $R_f = 0.68$. After 5 minutes, **2** is the sole product and only traces of **1** are detected. Reaction times longer than 5 minutes yield a mixture of **2** and **3** ($R_f = 0.45$) yielding pure **3** after ~15 minutes. From these results it can be inferred that **2** is a precursor to **3**. This is confirmed by the direct conversion of isolated **2** to **3** upon O_2 addition. Longer reaction times, 120 hours, under limiting O_2 conditions yield the disulfinato complex (bmmp- O_4 -TASN)RuPPh₃ (**4**), $R_f = 0.2$. Complex **4** can also be generated from isolated **3** or from **1** with excess O_2 . In the presence of water, **4** degrades to “intractable product” initially obtained in open-air oxygenation studies.¹²⁹

Limiting oxygen conditions

In the O_2 limited reactions, 5 equivalents of O_2 were added to a solution of **1** under an argon atmosphere. The solution was stirred for 5 minutes until the solution change from orange to claret and no solid is present in the solution. After that, the solution was filtered using a fritted filter flask under air-free conditions to remove any trace of unreactive staring material followed by evacuation of the solvent. The claret

crude product was dissolved in degassed methanol and purified using crystallization by solvent evaporation, which yielded yellow-orange crystals of the mono sulfinic acid derivative **2** in 72% yield after 72 hours. Further exposure of compound **1** to O₂ gives mixture products of compound **2** and **3**. The formation of a sulfinic acid motif in compound **1** changes its solubility properties. Compound **2** is partially soluble in water and as a consequence of this solubility compound **2** reacts with O₂ in aqueous solution and requires air-free conditions for its manipulation. The mechanism of oxygenation of the thiolate species is unknown. Mechanistic studies have been performed by Davinder Kumar, a current student in the Grapperhaus Group.

In the O₂ limited reactions, 5 equivalents of O₂ were added to a solution of **1** under an argon atmosphere. After 12 hours, the solution changed color from orange to claret and finally yellow. The solvent was removed under vacuum, and the yellow solid residue was dissolved in degassed methanol, which yielded crystals of the sulfinate/sulfinic acid derivative **3** in 82% yield upon slow evaporation under air-free conditions. The formation of a sulfinate motif in the compound **3** increases its solubility in water, a property that is used as a protocol of purification. Additional air or O₂ exposure results in complex degradation. While limiting the quantity of O-atom-transfer reagents is a common tactic in attempts to obtain partially sulfur-oxygenated derivatives of metal thiolates.⁷⁹ Intentionally limiting the O₂ supply for their controlled oxygenation has not been exploited.

The importance of limiting O₂/metal thiolate interactions to achieve partial oxygenation was suggested by the results with [Ru(DPPBT)₃]⁻. When suspensions of [Ru(DPPBT)₃]⁻ as the poorly soluble HNEt₃⁺ salt were exposed to air, the mixed sulfenic

acid/sulfinate product was obtained.¹⁰⁸ However, homogeneous solutions of the complex as the PPN⁺ (Bis(triphenylphosphine)iminium) salt reproducibly yield the disulfinate derivative.¹³⁰ As an additional example, the product distribution of singlet oxygen addition to an (N₂S₂)Ni complex shifts toward the sulfenate/sulfinate derivative as the complex concentration increases and the relative O₂ concentration decreases.¹³¹

To extend the family of oxygen derivatives, compound **1** was exposed to a gentle purge with O₂ for 2 hours and stirred for 120 hours. The product of the synthesis is air and moisture sensitive. During the reaction the compound change of color form orange to claret and to yellow in 72 hours. The yellow residue is compound **4**, and turns green when exposed to air and water.

FT-IR and isotopic labeling studies employing ¹⁶O₂ and ¹⁸O₂ confirm O₂ as the O-atom source in the conversion of **1** to **2** and **3**. In the Figure 14, the FT-IR of compound **1** displays a finger print of the compound between 500 and 1500 wavenumbers (cm⁻¹), C-H alkyl stretches between 2800 and 3000 wavenumbers (cm⁻¹) and C-H aromatic stretches above 3000 wavenumbers (cm⁻¹).

Figure 14. FT-IR of compound **1**.

In FT-IR of compound **2** displays sulfinate stretches as strong bands at 1139 and 1020 cm^{-1} attributed to asymmetric and symmetric S=O stretches, Figure 15. Synthesis of **2** employing $^{18}\text{O}_2$ as oxygen source shifts these bands to 1104 and 990 cm^{-1} , Figure 16. These shift of 35 and 30 cm^{-1} to 1104 and 990 cm^{-1} , respectively, for samples of **2** prepared with $^{18}\text{O}_2$ are based on a simple harmonic oscillator approximation. The isotopic shifts are consistent with those observed for ^{34}S -labeled NHase¹³² and other ^{18}O -labeled metal sulfinates.^{116,133}

Figure 15. FT-IR of compound **2** with $^{16}\text{O}_2$.

Figure 16. FT-IR of compound **2** with $^{18}\text{O}_2$.

In the Figure 17, the FT-IR of compound **3** displays a finger print of the compound between 500 and 1500 wavenumbers (cm^{-1}), C-H alkyl stretches between

2800 and 3000 wavenumbers (cm^{-1}) and C-H aromatic stretches above 3000 wavenumbers (cm^{-1}).

Figure 17. FT-IR of compound **3** with $^{16}\text{O}_2$.

The difference IR spectrum of **1** and **3** prepared with $^{16}\text{O}_2$ in Figure 18a displays intense bands at 1140 and 1020 cm^{-1} attributed to the asymmetric and symmetric S=O stretches of the sulfinate donor. These bands shift by 45 and 38 cm^{-1} to 1095 and 982 cm^{-1} , respectively, for samples of **3** prepared with $^{18}\text{O}_2$ in Figure 18b. The isotopic shifts are larger than those observed for ^{34}S -labeled NHase¹³² but consistent with a simple harmonic oscillator approximation and other ^{18}O -labeled metal sulfinates.^{116,133}

Figure 18. FT-IR difference spectra highlighting the $^{18}\text{O}_2$ -sensitive sulfinate stretching frequencies of (a) **1** and **3** prepared under $^{16}\text{O}_2$ (black line) and (b) **3** prepared under $^{16}\text{O}_2$ and $^{18}\text{O}_2$ (red line).

The FT-IR in the Figure 18 shows in the spectrum A, the two stretches for the symmetric and asymmetric frequencies of the SO of the sulfinate when the compound **3** is synthesized from $^{16}\text{O}_2$. This spectrum is the result of the subtraction of spectrum (compound **3** - compound **1**), to emphasize the sulfinate stretches.

In the FT-IR characterization of compound **4**, Figure 19, reveals four strong bands at 1136, 1120, 1029 and 1015 cm^{-1} attributed to the asymmetric and symmetric S=O stretches associated with two sulfinate stretches. The energies of sulfinate stretches are similar to those reported by Darensbourg in their complete series of nickel sulfur oxygenates.⁷⁹ Oxygen labeling studies were not performed in compound **4**.

Figure 19. FT-IR of compound **4** with $^{16}\text{O}_2$.

The identification and S-oxygenation of the complexes **1-4** was confirmed by mass spectroscopy. +ESI-MS was recorded for each complex prepared from natural abundance O_2 and 99.99 % $^{18}\text{O}_2$, Figures 20-29. The complex **1** displays a parent peak at m/z 684.1363, Figure 20, consistent with a theoretical value of 684.1369 for $[\mathbf{1}]^+$, Figure 21. The isotopical distribution shows an accuracy of 0.0006

Figure 20. +ESI-MS of **1**.

Figure 21. Calculated isotopic distribution for compound **1**.

Complex **2** displays a parent peak at $m/z = 715.6971$ consistent with a theoretical value of 716.1268 for $[2]^+$, Figure 22. The isotopical distribution shows and accuracy of 0.4297, Figure 23. While +ESI-MS typically yields $[M+H]^+$ or $[M+Na]^+$ ions, the direct oxidation of neutral species at the probe tip to yield $[M]^{++}$ is known for easily oxidized

samples such as **1-4**.¹³⁴ Samples of **2** prepared with $^{18}\text{O}_2$ show the expected shift to $m/z = 720.1338$ confirming O_2 as the source of both O-atoms in the product, Figure 24.

Figure 22. +ESI-MS of **2** prepared from $^{16}\text{O}_2$.

Figure 23. Calculated isotopic distribution for compound **2** using $^{16}\text{O}_2$.

Figure 24. +ESI-MS of **2** prepared from $^{18}\text{O}_2$.

The mixed sulfenate/sulfinate complex **3** displays a peak at $m/z = 731.1147$, Figure 25, the parent peak of the isotopic distribution is diphasic by $1.007\text{ }m/z$ of the experimental value, Figure 26. The experimental value shifts by 6.0116 to 737.1263 when the sample is prepared with $^{18}\text{O}_2$, Figure 27.¹²⁹ This results indicate that the thiolates of the complex uptake the oxygen from O_2 and no from the methanol.

Figure 25. +ESI-MS of **3** prepared from $^{16}\text{O}_2$.

Figure 26. Calculated isotopic distribution for compound **3** $^{16}\text{O}_2$.

Figure 27. +ESI-MS of **3** prepared from $^{18}\text{O}_2$.

The +ESI-MS of the disulfinate complex **4** has only small intensity at the theoretical value of $m/z = 748.1185$, Figure 28. A larger peak at $m/z = 485.6471$ associated with PPh_3 dissociation is observed along with free PPh_3 at $m/z = 262.0911$.

The isotopical distribution parent peak calculated for compound **4** is diphasic by 0.0019 m/z , Figure 29.

Figure 28. +ESI-MS of **4** prepared from $^{16}\text{O}_2$.

Figure 29. Calculated isotopic distribution for compound **4**.

Structural characterization.

Orange block shaped crystals of **1** in the monoclinic space group $P2_1/n$ were obtained upon slow evaporation of methanol solutions of the complex under air free

conditions. The final unit cell parameters: $a = 11.085(4) \text{ \AA}$, $b = 16.885(6) \text{ \AA}$, $c = 16.110(6) \text{ \AA}$, $\beta = 95.848(6)^\circ$, $V = 2999.7(19) \text{ \AA}^3$, $D_{\text{calc}} = 1.514 \text{ Mg/m}^3$, $Z = 4$. Complex **1** contains a six-coordinate ruthenium(II) ion in an $\text{N}_2\text{S}_3\text{P}$ donor set with one thioether (S1), one sulfinate (S2), and one thiolate (S3) sulfur donor, Figure 30. The TASN ligand backbone (N1, N2, S1) occupies one face of a distorted octahedron. The three sulfur donors are arranged in a meridional fashion as in other six-coordinate bmmp-TASN based complexes.^{78,93,96} The sulfinate sulfur S2 of **1** sits trans to the amine N2.¹²⁹ The thiolate sulfur S3 of **1** occupies the position trans to the thioether S1.

Figure 30. ORTEP representation of **1** showing 40 % probability ellipsoids. H atoms and methanol solvates have been omitted to clearly illustrate the oxygation of S2.

Orange block shaped crystals of **2** in the monoclinic space group $\text{P}2_1/n$ were obtained upon slow evaporation of methanol solutions of the complex under air free conditions. Complex **2** contains a six-coordinate ruthenium(II) ion in an $\text{N}_2\text{S}_3\text{P}$ donor set with one thioether (S1), one sulfinate (S2), and one thiolate (S3) sulfur donor, Figure 31.

The nine-membered heterocyclic TASN ring (N1, N2, S1) occupies one face of a distorted octahedron. The three sulfur donors are arranged in the same distribution as in other six-coordinate bmmp-TASN based complexes.^{78,93,96} The sulfinate sulfur S2 of **2** sits trans to the amine N2 in the same position as in **1**.¹²⁹ The thiolate sulfur S3 of **2** occupies the position trans to the thioether S1.

Figure 31. ORTEP representation of **2** showing 40 % probability ellipsoids. H atoms and methanol solvates have been omitted to clearly illustrate the oxygenation of S2.

A large yellow plate crystal of **3** in the monoclinic space group P-1 were obtained upon slow evaporation of methanol solutions of the complex under air free conditions. The complex **3** in Figure 32 contains a six-coordinate ruthenium(II) ion in an N₂S₃P donor set and reproduce the same structural arrangement that **1** and **2**. The two O atoms O1 and O2 of the sulfinate donor (S2) are directed roughly along the S1-Ru-S3 bond axis with torsion angles of -12.63(12)° and +35.55(13)° for O1-S2-Ru1-S1 and O2-S2-Ru1-

S3, respectively. The sulfenate oxygen (O3) is oriented toward N1 along the P1-Ru-N1 axis with an O3-S3-Ru1-N1 torsion angle of $-16.47(14)^\circ$. As shown in Figure 33, the triphenylphosphine donor restricts access to the remaining potential oxygenation site on S3, which may retard the rate of further oxygenation under limited O_2 .

Figure 32. ORTEP representation of **3** showing 40 % probability ellipsoids. H atoms and methanol solvates have been omitted to clearly illustrate the asymmetric oxygenation of S2 and S3.

Figure 33. Space-filling representation of **3** illustrating the steric crowding imposed by the phenyl substituents around the sulfenato sulfur, S3.

X-ray crystallographic analyses of **1**, **2** and **3** reveal similar $(\text{N}_2\text{S}_3)\text{RuPPh}_3$ donor environments, with a NS_3 square planar equatorial environment and an amine and phosphine donor in an axial positions. The S2 sulfur is oxidized in a sulfinate in **2** and **3** and S3 is the sulfur oxidized to sulfenato in **3**. As shown in the ORTEP representations of **1-3** in Figures 30-32, respectively all the complexes display a facially coordinated TASN ring (N1, N2, and S1), two pendant sulfur donors (S2 and S3), and a triphenylphosphine (P1) trans to the nitrogen (N1).

The sulfur-oxygenation of a metal coordinated thiolate eliminates a four electron $d\pi\text{-}p\pi$ antibonding interaction between the metal and the sulfur.^{66,80,133,135,136} Additionally, oxidation of the sulfur decreases its ionic radius. The net result is a decreased Ru-S bond distance.¹³³ The Ru-S bond distances to the oxygenated sulfur donors S2 and S3 are shorter in **3** than in **1**. The Ru-S_{sulfinate}, Ru-S2, bond distance decreases by 0.151(1) Å,

while the Ru-S_{sulfenate} bond distance, Ru-S3, shortens by only 0.026(1) Å. Consistent with this explanation, **3** displays significantly longer bond distances to its π -accepting ligands than **1**. The Ru-P1 bond distance to the triphenylphosphine increases by 0.088(1) Å, and the Ru-S_{thioether}, Ru-S1, bond distance similarly increases by 0.072(1) Å. This is similar to a recent theoretical prediction by Mascharak *et al.* of a 0.023 Å increase in the Fe-NO bond distance upon sulfur oxygenation of a dithiolate iron nitrosyl.¹¹² The average S-O distance for the sulfinate, S2, of 1.48 Å falls in the usual range (1.42-1.48 Å).^{82,133,137} The sulfenate S-O bond is more polarized, resulting in a longer S-O distance of 1.556(3) Å, which also lies in the typical range (1.50-1.60 Å).^{81,82,113,133} Additional comparison of crystallographic data of the family of compounds **1-3** reveals significant distinctions as a function of sulfur oxygenation. The Ru-S sulfinate distances of 2.2473(6) in **2** is 0.158(1) shorter than the corresponding Ru-S thiolate distance in **1**. Similarly, the Ru-S thiolate distances of 2.3943(6) in **2** is 0.045(1) longer than corresponding Ru-S sulfenate bond length in **3**.

Further, the loss of π -donating ability induced by S-oxygenation increases metal-ligand bond distances with traditional π -acceptors. The Ru-P bond distance consistently increases from 2.2911(10) to 2.3519(6) to 2.3790(9) Å for **1**, **2**, and **3**, respectively. The same trend is noted in the Ru-S thioether bond distances, as we can observe in Table 1.

	1		2		3		4
	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Theoretical
Ru1-S1	2.2900(10)	2.33949	2.3102(6)	2.36409	2.3622(9)	2.43248	2.40525
Ru1-S2	2.4057(9)	2.44426	2.2473(6)	2.32732	2.2548(9)	2.33608	2.34758
Ru1-S3	2.3754(10)	2.4401	2.3943(6)	2.43876	2.3493(9)	2.39406	2.38256
Ru1-P1	2.2911(10)	2.32479	2.3519(6)	2.3811	2.3790(9)	2.41051	2.44965
Ru1-N1	2.198(2)	2.25183	2.1927(19)	2.26026	2.178(3)	2.23921	2.25745
Ru1-N2	2.178(2)	2.22881	2.200(2)	2.26699	2.192(3)	2.2614	2.28146
S2-O1			1.4906(17)	1.53291	1.489(3)	1.5317	1.53436
S2-O2			1.4658(18)	1.5133	1.471(3)	1.5148	1.51018
S3-O3					1.556(3)	1.5755	1.53122
S3-O4							1.50548
P1-Ru-S2	95.44(2)	91.20	93.99(2)	93.43	90.72(3)	92.50	93.91
P1-Ru-S3	92.42(3)	93.34	93.16(2)	93.29	91.59(3)	91.10	94.06
S2-Ru-S3	94.93(3)	95.61	97.09(2)	97.81	94.13(3)	96.42	98.52

Table 1. Selected experimental and computational (BP86/LANL2DZ+6-31G(d)) bond distances (Å) and angles (deg) for **1-4**.

Computational investigations

The geometry optimization and subsequent molecular orbital analysis of complexes **1-4** were performed using the BP86 functional with the LANL2DZ basis set for Ru and the 6-31G(d) basis set for all other atoms. The calculated metal-ligand bond distances accurately reproduce the experimental values for complexes **1-3** within 0.02 to 0.08 Å, Table 1. Although no experimental data is available for **4**, the optimized bond distances are consistent with the trends observed for **1-3**, Figure 34. Calculated bond angles reproduce experimental values within 4°. Similar results were obtained when the B3LYP functional was analyzed.

The optimized metal ligand distances reflect changes in the electronic configuration as a function of sulfur oxygenation and its metal bond distances. As shown in Figure 34, the effects of sulfur oxygenation in the series **1-4** are revealed by the Ru-S2, Ru-S3, and Ru-P bond distances. As expected, large changes in Ru-S bond distances occur upon oxygenation of the sulfur donor. A decrease of 0.12 Å in the Ru-S2 bond distance occurs when S2 is oxygenated from a thiolate in **1** to a sulfinate in **2**. The Ru-S2 bond distance then only slightly increases in **3** and **4**. The largest decrease in the Ru-S3 bond distance, 0.04 Å, is observed when the thiolate of **2** is oxidized to a sulfenate in **3**. Only small changes are observed between the S3-thiolates of **1** and **2** and the S3-oxygenates of **3** and **4**. While changes in the Ru-S bond distances reflect bonding changes at that specific atom, the Ru-P bond distance consistently increases with each subsequent O-atom added to the sulfur donors. As shown in Figure 34, there is a direct correlation between the Ru-P bond distance and the level of sulfur oxygenation. The data fits a straight line according to the equation $y = 2.331 + (0.040) x$ ($R^2=0.98$), where y is the Ru-P bond distance in Å and x is the number of O-atoms added to sulfur. For the bis-sulfinate complex **4**, the theoretical bond length increases to 2.450 Å. The elongation of the Ru-P bond as a function of sulfur oxygenation supports the suggestion that post translational modifications in NHase or SCNase regulates substrate/product binding.

Figure 34. Plot of optimized (BP86/LANDZ+6-31G(d)) Ru-Lbond distance versus number of oxygen atoms in **1-4**. Ru-P (black), Ru-S2 (red), Ru-S3 (blue).

Analysis of the frontier orbitals of **1-4** shows a direct connection between sulfur oxygenation and changes in the Ru-P bonding. In **1**, the occupied frontier molecular orbitals are dominated by metal-sulfur interactions as observed in other metal-thiolates.^{66,78,136,138-140} The highest occupied molecular orbital (HOMO) and HOMO-1, Figure 35, show π^* interactions between filled “ t_{2g} ” orbitals on the metal and p-type lone pairs on the sulfur on S2 and S3, respectively. Additionally, the HOMO-1 includes a significant σ -bonding interaction between metal-centered orbital and the phosphine ligand that strengthens the Ru-P bond. This σ -bonding interaction can be considered as an “outlet” for the 4 electron $d\pi$ - $p\pi$ repulsion described for “ t_{2g} -rich” metal-thiolates. A similar σ -donation is observed in the HOMO between the metal and the thioether sulfur S1, with an additional polarization of the metal orbital toward the phosphine donor. In

(**2**), one of the thiolates, S2, has been oxygenated and no longer participates in π -bonding/antibonding with Ru. The HOMO of **2** is localized on the remaining thiolate, S3, and Ru. The HOMO of **2** is similar to the HOMO-1 of **1** with a π^* interaction between Ru and S and a strong σ -bonding interaction between Ru and P. Complexes **3** and **4** lack thiolate donors and do not show the same type of interactions as **1** and **2**. Rather, the HOMOs of **3** and **4** are dominated by S-O π^* interactions that are σ -bonding with respect to the metal sulfur-oxygenate bond. As in the HOMO of **1**, the metal centered orbital is slightly polarized toward the phosphine ligand. Overall, Ru-S interactions reinforce the Ru-P bond through the HOMO and HOMO-1 of **1** and the HOMO of **2**. The Ru-P bond is only weakly affected by Ru-S interactions in the HOMOs of **3** and **4**.

Figure 35. Homo surfaces of 1-4 and Homo-1 of 1.

Sulfur oxygenation effect on the complex (bmmp-TASN)RuPPh₃ probed by multi-edge X-ray absorption spectroscopy

In collaboration with Jason Shearer at University of Nevada Reno, it was investigated the effect of the sulfur oxygenation in compound **1**. These studies used Ru L-edge, and ligand (N-, S- and P-) K edge X-ray absorption spectroscopies to investigate the effect of the sulfur oxygenation in the electronic structure of compound **1-3**. In this

study is included N K-edge spectroscopy, technique that is used for first time to obtain N-metal covalency parameters. The most relevant result was that the complexes becomes progressively more ionic, and hence the Ru(II) center becomes a harder Lewis-acid.

In the X-ray absorption studies performed in the National Synchrotron Light Source, Brookhaven National Laboratory, it was demonstrated that the bonding in the complex **1-3** is dominated by S-Ru interactions. The Ru-P and Ru-N interaction contribute in a lesser degree in the bonding interactions. Upon oxygenation of compound **1** the thiolates-ruthenium bond distance decrease in S2 and S3 for compound **2** and **3**. As this occur the covalency of the compound decrease and the charge of the ruthenium center increase. The ruthenium increase charge goes from -0.073 in RuS to + 0.0831 in RuSO₂ to + 0.263 in RuSO₂/SO and as consequence the ruthenium center become more Lewis-acid. One of the consequences of the harder ruthenium is the week interaction with the soft phosphine and increase interaction with harder amines (relative to phosphine), both effects were observed in X-ray and DFT calculations.

From a mechanistic perspective, the increase in the hard Lewis acidity nature of the metal ion would aid to the catalysis. In a nitrile metal bond mechanistic model, the increased hardness of the metal would better polarize the nitrile CN bond aiding in attack by free water. In a water bind mechanism, the coordination of the water is favored over the coordination of a soft nitrile. Furthermore this last mechanism is favored for the increased charge in the metal as consequence of the sulfur oxygenation. The increase in charge will lower the *pKa* of the water generating the hydroxide for a nitrile attack.

Voltammetric studies.

Electrochemical studies of **1-3** were conducted in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte under air-free conditions in the glovebox. All potentials are referenced to the ferrocenium/ferrocene (Fc⁺/Fc) couple. The square wave voltammograms, Figure 36, clearly outline the changes in the Ru(III/II) reduction potential as a function of sulfur oxygenation. The Ru(II)-dithiolato precursor **1** displays a Ru(III/II) redox couple with $E_{1/2} = -851$ mV. Oxygenation of **1** to **2** stabilizes the lower oxidation because of electron withdrawing effects of the two O atoms. The $E_{1/2}$ of **2** is shifted by +458 mV with respect to **1** resulting in a Ru(III/II) potential of -393 mV. The shift is similar to that observed upon oxygenation of other Ru thiolates.¹³⁰ The $E_{1/2}$ of **3**, -263 mV, reflects an additional shift of +130 mV as compared to **2** as another O-atom is added. The cathodic shift for a single sulfenate O-atom is less than half of the shift induced by the two O-atoms of the sulfinate as previously noted by Darensbourg *et al.*⁷⁹ The reversibility of each redox event was established by cyclic voltammetry, Supporting Information, Figures A2-A4. Each complex displays a quasi-reversible Ru(III/II) couple with ΔE values of 109, 73, and 79 mV for **1**, **2**, and **3** at a scan rate of 200 mV/s.

Figure 36. Square voltammograms **1-3**.

Summary.

We reported the synthesis of (bmmp-TASN)RuPPh₃ (**1**) and its derivation under limiting dioxygen conditions to (bmmp-O₂-TASN)RuPPh₃ (**2**), (bmmp-O₃-TASN)RuPPh₃ (**3**), and (bmmp-O₄-TASN)RuPPh₃ (**4**).^{129,141} The sulfenate/sulfinate (RSO⁻)/(RSO²⁻) donor set of **3** mimics the unusual post-translational modification of the NHase and SCNase active sites. The asymmetric sulfur-oxygenate **3** represents one of only three sulfenate/sulfinate derivatives prepared by direct reaction with dioxygen.^{79,108} High yields of **3** were obtained by limiting the quantity (5 equivalents) and duration (12 hours) of dioxygen exposure.

This research work offers insight into the controlled sulfur oxygenation of metal thiolates and the resulting changes in the electronic structure. The previous hypothesis of the Grapperhaus group that “t_{2g}-rich” low-spin complexes favor sulfur oxygenation is

supported by the reactivity of **1** with O₂. Further, partial sulfur oxygenation is achievable using limited O₂ conditions, as demonstrated by **3** and other reported sulfenate/sulfinate complexes. In **1**, the steric bulk of PPh₃ slows oxygenation beyond **3** but does not prevent it, as demonstrated under excess O₂ conditions. These results suggest that asymmetric oxygenation of nitrile hydratase and thiocyanate hydrolase may also be facilitated by limited O₂ at the active site without the necessity for single O-atom-transfer reagents. Structurally sulfur oxygenation shortens the M-S bond while lengthening the metal-ligand bonds to π acceptors. In combination with the previously documented labilizing effect of the trans-thiolate,^{142,143} sulfur oxygenation may promote ligand exchange. As demonstrated by Mascharak, sulfur oxygenation facilitates photodissociation of NO.¹¹² It is also expected to enhance coordination of π donors, such as HO⁻, and may help to discriminate substrate coordination.

Finally, we report systematic studies under limited O₂ conditions. By fixing the quantity of O₂ and the duration of the reaction, conditions were optimized to reproducibly obtain the monosulfinate (bmmp-O₂-TASN)-RuPPh₃ **2**, the asymmetric sulfenate/sulfinate (bmmp-O₂-TASN)-RuPPh₃ **3** and bissulfinate (bmmp-O₄-TASN)RuPPh₃ **4** derivatives without the need for O-atom transfer reagents or purification by column chromatography. This approach has yielded a unique “family” of complexes, **1-4**, that differ only in the degree of S-oxygenation, Scheme 4. Although the number of reported S-oxygenates is growing, families containing three or more oxygenated derivatives are scant.¹⁴⁴ Based on a systematic synthesis design, the pioneering Ni- and Pd-dithiolate systems developed by Darensbourg provide a benchmark for completeness, because they offer no prospects to probe the effects of S-oxygenation at a variable ligand

site. Challenge that it is being addressed in this research, analysis of the structural parameters of **1- 4** reveals a systematic increase in the Ru-P bond distance as a function of S-oxygenation. This trend is reproduced computationally by density functional theory calculations providing insight into the potential of S-oxygenation to regulate substrate/product binding at the NHase active site and to formulate the hypothesis that this sulfur oxygenation allows exchange substrate in our model, this hypothesis will be tested in the next chapter.

CHAPTER IV

REACTIVITY BEHAVIOR OF (bmmp-TASN)RuPPh₃

The stabilization, coordination and activation of small molecules such as NO, RCN, RC(O)NH₂, H₂O by transition metal with sulfur-nitrogen coordination complexes such as the (bmmp-TASN)Ru is of critical interest for understanding the molecular mechanisms of NHase and SCNase. It is proposed that these molecules interact with a low spin Fe(III) or Co(III) in the first coordination sphere of the NHase. The NHase of *Rhodococcus erythropolis* N771 exhibit catalytic activity converting tert-butylisonitrile (*t*BuNC) to tert-butylamine; its nitrile substrate was structurally characterized by time-resolved X-ray crystallography.⁵⁰ These studies address a nitrile mechanism where the substrate was coordinated to the iron and then attacked by a solvent molecule activated by α Cys¹¹⁴-SO(H).

In a recent published, studies achieved by the Kovac's group supported the proposed role of the sulfenate as a proximal base. Kovac et al trapped and structurally characterized a Co-iminol and Co-amidate, which is tautomer of the imidate intermediate by using alkoxide and amine donor in place of the sulfenate.⁶⁵ However, there are no available catalytic models that reproduce the activity of the enzyme and at the same time the functionality of the post-translational modification remains unexplained.

At the moment there is not a synthetic compound that model, the basic structural and functional properties of the NHase metal center. To be more specific, the basic features are the metal thiolate-nitrogen coordination, systematic oxygenation of the thiolate, substrate-product exchange in the active site and catalytic activity of the model. In the search for such models, we found that the (bmmp-TASN)RuX is an unequal example in the research community that satisfies the coordination and structural requirement for a catalytic model of the NHase.

Substrate exchange in bmmp-TASN models preliminary results

The Grapperhaus group has been performing studies in the NHase (bmmp-TASN)Fe(III) model in the area of exchange substrate reactivity, using NaOH, NO, Et₄NCN and TlOTf. In the latter, the trifluoromethanesulfonate (OTf) was used as a weakly coordinated ion to test solvent coordination solvent and binding reactivity. These studies cover the first NHase model complex [(bmmp-TASN)Fe]OTf reported to coordinate nitrile and water, both substrates of the enzyme, and achieved broad substrate binding studies.¹⁰⁹

Figure 37. Substrate ligand exchange reactions of (bmmp-TASN)FeCl yield derivative complexes with spin-states that are dependent on the variable ligand allowing comparisons of spin-state effects for closely related complexes. Metathesis of chloride with thallium triflate yields $[(\text{bmmp-TASN})\text{Fe}]^+$ with an open-coordinate site available for solvent (substrate) binding.

The Grapperhaus groups preliminary studies utilized a penta-coordinated, square pyramidal $(\text{N}_2\text{S}_3)\text{Fe}$ core to bind coordination solvents in the 6th axial position. Solvents that coordinate include H_2O , CH_3CN , DMF, MeOH, DMSO and pyridine. The triflate derivative was synthesized using a suspension of LFeCl and dropwise cannula addition of thallium triflate in acetonitrile under air free conditions. Several trials to synthesize the $(\text{bmmp-TASN})\text{FeOTf}$ with traditional Ag^+ salts failed due to Ag^+ thiolate reactivity. In a series of competition evaluation of binding preference of $\text{H}_2\text{O} > \text{amide} > \text{nitrile}$, it was determined that the Fe(III) model supports a water bound mechanism. However, no evidence of hydrolysis was observed in this iron model.

Figure 38. [(btmp-TASN)Fe]Tf is the first NHase model complex that coordinates water and nitrile. Nitrile coordination is only observed at low temperature. DMF readily displaces nitriles and H₂O displaces both nitriles and DMF.

The aqua derivative [(btmp-TASN)Fe-OH₂]⁺ reveals reversible deprotonation events that include the formation of a μ -hydroxo [[(btmp-TASN)Fe]₂OH]OTf, μ -oxo [(btmp-TASN)Fe]₂O complexes. These events take place with biologically relevant pK_a values (pK_{a1} = 5.4(1), pK_{a2} = 6.52(1)). The first deprotonation yields an unsupported μ -OH bridge di-iron complex that was structurally characterized by X-ray crystallography. Subsequent deprotonation yields the μ -oxo bridge complex [(btmp-TASN)Fe]₂O in a reversible process. The [(btmp-TASN)Fe]X (X = H₂O, μ -OH and μ -O) complexes lack of hydrolytic activity at a variety of pH values covering the two protonation states indicating insufficient nucleophilicity of the bridging HO⁻ and strong substrate coordination.

The Grapperhaus group performed EPR experiments in collaboration with Prof. Brian Bennett from the National Biomedical EPR center, Medical College of Wisconsin to study substrate exchange properties in the penta-coordinated model [(bmmp-TASN)Fe]⁺OTf⁻. The spin-state of [(bmmp-TASN)Fe-Solvent]OTf depends on the substrate (coordination solvent) with low-spin Fe(III) complexes observed in acetonitrile ($g_1 = 2.27$, $g_2 = 2.18$, and $g_3 = 1.98$) or benzonitrile ($g_1 = 2.28$, $g_2 = 2.18$, $g_3 = 2.00$). The nitrile derivatives are in equilibrium with a low-spin 5-coordinate species, [(bmmp-TASN)Fe]⁺ ($g_1 = 2.04$, $g_2 = 2.02$ and $g_3 = 2.01$); this equilibrium is supported by spectroscopic characterization at 40 °C in acetonitrile, solutions of [LFe]⁺ are green with absorbance bands at 315, 427, and 603 nm; similar to the spectrum observed in dichloromethane and consistent with a five coordinate complex. Nevertheless, upon cooling to room temperature and below, the acetonitrile solution turns blue color as the peak at 427 nm loses intensity and the low energy band shifts toward 596 nm. Using other donor solvents such as H₂O, DMF, DMSO, MeOH or pyridine, 6-coordinated high spin Fe(III) complexes with the substrate *cis* to the thiolates show significant strain in the rhombic zero-field splitting term E/D. These results helped to narrow our study of the (bmmp-TASN)FeX NHase system to focus on (bmmp-TASN)RuPPh₃ which will maintain a low-spin state and would facilitate substrate exchange property required for a catalytic turnover and avoid metal oxo bridged species due to the high Lewis acid character of iron compare with ruthenium.

On the road to synthesize a functional model of NHase capable of exchanging substrates and displaying has hydrolytic activity, we decided to explore the sulfur oxygenation of the model (bmmp-TASN)RuPPh₃. The bmmp-TASN ligand has been a

focus of the Grapperhaus group with the objective to reproduce the unusual and synthetic challenging post-translational modification of the nitrile hydratase enzyme. The structural and spectroscopic characterizations of the family derivatives from the thiolate complex (bmmp-TASN)RuPPh₃ has been described in the previous chapter. As noted previously, low spin Fe(III) complexes favor S-oxygenation and not disulfide formation or oxo clusters, inspiring investigations with (bmmp-TASN)RuPPh₃.

Analysis of the structural parameters using X-ray crystallography and Density Functional Theory calculations in the family of S-oxygenates reveals a systematic increase in the Ru-P bond distances as a function of S-oxygenation. This trend, which is in opposition to some expectations of tighter Ru-P binding resulting from decreased S-donation, is supported experimentally by multi-edge X-ray absorption spectroscopy in collaboration with Prof. Jason Shearer of the Chemistry Department at University of Nevada, Reno. The XAS studies include N K-edge spectroscopy, which to our knowledge, has not been previously utilized to extract covalency parameters in metal complexes. The results demonstrate dramatic reduction in metal-ligand covalency with each sequential oxygenation with significant hardening of Ru. This leads to enhanced lability of the soft PPh₃ donor.

The sequence of S-oxygenates LⁿRuPPh₃ (n = 1–4) synthesized in the Grapperhaus' Lab, make available an unparalleled set of functional complexes to study the outcome of S-oxygenation on catalytic activity, substrate binds, structural rearrangement of the ligand due to substrate binding, coordination solvent preference, and ligand exchange. Even though the number of reported S-oxygenated is growing, families of three or more oxygenated derivatives are scarce and just few successful studies

have reproduced the sulfenate/sulfinate first metal coordination sphere. The groundbreaking Ni- and Pd-dithiolate systems developed by Darensbourg group helped establish this field, such as (N,N'-bis(2-mercaptoethyl)-1,5-diazacyclooctanato)Ni(II) (Ni(bme-daco)), (N,N'-2-mercaptoethyl-2-sulfinatoethyl-1,5-diazacyclooctanato)Ni(II) (Ni(mse-daco)), and [N,N'-bis(2-sulfinatoethyl)-1,5-diazacyclooctanato]Ni(II) (Ni(bsp-daco)),^{116,135} However these models offer no opportunity for substrate coordination or ligand exchange reactions. Our system masters this limitation with a variable donor site. As we will described in our results below, ligand exchange of PPh₃ for other donors provides functional hydrolytic mimic and establish unprecedented synthetic routes to S-oxygenates derivatives. Phosphine exchange reactions are known for select Ru-thiolates reported by Sellmann.^{145,146} In this study we found that the model (bmmp-TASN)RuPPh₃ and its family of derivatives can exchange its triphenylphosphine by other phosphines, CO and the models (**1-3**) are hydrolytically active. We proposed to exploit the enhanced lability of our S-oxygenates to initiate similar ligand exchanges to obtain hydrolytically more active complexes and understand the functional effects of posttranslational oxygen modification in thiolates.

Phosphine exchange in the metal complexes (bmmp-TASN)RuPPh₃ and derivatives

In this section we will present ³¹P NMR spectra and +ESI-MS results that support the triphenylphosphine exchange in compound **1**, **2** and **3**. These results are consequence of preliminary results presented in the last chapter. The preliminary results that support this study include the Ru-P bond distances elongation calculated from X-ray analysis and DFT calculations. Also, the increase in the bond covalencies and metal hardening observed in the XAS studies suggest phosphine lability. Finally, experimentally it was

observed that under air free conditions compound **3** change colors from orange to green upon heating, with a return to orange **3** upon cooling.

Results of our initial synthetic trails at 50 °C are summarized in Figure 39 and +ESI-MS spectrums in A5 and A6. Phosphine exchange readily occurs for compound **2** and **3** using 5 equivalents of PMePh₂ at 50 °C in MeOH. These results confirms our hypothesis that triphenylphosphine can be exchanged in sulfur-oxygenated compounds. In these experiments, the sulfinate/thiolate compound **2** and the sulfinate/sulfenate compound **3** exchange triphenylphosphine for methyl diphenylphosphine as confirmed by + ESI-MS, Figure 39.

The identification of phosphine exchange in the complexes (bmmp-O₂-TASN)RuPMePPh₂ (**8**) and (bmmp-O₃-TASN)RuPMePPh₂ (**9**) were confirmed by mass spectroscopy. +ESI-MS was recorded for each complex after the phosphine exchange reaction. Compound **8** displays a parent peak at m/z 677.1140, Figure A5, consistent with a theoretical value of 677.1009 m/z for [**8**+Na]⁺. The isotopical distribution shows and accuracy of 0.0131 m/z . Compound **9** displays a parent peak at m/z 693.1192, Figure A6, consistent with a theoretical value of 693.0958 m/z for [**9**+Na]⁺. The isotopical distribution shows and accuracy of 0.0234 m/z .

Figure 39. Sulfur-oxygenation increases the lability of PPh_3 allowing a series of S-oxygenates to be prepared.

Further investigation in phosphine exchange required the assessment of other phosphines. For this reason, we used the bulky phosphine, methylenebis[diphenylphosphine]. The +ESI-MS results shows that phosphine exchange was again successful for **2** and **3**, but not for **1**, Figure 40 and +ESI-MS spectrums in A7 and A8.

The identification of phosphine exchange in the complexes $(\text{bmmp-O}_2\text{-TASN})\text{Ru}(\text{MePPh}_2)_2$ and $(\text{bmmp-O}_3\text{-TASN})\text{Ru}(\text{MePPh}_2)_2$ were confirmed by mass spectroscopy. (+)ESI-MS was recorded for each complex after the phosphine exchange reaction. Compound $(\text{bmmp-O}_2\text{-TASN})\text{Ru}(\text{MePPh}_2)_2$ displays a parent peak at m/z 839.1629, Figure A7, consistent with a theoretical value of 838.1553 m/z for $[(\text{bmmp-O}_2\text{-TASN})\text{Ru}(\text{MePPh}_2)_2]^+$. The isotopical distribution shows an accuracy of 1.0076 m/z . Compound $(\text{bmmp-O}_3\text{-TASN})\text{Ru}(\text{MePPh}_2)_2$ displays a parent peak at m/z 855.1582,

Figure A8, consistent with a theoretical value of 854.1502 m/z for [(bmmmp-O₃-TASN)Ru(MePPh₂)₂]⁺. The isotopical distribution shows and accuracy of 1.0008 m/z .

Figure 40. Triphenylphosphine exchange using methylenebis[diphenylphosphine]

To achieve the triphenylphosphine exchange in **1** extensive heating was applied. Compound **1** has the smallest Ru-P bond distance in the sulfur oxygenated series. Complex **1** was heated to 100 °C in the presence of 5 equivalents of methylbis(diphenyl)phosphine in chlorobenzene. The mixture was heated at 100 °C for 36 hours under an argon atmosphere. After this period of time the chlorobenzene was removed under a vacuum at room temperature. The yellow-amber solid was transferred to a glovebox.

Phosphine exchange experiments were performed using ^{31}P NMR in deuterated methanol. The ^{31}P NMR spectrum shows free triphenylphosphine at -6.23 ppm, excess methyldiphenylphosphine at -27.83 ppm and the exchange product (bmmp-TASN)RuPMePh₂ 34.64 ppm. Similar experiments over a temperature range of 50 °C and 100 °C indicates that the phosphine exchange is temperature dependent. The dissociation of the ligand at moderate temperatures allows the exchange of phosphine, while the product are stable with respect to phosphine or solvent exchange at 25 °C. This is confirmed by electrochemical studies at room temperature. Both cyclic voltammetry and square wave voltammetry reveals a single oxidation-reduction event in compounds **1**, **2** and **3**. As we can observe in the CV of the (bmmp-TASN)RuPPh₃ and derivatives, Figures A2-A4.

The ^{31}P NMR spectrum for **1**, **2** and **3** and free triphenylphosphine is presented in Figure 41. The free triphenylphosphine displays a peak at -6.23 ppm. The ^{31}P NMR experiment was performed in an air free J-young NMR tube using degassed deuterated methanol at 50 °C after 1024 repetitions to observe the peaks in the NMR due to the low solubility of the complex in methanol. The results of ^{31}P NMR experiments show a tendency with, a ruthenium dithiolate (bmmp-TASN)RuPPh₃ at 43.37 ppm, a ruthenium thiolate/sulfinate (bmmp-O₂-TASN)RuPPh₃ at 34.343 ppm and a ruthenium sulfinate/sulfenate (bmmp-O₂-TASN)RuPPh₃ at 33.68 ppm.

Figure 41. ^{31}P NMR of free triphenylphosphine and compounds **1**, **2** and **3** at 50 °C.

To a mixture of **1**, **2** and **3** in chlorobenzene were added PMePh_2 . The solution was stirred for 36 hours at 100 °C and the solvent was removed via vacuum under air free conditions. The residue was dissolved in deuterated methanol in a J-young tube and the ^{31}P NMR spectrum was collected. The results show excess PMePh_2 at -27.83 ppm, the ruthenium dithiolate exchange product $(\text{bmmp-TASN})\text{RuPMePh}_2$ at 34.64 ppm, the ruthenium thiolate/sulfinate exchange product $(\text{bmmp-O}_2\text{-TASN})\text{RuPMePh}_2$ at 25.54 ppm, and the ruthenium sulfinat/sulfenat exchange product $(\text{bmmp-O}_2\text{-TASN})\text{RuPMePh}_2$ at 22.54 ppm. The free PPh_3 in this experiment is observed at -6.23 ppm. For each complex the ^{31}P resonance is shifted by - 0.488 ppm with respect to the PPh_3 precursor, Table 2.

Figure 42. ^{31}P NMR of free triphenylphosphine PMePh_2 and compounds **7**, **8** and **9** at 50 °C.

	PPh_3	PMePh_2
Free PPh_3	-6.229	-6.229
Free PMePh_2		-27.831
Thiolate	43.374	34.640
SO_2	34.343	25.494
SO_3	33.675	22.539

Table 2. ^{31}P NMR assignments for Figures 37 with the use of PPh_3 and for Figure 38 with the use of PMePh_2 . ^{31}P NMR values were internally referenced to free PPh_3 .

X-ray structure analyses of $(\text{bmmp-O}_2\text{-TASN})\text{RuPMePh}_2$ (8**), $(\text{bmmp-O}_3\text{-TASN})\text{RuPMePh}_2$ (**9**), their analogues precursors and $[(\text{bmmp-TASN})\text{Ru}]_2$ (**10**)**

The phosphine exchange studies resulted in the syntheses of new ruthenium complexes with the $[(\text{bmmp-TASN})\text{Ru}]$ framework. Of these, two new compounds were structurally characterized by X-ray diffraction studies; $(\text{bmmp-O}_2\text{-TASN})\text{RuPMePh}_2$ **8**

and (bmmp-O₃-TASN)RuPMePh₂ **9**. X-ray quality crystals of **7** were not obtained. The molecular structures of **8** and **9** were elucidated by X-ray structure determination. Complex **8** crystalize in a triclinic space group P-1; with $a = 9.7483(3) \text{ \AA}$, $b = 14.4088(5) \text{ \AA}$, $c = 24.8048(7) \text{ \AA}$; $\alpha = 75.203(3)^\circ$, $\beta = 80.610(3)^\circ$, $\gamma = 81.507(3)^\circ$; $Z = 2$; $R1/wR2 = 0.0532/0.1279$. Complex **9** crystalize in a triclinic space group P-1; $a = 8.7767(3) \text{ \AA}$, $b = 15.8615(5) \text{ \AA}$, $c = 21.4533(7) \text{ \AA}$; $\alpha = 89.823(3)^\circ$, $\beta = 79.435(3)^\circ$, $\gamma = 76.449(3)^\circ$; $Z = 4$; $R1/wR2 = 0.0289/0.0584$. Compound **8** and **9** exhibit pseudooctahedral six-coordinated Ru(II) centers.

The molecular structure of **8** with selected distances is shown in Figure 43 and Table 3. The ruthenium center is in a pseudo octahedral environment. As in the precursor complex **2**, compound **8** displays a facially coordinated TASN ring (N1, N2, and S1), two pendant sulfur donors (S2 and S3), and a single phosphorus donor (P1). The two oxygen atoms, O1 and O2, of the sulfinate donor (S2) are directed roughly along the S1-Ru-S3 bond axis with torsion angles of $-11.74(13)^\circ$ and $+40.42(12)^\circ$ for O1-S2-Ru1-S1 and O2-S2-Ru1-S3, respectively.

Table 3. Selected bond lengths determined by X-ray of compound **8**.

Ru1-N1	2.188(3)	Å
Ru1-N2	2.190(3)	Å
Ru1-P1	2.3045(8)	Å
Ru1-S1	2.3163(8)	Å
Ru1-S2	2.2384(8)	Å
Ru1-S3	2.3940(8)	Å
S2-O1	1.478(3)	Å
S2-O2	1.485(3)	Å

Figure 43. ORTEP representation of (bmmp-O₂-TASN)RuPMePh₂ (**8**).

The yellow plate crystals of **9**, Figure 44, are similar to **1**, **2**, **3** and **8** with a facially coordinated TASN ring (N1, N2, and S1), two pendant sulfur donors (S2 and S3), and a single phosphine (P1). The two oxygen atoms O1 and O2 of the sulfinate donor (S2) are directed roughly along the S1-Ru-S3 bond axis with torsion angles of $-12.31(6)^\circ$ and $+35.82(6)^\circ$ for O1-S2-Ru1-S1 and O2-S2-Ru1-S3, respectively. The sulfenate oxygen (O3) is oriented toward N1 along the P1-Ru-N1 axis with an O3-S3-Ru1-N1 torsion angle of $-16.46(8)^\circ$. These result clearly show that the formation of S3-O3 bond in compound **9** release a structural stress in the penta heteroatom member ring Ru1-N2-C9-C10-S3. The loss of a π coordination orbital between a d-Ru and a p-S allows a decrease in the torsion angle O2-S2-Ru1-S3 from $+40.42(12)^\circ$ in **8** to $+35.82(6)^\circ$ in **9**. The loss of π -donating ability induced by the S-oxygenation increases the metal-ligand bond distances with traditional π -acceptors. The Ru-P1 bond distance consistently increases from 2.3045(8) to 2.3276(4) Å for **8**, and **9**, respectively. The same trend is

noted in the Ru-S1 thioether bond distances from 2.3163(8) to 2.3508(4) Å for **8**, and **9**, respectively.

Table 4. Selected bond lengths determined by x-ray of compound **9**.

Ru1-N1	2.1746(13)	Å
Ru1-N2	2.1852(14)	Å
Ru1-P1	2.3276(4)	Å
Ru1-S1	2.3508(4)	Å
Ru1-S2	2.2562(4)	Å
Ru1-S3	2.3532(4)	Å
S2-O1	1.4862(12)	Å
S2-O2	1.4767(12)	Å
S3-O3	1.5197(14)	Å

Figure 44. ORTEP representation of (bmmp-O₃-TASN)RuPMePh₂ (**9**).

The structural comparison between the two series of phosphine sulfur oxygenated show that the methyldiphenylphosphine is a better base than triphenylphosphine due to the increase in electronic donation from the methyl group into the σ orbital between the Ru-P. This σ donation effect can be observed through the reduction in the bond distance between Ru1-P1. For compound **2** and **8**, these bond distance are 2.3519(6) Å and 2.3045(8) Å respectively, this make a 0.0474 Å of difference; for compound **3** and **9** the bond distance are 2.3790(9) Å and 2.3276(4)Å respectively, this make a 0.0514 Å of difference. This approximately 0.05 Å units bond distance effect can be explained as result of small cone angle between the PPh₃ with a cone angle of 145° and PMePh₂ with a cone angle of 136° this reduction of volume allow a better accessibility into the axial pocket of the metal center. Further investigation has to be performed to clearly determine if this bond reduction is caused by an electronic or steric effect or a combination of both.

The ORTEP representations of **3** and **9** are shown in Figure 32 and 44 respectively. Selected distances are listed in Table 1 and 4. The comparison of the two structures indicates a zero net effect in the bond distance of the ligand frame due to exchange of the triphenylphosphine for a better nucleophile such as methyl diphenylphosphine. This result suggests that a Ru1-P1 bond distance dependent of the steric effect or cone angle of the substrate. The average Ru-S 2.390 Å and Ru-N 2.192 Å distances are statistically the same as those in Ru1-N2 2.192(3) Å and 2.1852(14) Å for **3** and **9** respectively. For the Ru1-N1 bond trans to the phosphine those values are 2.178(3) Å and 2.1746(13) Å for **3** and **9** respectively. In Ru1-S2 the bond distances are 2.2548(9) Å and 2.2562(4) Å for **3** and **9** respectively, and for Ru1-S3 2.3493(9) Å and 2.3532(4) Å are **3** and **9** respectively. The direct effect on the ligand frame due to the exchange of the triphenylphosphine is observed in Ru-S1 (thioether) with 2.3622(9) Å and 2.3508(4) Å for **3** and **9**.

In addition to the phosphine exchange compounds **8** and **9**, the phosphine free bimetallic complex [(bmmp-TASN)Ru]₂ (**10**) was structurally characterized, Figure 45. Complex **10** was obtained upon slow crystallization of compound **1** through solvent diffusion of methanol-ether under air-free condition for a period of one month. Repeated attempts to reproduce **10** were unsuccessful.

Figure 45. Bimetallic complex $[(\text{bmmp-TASN})\text{Ru}]_2$ (**10**).

Reactivity of $(\text{bmmp-TASN})\text{RuPPh}_3$ (**11**) with CO

The exchange properties of the compounds **1**, **2** and **3** were confirmed by the replacing of the triphenylphosphine with other phosphines. It was of interest to the Grapperhaus group to evaluate strategic routes to remove the phosphine donors all together to promote substrate binding. If obtained transition metal complexes with sulfur and nitrogen coordination spheres similar to the NHase or SCNase could be realized. As noted previously complexes which model structural and functional features of these active sites are of interest for biochemistry, spectroscopic and technological reasons. The relevant post-translational modification of the cysteines in these enzymes was systematically reproduced in the $(\text{bmmp-TASN})\text{RuPPh}_3$ model. In this section efforts to prepare and isolate $(\text{bmmp-TASN})\text{RuCO}$ (**11**) are described. The CO derivative represents an alternative to synthesis of analogue derivatives after the remotion of CO thermally, photochemically or by chemical oxidation. Once the CO is removed from the

metal center, it will be of special interest the synthesis of nitrile, amide, nitric oxide and H₂O derivatives.

The thiolate complex **1** was treated with CO for 20 minutes and then stirred for 20 hours at 70 °C in degassed methanol to yield (bmmp-TASN)RuCO derivative. Interestingly, the bmmp-TASN ligand has rearranged in this complex to generate an N₂S₂ donor plane with a single S (thioether) donor trans to the variable coordination site alike to the NHase and SCNase active sites, Figure 46 and 47.

Figure 46. Synthesis of (bmmp-TASN)RuCO and ligand frame rearrangement.

(bmmp-TASN)RuCO has
the same N_2S_3 donor
arrangement as NHase

$[(bmmp-TASN)FeNO]^+$ has
the typical ligand
arrangement of our ligand

Figure 47. NHase enzyme and $[(bmmp-TASN)FeNO]^+$ analogue of **11**.

The CO-bound derivative of **1** is room temperature stable, making it easy to isolate as a yellow solid. The UV visible spectrum of **11** shown in Figure 48 is dominated by a band at 331 nm. As the solution is compared with its precursor analogue **1**, the band at 438 nm is absent. The identity of the product **11** as a ruthenium-bound CO species is supported by the appearance in IR of an intense band at 1888 cm^{-1} , Figure 49. A band in this region is characteristic of Ru(II)-CO species.^{147,148} The ν_{CO} stretching frequency 1888 cm^{-1} indicates strong π -back-bonding, as compared to free CO 2155 cm^{-1} . The two thiolates stabilize the π -interaction between the ruthenium(II) center and CO.

Figure 48. UV visible of (bmmp-TASN)RuCO.

Figure 49. FT-IR of (bmmp-TASN)RuCO.

The displacement reaction and rearrangement of the compound (bmmp-TASN)RuCO can be explained for two different routes. The first, Scheme 6, it is a

dissociative mechanism in which PPh_3 is displaced making a pentacoordinate or methanol coordinate complex. Binding of the CO causes a structural rearrangement of the ligand frame by electronic effect. The second route, Scheme 7, is an associative or interchange mechanism. The coordination of CO to the octahedral complex initiates displacement and elimination of the PPh_3 with structural rearrangement of the complex.

Scheme 6. Dissociative mechanism for the formation of compound **11**.

Scheme 7. Associative or interchange mechanism for the formation of compound **11**.

It is expected that the differences in the overall ligand field strength will weaken CO coordination upon sulfur oxygenation. We expect to observe the weakening of the CO through X-ray crystallography and the IR stretches shift around 1900-1940 cm^{-1} . The complexes will be investigated by Davinder Kumar.

Structural description of the (bmmp-TASN)RuCO (11**)**

Yellow plate crystals of **11** in the space group $P 1 21/n 1$ were obtained upon slow evaporation of methanol solutions of the complex under air free conditions. The final unit cell parameters: $a = 9.2404(2) \text{ \AA}$, $b = 20.7973(4) \text{ \AA}$, $c = 10.6722(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 94.916(2)^\circ$, $\gamma = 90^\circ$, $V = 2043.40(8) \text{ \AA}^3$, $D_{\text{calc}} = 1.553 \text{ Mg/m}^3$, $Z = 4$. Complex **11** contains a six-coordinate ruthenium(II) ion in an $\text{N}_2\text{S}_3\text{C}$ donor set with one thioether (S1), two thiolate (S2 and S3), sulfur donor, Figure 50. The TASN ligand backbone (N1, N2, S1) occupies one face of a distorted octahedron. The three sulfur donors occupy other face of the octahedron. The thiolate sulfur S2 and S3 are trans to the nitrogen N1 and N2 respectively. The thioether S1 is trans to the C15 of the CO.

The ν_{CO} stretch of **11** suggests that there is significant π back-donation to the CO ligand from the Ru, reflecting the strong electron donating properties of the thiolate ligands and the effect of the thioether trans to the CO. This π back donation is reflected in the small reduction in the bond distance between the metal center and atoms of the equatorial plane N_2S_2 . As we observe in the Figure 50 compound **11** has a distorted octahedral configuration with the two thiolate S2 and S3 ligands in cis configuration and the thioether trans to the carbon monoxide ligand, This arrangement of atoms is altered from the analogue precursor compound **1**.

Table 5. Selected bond lengths determined by x-ray of compound **11**.

C15-O1	1.158(3)	Å
Ru1-C15	1.822(2)	Å
Ru1-N1	2.1354(19)	Å
Ru1-N2	2.1215(19)	Å
Ru1-S1	2.4379(6)	Å
Ru1-S2	2.3854(6)	Å
Ru1-S3	2.3854(6)	Å

Figure 50. ORTEP representation of (bmmp-TASN)RuCO (**11**).

The bond distances presented in Table 5 indicate an almost symmetric bond distance in the square planar N_2S_2 . The ligand rearrangement that is observed in the complex (bmmp-TASN)RuCO is proposed in the reactivity cycle upon nitrile coordination. The previous reported coordination of nitrile, water, and amides of [(bmmp-TASN)Fe]OTf suggest similar binding may occur for the (**1-4**) upon PPh_3 dissociation. This supposition is supported by the catalytic activity and +ESI-MS of the product of the catalysis as it will be described in the next section.

Hydrolysis studies of **1**, **2** and **3**.

Hydrolysis activity was investigated through the evaluation of a series of substrate candidates to test the activity of the family of S-oxygenated **1**, **2** and **3**. The substrates investigated include *p*-nitrophenylacetate, which was followed by UV-visible, acetonitrile, acrylonitrile and benzonitrile with the exception of the ester all reactions were followed by 1H NMR, FT-IR and GC-MS. The results support that the phosphine lability

at elevated temperatures is required for hydrolysis activity. At this time, it remains unclear if the coordinated substrate is water or nitrile.

Hydrolysis of the *p*-nitrophenylacetate

We began our hydrolysis studies with the *p*-nitrophenylacetate. This ester is excellent candidates for hydrolysis test since it is relatively easy hydrolyze. The concept being that if the ruthenium complexes cannot hydrolyze the ester, it will be less probable to hydrolyze a nitrile. The use of this ester provides us with a versatile strategy to screen our complex in a short time frame and with the use of a minimal amount of complex in each trial. This hydrolysis trial has the advantage that use tractable compound in UV-Visible, the *p*-nitrophenylacetate and its product of hydrolysis the *p*-nitrophenol. The absorption bands for both structures are well resolved and significantly separated, the *p*-nitrophenyl acetate compound has a band at 276 nm, *p*-nitrophenolate at 317 nm and *p*-nitrophenol at 405 nm.

The initial studies involve the test of hydrolysis activity at low temperature; a mixture of **1** (5 mg, 7 μ mol) and 4-nitrophenyl acetate (16 mg, 0.088 mmol) in MeOH/H₂O (8.2 mL/8.2 mL) and citrate buffer (1 M, pH=4.8, 1.8 mL) was stirred at 4°C and at room temperature for 5 days. The reaction was monitored by UV-visible spectroscopy, and results were compared to a control sample with no added metal complex. The same methodology was applied to solutions containing **2** and **3**. From these studies with the *p*-nitrophenylacetate, we concluded that the hydrolysis reaction at 4 °C and at room temperature show not reactivity for the three compounds, indicating the necessity to raise the temperature to release the triphenylphosphine and expose the metal center to the substrate.

The next hydrolysis reactions were performed at 50° C, following the same basic procedure but with pipes buffer at pH = 6.75. The substrate was added to the solution, and the UV-visible absorption spectra were recorded at regular intervals. Hydrolysis of *p*-nitrophenylacetate in the presence of **3** is confirmed by the changes in the UV-visible spectrum. Spectra were recorded every 3000 seconds for 10 hours. These results are shown in the figure below.

Figure 51. Hydrolysis of *p*-nitrophenylacetate in the presence of **3** is confirmed by the changes in the UV-visible spectrum. Spectra were recorded every 3000 s. Control experiments in the absence of **3** do not show hydrolysis.

As it can be observed from the figure 51, the *p*-nitrophenylacetate at 276 nm is converted to *p*-nitrophenolate at 317 nm and *p*-nitrophenol at 405 nm. The presence of an isosbestic point at 292 nm suggests that the substrate is being hydrolyzed to the product

without intermediate as it is not observed any other additional band. These experiments show that compound **3** can hydrolyze at least 2 equivalents of substrate over a period of 10 hours. Control experiments in the absence of **3** do not show hydrolysis. Condition improvements like pH, temperature or increasing of substrate concentration have not been tested.

This preliminary screening was designed to prove the hydrolytic catalytic activity of compound **3**. The kinetic data indicate low turnover and for this reason we decided to not to pursue further studies. However the result obtained in this experiment show that compound **3** is a promising candidate for further hydrolysis studies.

Nitrile hydrolysis

The polarized S-O bond of the sulfenate has been suggested as a nucleophile for nitrile hydrolysis.⁸⁰ Previously, Chottard *et al.* reported the slow, catalytic (18 turnovers after 17 h) hydrolysis of acetonitrile in a coordinatively saturated, exchange-inert cobalt(III) sulfenate.⁸⁹ Attempts to hydrolyze acetonitrile with **3** following the same protocol yielded no quantifiable acetamide at 4° C. This may be attributed to steric influences of the PPh₃ ligand or the reduced Lewis acidity of ruthenium(II) in **3** as compared to cobalt(III) in the Chottard system or mainly due to the coordination of the PPh₃ to the metal.

The initial trials of hydrolysis of CH₃CN involve the use of a mixture of **1** (5 mg, 7 µmol) and 1,4-dimethoxybenzene (internal reference) (7 mg, 0.050 mmol) in CH₃CN (0.5 mL) and an HOAc/NaOAc (1 M, pH=4.8, 0.5 mL) or PIPES (1 M, pH = 7.0, 0.5 mL) buffer, solution that was stirred at 4 °C for 5 days. After chloroform extraction, the organic soluble residue was dissolved in CD₃OD for ¹H and ¹³C NMR analysis. The same

procedure was applied to **2** and **3**. As mentioned above acetamide was not detected in ^1H or ^{13}C NMR.

The compounds **1-3** were investigated in solution to probe their potential hydrolytic activity. Metal complex that promoted hydrolysis requires dissociation of the phosphine to provide an open coordination site for substrate binding or direct participation of the S-oxygenate moieties in the hydrolysis. Structural studies (*vide infra*) reveal an increased Ru-P bond distance as a function of S-oxygenation suggesting the phosphine may become labile in solution generating a transient five-coordinate intermediate.

Solutions of **2** and **3** in 1:1:1 mixture of acetonitrile, methanol, and PIPES buffer (pH = 7.0) yield small quantities of acetamide after stirring under inert conditions for 5 days at 25 °C. The identity of the acetamide was confirmed by ^1H and ^{13}C NMR, Figure 52, following evaporation of solvent and extraction of soluble products into CDCl_3 . Attempts to quantify acetamide using 1,4-dimethoxybenzene as an internal standard yielded inconsistent results.¹⁴¹ In all cases, the acetamide integration was significantly greater than the standard, but proportional to free PPh_3 . No acetamide is observed for **1** under identical conditions. In contrast, the acetonitrile hydrolysis activity of **2** and **3** is consistent with partial PPh_3 dissociation in solution. It should be noted that exchange inert Co(III) sulfenate complexes have been reported to hydrolyze nitriles via a ligand-centered mechanism in buffers at pH=4.8.⁸⁹ However, under these conditions no hydrolysis was observed for **1-3**. Further studies are underway to exchange the coordinated phosphine for more labile ligands. Complex **4** degraded to an intractable orange product upon the addition of water precluding catalytic attempts.

Figure 52. ^1H NMR of CDCl_3 extract after acetonitrile hydrolysis trial with **3** reveals peaks at 1.98 and 5.34 ppm associated with acetamide at 25 °C.

Further catalytic studies involve the use of higher temperature to evaluate hydrolysis activity; as result of these studies we detect the formation of acetamide in compound **3** at 75 °C as we observe in the Figure 53. The temperature in this experiment is above the 50 °C required to exchange the triphenylphosphine. This result strongly suggests the necessity to expose the metal center to generate any catalytic activity.

The experiment was performed in a NMR J-young tube in a mixture of 500 μl of MeOH deuterated and 200 μl D_2O . It was used 2.2 mg (3.0 μmol) of compound **3** and 2.2 mg (6.7 μmol) of $(\text{C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-$ as reference. The substrate was acetonitrile 5 μL (94.6 μmol). The mixture MeOH and D_2O was used to help to solubilize the compound **3**. The reference $(\text{C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-$ was integrated in the region 0.94 ppm to 1.01 for the equivalent of 3 protons. The experiment was performed for 11 day in an oil bath. The sample was only removed from the bath for ^1H NMR determinations of 20 minutes. The ^1H NMR was performed with a relaxation delay of 1.0 seconds, 256 repetitions with a total time of 15 minutes, at 25 °C in a 400 MHz instrument.

Unfortunately, besides being a positive test of nitrile active complex the yield obtained indicates 2 turnovers after 11 days for the hydrolysis reaction and for this reason it was required to evaluate other nitriles that are easier to hydrolyze.

Figure 53. Hydrolysis of acetonitrile to acetamide by compound **3**.

The two other substrate candidates that we decided to analyze were acrylonitrile and benzonitrile; both compounds are easy to hydrolyze for NHases models. Shearer *et al* in a recent publication reported 58 turnovers at 25 °C in 18 hours for the formation of acrylamide. The acrylonitrile unfortunately present an inconvenient, it is thermal unstable and polymerize around 50 °C, as result of the polymerization during the hydrolysis studies at 75 °C, it was observed a decrease in the starting material faster than acrylamide formation. The hydrolysis of acrylonitrile to acrylamide is observed for **3** (2.2 mg, 3 μmol) in a 5:2 mixture of MeOH:Water (Total volume 0.7 mL). Using as reference 3.7 mg, 11.2 μmol $(\text{C}_4\text{H}_9)_4\text{N}^+\text{BF}_4^-$ at reflux temperature (75°C) and 50:1 substrate 10 μL , 150

μmol of acrylonitrile to catalyst. No acrylamide was detected in control reactions. After 2850 minutes the hydrolysis stops with 25 turnovers as it can be observed in Figure 54.

Figure 54. ^1H NMR in CD_3OD of acrylonitrile hydrolysis trial with **3** reveals groups peaks at 5.84 q and 5.76 dd ppm associated with CH_2CHCN and $\text{CH}_2\text{CHC}(\text{O})\text{NH}_2$.

The other candidate, benzonitrile is easy to hydrolyze in a matrix of water and ruthenium complex at $100\text{ }^\circ\text{C}$ and $124\text{ }^\circ\text{C}$. The results of these studies indicate an hydrolyze activity in the three compounds **1-3** with the highest activity in compound **3**. In the Figure 55, it is presented the FT-IR of the product isolated after the reaction at $100\text{ }^\circ\text{C}$ for compound **3** with 9 ± 1 turnovers. The FT-IR matches the spectrum of a pure benzamide. Compound **2** shows 10 ± 1 turnovers and compound **1** show 6 turnovers. The protocol involve in this reaction required the use $1200\text{ }\mu\text{l}$ benzonitrile and $2000\text{ }\mu\text{l}$ of D_2O using a reaction flask at $100\text{ }^\circ\text{C}$ for 5 days.

Figure 55. FT-IR of benzamide isolated from hydrolysis of benzonitrile in the presence of **3**.

Additional trials performed at 124 °C indicate 65 ± 1 turnovers for compound **1**, 86 ± 9 for compound **2** and 85 ± 11 for compound **3**. It was observed that the ruthenium complex **1** has the low solubility in polar solvents and at the same time the low reactivity with 65 turnovers by 18 hours at 124 °C. The likely reason for this reactivity is the competition between the PPh_3 substrate and the benzonitrile or water. In presence of air the activity of **1** drop to 29 ± 2 turnovers. This result can be explained based on the sulfur oxygenation of the complex and water sensitivity of complex **4**. The number of moles of catalyst used in these trails was 2.7×10^{-7} , the number mmoles of benzonitrile substrate was 4.9 and the number of mmoles of D_2O 82.9. The quantification was performed by GC-MS. The calibration curve is presented in the Figure 56.

Figure 56. GC-MS calibration curve for benzamide.

Preliminary results of +ESI-MS in the product of the benzonitrile hydrolysis reaction with compound **1** indicate a nitrile bound mechanism. The mass spectral analysis of an isolated green residue product of the hydrolysis of benzonitrile with complex **1** displays a m/z peaks at 574.15 and 590.16 consistent with (bmmp-TASN)RuNCPh and (bmmp-TASN)RuNH₂C(O)Ph, respectively, suggesting discreet substrate and product derivatives Figure 57, further research is underway to isolated and fully characterized these new compounds.

Figure 57. +ESI-MS of benzonitrile hydrolysis reaction with compound **1**.

Summary

Studies with (bmmp-TASN)RuPPh₃ and S-oxygenates **2-3** reveal significant benzonitrile hydrolysis at moderate temperatures 124 °C. Benzonitrile is an ideal substrate due to its product the benzamide is easily isolated by sublimation from the crude reaction mixture and because after the hydrolysis reaction the benzamide precipitate from the reaction matrix. The sulfenate/sulfinate complex **3** shows up to 85 ± 11 turnovers in 18 hours. Control reactions without Ru catalyst yield 7 ± 2 Turnovers. Turnovers numbers have not yet been optimized, but some hydrolysis is also observed for (**1-2**) We have also examined hydrolysis of acrylonitrile, which offer the advantage of in situ reaction monitoring by ¹H NMR. As shown in Figure 54, the relative intensity of the acrylamide vinyl protons increases with time, when compound **3** promoted hydrolysis. It

is expected the hydrolysis proceeds via a nitrile- or water-bound complex following thermally induced PPh_3 dissociation. As mentioned in this chapter the thermally dissociation of PPh_3 for phosphine exchange has an inverse correlation with the oxygenation of thiolates, at 100 °C, for the thiolate ligand and 50° C for sulfenate/sulfinate derivate for phosphine exchange.

CHAPTER V

CONCLUSIONS AND FUTURE DIRECTIONS

The research in the area of nitrile hydratase has been fruitful in the last 20 years. From the beginning, this area of study has been oriented in both industrial and academic direction. It was remarkable that nitrile hydratase was the first enzyme used in a biotechnological process; the transform of acrylonitrile to acrylamide. It was this process that demonstrated the technological advantage of the nitrile hydratase enzyme to produce acrylamide at industrial level. This process cannot be accomplished by chemical means due to the highest temperatures of 200 to 300 °C and higher pressures required in the chemical hydrolysis. Since under these conditions acrylonitrile will polymerize and decompose.

It was the NHase, with its low temperature range of hydrolysis activity between 25 to 35 °C, that allowed the industrial synthesis of acrylamides. This technological breakthrough and the unusual active center of the NHase drove the research in academia. At the academic level, the NHase represent an ideally case of study to understand metal thiolate reactivity and post-translational modifications.

The main targets of study in the area of metal thiolate reactivity and NHase are the understanding of the metal thiolate reactivity with oxygen, the reproduction of the

synthetically challenge sulfenate/sulfinate active site of the NHase enzyme, the study of the NHase mechanism and the designing of a more efficient NHase synthetic model.

As a bioinorganic synthetic chemistry group, we took the challenge to study the NHase system and respond some of the unsolved question in the area. This thesis was oriented to synthesize the best functional synthetic NHase model in the research community. The conclusion and future direction of this research are presented in the next paragraphs.

Synthesis of (bmmp-TASN)RuPPh₃ and sulfur oxygen derivatives

In this research we reported the synthesis of (bmmp-TASN)RuPPh₃ (**1**) and its derivatives compounds under limiting dioxygen conditions. The family of oxygen derivatives include (bmmp-O₂-TASN)RuPPh₃ (**2**), (bmmp-O₃-TASN)RuPPh₃ (**3**), and (bmmp-O₄-TASN)RuPPh₃ (**4**).^{129,141} The sulfenate/sulfinate (RSO[•])/(RSO²⁻) donor set of **3** mimics the unusual post-translational modification of the NHase and SCNase active sites. The asymmetric sulfur-oxygenate **3** represents one of only three sulfenate/sulfinate derivatives prepared by direct reaction with dioxygen.^{79,108} High yields of **3** were obtained by limiting the quantity (5 equivalents) and duration (12 hours) of dioxygen exposure. The sulfur oxygen derivate are oxygen sensible and their synthesis required a new synthetic approach.

O₂ delivery an innovative approach for the synthesis of sulfur oxygen derivatives

The typical approach to prepare sulfur-oxygenated mimics of NHase or SCNase involves the reaction of metal-thiolate precursors with O-atom transfer agents such as H₂O₂, *N*-sulfonyloxaziridine, (1*S*)-(+)-(10-camphorsulfonyl)oxaziridine, or urea hydrogen peroxide.^{80,82,88,89,112,118} These efforts have been successful for the isolation of

sulfenate,^{80,89,112,118} sulfinate,^{88,89} and a mixed sulfenate/sulfinate complex with η^2 -sulfenate coordination.⁸² A major advantage of O-atom transfer agents is the ability to quantitatively add oxidizing equivalents at controlled rates. However the application of this approach in our system was not successful. A new synthetic strategy was applied for the synthesis of the sulfur oxygenated reactive products. Less well developed are reactions employing dioxygen, which is the proposed reagent in the enzymatic systems.^{42,46,56} While several sulfinate complexes have been reported upon O₂ exposure of thiolate precursors,^{82,116,119-127} isolation of sulfenate^{120,128} or mixed sulfenate/sulfinate complexes from O₂ are rare due to the reactivity of the sulfenate.^{79,108,129,142,143} Our strategy for the synthesis of a family of sulfur oxygen derivative involves the quantitative delivery of oxygen using an oxygen transfer bulb. The optimizations of the conditions for a sequential oxygenation were obtained with the use of FT-IR and TLC.

As part of the sulfur oxygenation study, we report this innovative approach to synthesize sulfur oxygen derivatives. A family of sulfur oxygenated derivatives has been prepared through the controlled oxygenation of **1** under limiting O₂ conditions. The key synthetic features of our approach include restricted quantities of O₂ and short reaction times. Prior studies were largely conducted open to air or in oxygen saturated solutions under an O₂ atmosphere for hours or days. By fixing the quantity of O₂ and the duration of the reaction, conditions were optimized to reproducibly obtain high yields of **2**, **3**, or **4** without the need for O-atom transfer reagents or purification by column chromatography. The S-oxygenation of **1** proceeds in a series of stepwise additions. Rapid addition of O₂ to **1** yields **2**. This step is promoted by the t_{2g}^6 electron configuration of Ru(II). As reported previously, the π and π^* interactions between thiolate sulfur donors and t_{2g} -rich

metal ions increase the covalency of the metal-sulfur bond and promote sulfur oxygenation. The second oxygenation step, **2** to **3**, proceeds significantly more slowly than the first. This is attributable, at least in part, to steric interactions between the remaining thiolate and PPh₃. Further oxygenation of **3** to **4** is further hindered by the PPh₃ and occurs only on longer time scales. Each S-oxygenate, **2-4**, is stable in acetonitrile and methanol solutions in the absence of O₂. Complex **4** degrades in the presence of water. This approach has yielded a unique “family” of complexes, **1-4**, that differ only in the degree of S-oxygenation. Although the number of reported S-oxygenates is growing, families containing three or more oxygenated derivatives are scant.¹⁴⁴

Relevance of the oxygenation study of metal-thiolate complexes

With the synthesis of the family of sulfur oxygen derivatives, this thesis offers insight into the controlled sulfur oxygenation of metal thiolates and the resulting changes in the electronic structure. The relevance of this study is not only subscribed to the NHase or SCNase systems but also to post-translational modification of cysteines during redox signaling and oxidative stress. The cysteine residues, thiolates, suffer oxidative modification that will lead to functional alterations in the proteins. This modification has a broad biological impact in health and diseases from molecular to the cellular and organismal level. In our study we observe and characterize the effect of the oxidation with O₂ of two thiolates in a NHase model system using for a first time a family of sulfur oxygen derivatives to understand the effect of this oxidation. Until now the oxidative modification in cysteine has been reviewed from a biochemistry approach with reactive oxygen species, in cellular redox systems and in apoptosis¹⁴⁹ but not in a synthetic catalytic center. One of the results of this oxidative modification in our NHase synthetic

model is the improvement in catalytic activity in a 25% for the NHase analogue with respect to the thiolate derivative. It can be speculated that the activation of the NHase is due to the effect of sulfur oxygenation and the elongation of the Metal-NO bond distance and subsequent exposure of the metal to the substrate.

Low spin state configuration leads to metal-thiolate oxygenation complex

Through our studies of the ruthenium dithiolate oxygen reactivity we confirm the previous hypothesis of the Grapperhaus group that “ t_{2g} -rich” low-spin complexes favor sulfur oxygenation. This hypothesis is supported by the reactivity of **1** a ruthenium(II) low spin complex with O_2 . Further, partial sulfur oxygenation is achievable using limited O_2 conditions, as demonstrated by **2** **3** and **4**. In **1**, the steric bulk of PPh_3 slows oxygenation beyond **4** but does not prevent it, as demonstrated under excess O_2 conditions. These results suggest that asymmetric oxygenation of nitrile hydratase and thiocyanate hydrolase may also be facilitated by limited O_2 at the active site without the necessity for single O-atom-transfer reagents. Structurally sulfur oxygenation shortens the M-S bond while lengthening the metal-ligand bonds to π acceptors. In combination with the previously documented labilizing effect of the trans-thiolate,^{142,143} sulfur oxygenation may promote ligand exchange. It is also expected to enhance coordination of π donors, such as HO^- , and may help to discriminate substrate coordination.

Study of a pentacoordinate system that allow substrate exchange

Based on a systematic synthesis design, the pioneering Ni- and Pd-dithiolate systems developed by Darensbourg provide a benchmark for completeness, because they offer no prospects to probe the effects of S-oxygenation at a variable ligand site. To face this challenge we used a pentacoordinate ligand designed for the Grapperhaus group to

allow us exchange the six coordinate substrate. The analysis of the structural parameters of **1-4** reveals a systematic increase in the Ru-P bond distance as a function of S-oxygenation. This trend is reproduced computationally by density functional theory calculations providing insight into the potential of S-oxygenation to regulate substrate/product binding at the NHase active site and exchange substrates.

The ligand bmmp-TASN has been employed to model the donors at active sites of NHase and SCNase. As in the enzymes, ligand coordination positions two reactive thiolate donors on the same octahedral face as a sixth, variable ligand. The t_{2g}^6 electron configuration of Ru(II) in **1-3** reproduces key electronic features of the low-spin t_{2g}^5 and t_{2g}^6 configurations of Fe(III) and Co(III) at the enzyme active sites. Further, as noted in the current thesis, the Ru-S π^* interactions stabilizes Ru-P σ -bonding. Upon oxygenation, the Ru-S π^* interaction is relieved, weakening the Ru-P bond as evidenced by the direct correlation between the oxygenation level and Ru-P bond distance. These results allow us postulate our complexes **1-3** as ideal candidates to analyze H₂O, nitriles and NO derivatives. These substrates are postulated as part of the NHase mechanism.

Sulfur oxygenation X-ray absorption studies in a ruthenium NHase mimic

NHases require oxygenated cysteinate residues to be catalytically activity. The functional reasons for these post-translational modifications are on debate. In this thesis, It was investigated the influence of sequential thiolate oxygenation on a series of Ru(II) complex **1**, **2** and **3**. It had previously been observed by X-ray and by computational calculations that upon sequential oxygenation the Ru-P bond-length increased.

Through the use of X-ray absorption spectroscopy it has been confirmed that the bonding in these complexes is largely dominated by S-Ru interactions, with the Ru-P

and Ru–N interactions contributing to a lesser degree. Upon oxygenation the bonding interactions between the oxygenated thiolates and the Ru-center decreases. As this occurs the covalency of the complex decreases overall and the charge on the Ru-center increases as a result; the atomic charge on Ru increases from -0.073 in **1** to +0.0831 in **2** to +0.263 in **3**. In terms of hard/soft acid/base chemistry the Ru-center is becoming a harder Lewis-acid. Thus, bonding between the progressively harder Ru-center and the soft PPh₃ ligand would be expected to become weaker, which is what is observed.

Compound 3 mimic the asymmetric environment of the catalytic center of the NHase

One of the most remarkable result in this thesis was the synthesis of the sulfenate/sulfinate (bmmp-O₃-TASN)RuPPh₃ compound **3**. The compound **3** provide us with an unusual synthetic model with a mixed S-oxygenation environment observed at the active site of NHase and SCNase. This model complex situates the Grappaerhus' group in an ideal position to investigate the effects of the sulfur oxygenation in a NHase mimic with catalytic activity. To our knowledge, only three mixed sulfenate/sulfinate complexes have been structurally characterized. Of these, only one is isolated from aerobic oxidation, but that complex is coordinative saturated and not provide an exchange substrate position as consequence it is not a useful mimic. This complex is a NHase model complex reported by Kovacs, that is isolated via H₂O₂ oxidation of the thiolate - sulfinate precursor, but the generated sulfenate ligand is coordinated in a side-on, η^2 -fashion that saturates the metal coordination sphere and prevents further reactivity studies as mentioned in chapter one. We state that our (bmmp-O₃-TASN)RuPPh₃ complex best mimics the S-oxygenation of NHase and SCNase as: it is isolated directly from aerobic

oxidation; it maintains η^1 -coordination of the sulfenate ligand and specially because it is built on a pentadentate ligand framework that allows a variable coordination site cis to the S-oxygenates. Finally this model is hydrolytically active and it is functional catalyst.

Sulfur oxygen derivatives 2 and 3 facilitate phosphine exchange

Notably, the increase in bond length in the family of sulfur oxygen derivatives correlates with the phosphine exchange reactivity with compound **2** and **3** at 50 °C in methanol and for compound **1** at 100 °C chlorobenzene. It is expected that the same M-L bond distance trend would be observed for Fe(III) and Co(III). In support of this, Mascharak et al. have shown that S-oxygenation of an iron-thiolate facilitates photodissociation of NO. Our series of complexes confirms the observation for that isolated example to show a direct correlation between the number of O-atoms and the M-L bond distance. These results are consistent with the notion that sulfur oxygenation increases substrate/product lability as it is the case of exchange of triphenylphosphine by methyldiphenylphosphine. Synthesis of a thiolate derivative is accomplished with the use of CO in methanol at 70 °C.

(bmmp-TASN)RuPPh₃ and sulfur oxygen derivatives are hydrolysis active catalyst

The hypothesis of hydrolysis activity has been investigated through the evaluation of a series of hydrolysable substrate candidates, such compounds were screening to test its activity, and between them we can mention *p*-nitrophenylacetate with the UV-visible studies, acetonitrile, acrylonitrile and benzonitrile with ¹H NMR and FT-IR studies.

Studies with (bmmp-TASN)RuPPh₃ (**1**) and S-oxygenates (**2-3**) reveal significant benzonitrile hydrolysis at moderate temperatures 124 °C. Benzonitrile is an ideal substrate due to its product the benzamide is easily isolated by sublimation from the crude reaction mixture and because after the hydrolysis reaction the benzamide

precipitated from the reaction matrix. The sulfenate/sulfinate complex (**3**) shows up to 85 ± 11 turnovers over 18 hours. Control reactions without Ru catalyst yield 7 ± 2 Turnovers. Turnovers numbers have not yet been optimized, but some hydrolysis is also observed for (**1-2**). Compound **2** generates 86 ± 9 turnovers, and compound **1** generates 65 ± 1 turnovers.

We have also examined hydrolysis of acrylonitrile, which offer the advantage of in situ reaction monitoring by ^1H NMR. The relative intensity of the acrylamide vinyl protons increases with the time, when compound **3** promoted hydrolysis. It was reported 25 turnovers after 2850 minutes. It is expect the hydrolysis proceeds via a nitrile- or water-bound complex following thermally induced PPh_3 dissociation. As mentioned above the thermally dissociation of PPh_3 for phosphine exchange has an inverse correlation with the oxygenation of thiolates, at 100°C for the thiolate and at 50°C for sulfenate/sulfinate derivate for phosphine exchange.

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Figure A1. FT-IR of $\text{O}_2 + (\text{bmmp-TASN})\text{RuPPh}_3$ after 96 hours as KBr pellets.

Figure A2. Cyclic voltammogram of **1** in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Potentials referenced to Fc/Fc^+ .

Figure A3. Cyclic voltammogram of **2** in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Potentials referenced to Fc/Fc^+ .

Figure A4. Cyclic voltammogram of **3** in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Potentials referenced to Fc/Fc^+ .

+TOF MS: 0.017 to 0.183 min from 07211020.wiff
a=3.55581864568315810e-004, t0=4.64411847614901490e+001

Max. 1010.9 counts.

+TOF MS: 0.017 to 0.183 min from 07211020.wiff
a=3.55581864568315810e-004, t0=4.64411847614901490e+001

Max. 1010.9 counts.

Figure A5. +ESI MS for compound 8.

+TOF MS: 0.083 to 0.167 min from 07211021.wiff
a=3.55581864568315810e-004, t0=4.64411847614901490e+001

Max. 469.3 counts.

+TOF MS: 0.083 to 0.167 min from 07211021.wiff
a=3.55581864568315810e-004, t0=4.64411847614901490e+001

Max. 469.3 counts.

Figure A6. +ESI MS for compound **9**.

+TOF MS: 0.917 to 1.417 min from 01251029.wiff
a=3.55591072036392090e-004, t0=4.71856293243654360e+001 R;

Max. 40.0 counts.

Figure A7. +ESI MS for compound (bmmp-O₂-TASN)Ru(Me(PPh₂)₂).

+TOF MS: 0.417 to 1.783 min from 01251032.wiff
a=3.55603402798775250e-004, t0=4.71856293243654360e+001

Max. 2.9 counts.

Figure A8. +ESI MS for compound (bmmp-O₃-TASN)Ru(Me(PPh₂)₂).

TABLE A1 Optimized coordinates of **1** (B3LYP)

C	-2.140479	-3.835227	1.847745
C	0.297767	-3.589939	2.173125
C	-0.917465	-2.987333	1.434361
C	2.039153	0.854411	4.097420
C	3.301908	0.320181	4.360255
C	-0.613516	-3.069885	-0.084967
C	-3.571911	-1.364095	-0.193658
C	-3.318107	2.447163	2.663376
C	-2.745212	-2.280445	-1.087370
C	-3.703127	0.811114	0.848766
C	1.492245	0.781115	2.816152
C	4.025498	-0.275513	3.327261
C	-3.123587	2.206678	1.150846
C	2.211772	0.181743	1.769189
C	3.487606	-0.337598	2.039182
C	-3.848526	3.343469	0.402970
C	-0.662705	-2.109464	-2.335331
C	-3.636171	0.592262	-1.650032
C	2.845440	-2.209687	-0.493640
C	3.486717	-3.120576	-1.338171
C	2.461357	-0.937758	-0.951386
C	-1.086656	-0.949513	-3.247982
C	-2.620699	1.403362	-2.453635
C	3.751160	-2.784448	-2.666199
C	2.218108	1.851854	-0.526729
C	3.614874	2.014075	-0.466673
C	2.738502	-0.615193	-2.293366
C	1.449893	2.908704	-1.028257
C	3.372635	-1.526169	-3.140168
C	4.220992	3.189502	-0.903505
C	2.057779	4.091449	-1.463902
C	3.441851	4.235417	-1.407232
H	-2.299349	-3.745959	2.926897
H	-1.971161	-4.898038	1.618775
H	0.098290	-3.629604	3.248540
H	-3.071905	-3.536418	1.361729
H	0.509947	-4.614920	1.830342
H	1.467904	1.322992	4.894432
H	3.720573	0.369953	5.362337

H	1.190665	-2.976085	2.033020
H	-3.407762	-1.628208	0.848603
H	-4.383546	2.409366	2.938862
H	-0.862292	-4.081357	-0.454653
H	-2.779504	1.696753	3.249035
H	-2.978713	-3.325520	-0.850365
H	-3.474561	0.174661	1.704052
H	-4.642103	-1.489406	-0.429563
H	-4.801168	0.872349	0.747660
H	0.456738	-2.926496	-0.228050
H	-2.933225	3.433839	2.940733
H	0.508410	1.195875	2.621763
H	5.013173	-0.688708	3.516842
H	-3.032985	-2.141289	-2.132114
H	-4.911631	3.379880	0.684406
H	2.655485	-2.494394	0.535271
H	-0.924170	-3.057785	-2.836868
H	-3.965862	-0.254257	-2.259305
H	3.781997	-4.092570	-0.951170
H	-4.527764	1.209741	-1.484632
H	4.076384	-0.791703	1.249360
H	-3.398617	4.306405	0.665084
H	0.420301	-2.088856	-2.214687
H	-3.790870	3.248932	-0.684601
H	-2.114866	-1.045630	-3.607629
H	-2.462406	2.389073	-2.010081
H	4.238430	1.218833	-0.071383
H	-0.437947	-0.944019	-4.128850
H	4.251518	-3.491304	-3.322654
H	-2.967276	1.531934	-3.485397
H	0.370286	2.828873	-1.048295
H	2.468219	0.363730	-2.678027
H	5.301866	3.290938	-0.846169
H	3.580824	-1.245683	-4.169781
H	1.437986	4.901281	-1.840247
H	3.913369	5.155006	-1.744648
N	-1.264039	-2.054535	-0.972994
N	-3.155823	0.058210	-0.330122
P	1.447078	0.250397	0.076453
S	-1.121851	-1.204769	1.993296
S	-1.291696	2.262745	0.765757
S	-0.914853	0.716503	-2.420997
Ru	-0.909045	0.006284	-0.139162

TABLE A2 Optimized coordinates of **1** (BP86)

C	-2.131546	-3.825739	1.859745
C	0.309585	-3.548301	2.217010
C	-0.905619	-2.975099	1.447133
C	1.990536	0.844279	4.120143
C	3.261510	0.308356	4.385356
C	-0.579889	-3.067921	-0.068478
C	-3.546896	-1.389451	-0.206361
C	-3.325452	2.437085	2.649352
C	-2.711305	-2.294095	-1.105908
C	-3.706260	0.794377	0.827868
C	1.442710	0.773219	2.830520
C	3.993437	-0.285406	3.346251
C	-3.131202	2.191428	1.133488
C	2.171548	0.174794	1.778637
C	3.455294	-0.345529	2.048944
C	-3.838679	3.334896	0.372582
C	-0.608018	-2.117080	-2.335872
C	-3.618647	0.569514	-1.683730
C	2.842165	-2.203098	-0.501847
C	3.493876	-3.107861	-1.358328
C	2.447561	-0.922092	-0.952486
C	-1.034720	-0.960764	-3.253247
C	-2.597980	1.392660	-2.471701
C	3.757891	-2.757005	-2.691434
C	2.178995	1.862695	-0.512140
C	3.582600	2.023532	-0.435675
C	2.725832	-0.584094	-2.299331
C	1.409630	2.926892	-1.017881
C	3.369853	-1.489393	-3.157720
C	4.196185	3.208867	-0.861974
C	2.025036	4.119049	-1.441598
C	3.416991	4.263596	-1.369297
H	-2.320349	-3.700518	2.939824
H	-1.940753	-4.902089	1.670682
H	0.091607	-3.570727	3.298641
H	-3.061708	-3.554919	1.334987
H	0.544624	-4.584647	1.894622
H	1.412725	1.313907	4.924677
H	3.681700	0.356470	5.397016
H	1.201331	-2.915580	2.078293

H	-3.356250	-1.645600	0.847201
H	-4.400029	2.409622	2.926911
H	-0.826135	-4.090189	-0.440943
H	-2.787800	1.676413	3.239814
H	-2.936428	-3.354498	-0.881418
H	-3.478242	0.149986	1.692588
H	-4.628114	-1.526286	-0.430022
H	-4.813420	0.849766	0.712386
H	0.501512	-2.918275	-0.203120
H	-2.928310	3.429042	2.926730
H	0.451039	1.194032	2.625971
H	4.990505	-0.699787	3.538061
H	-2.987926	-2.141395	-2.162621
H	-4.908303	3.396225	0.660689
H	2.653218	-2.496748	0.535683
H	-0.864139	-3.081009	-2.831792
H	-3.930668	-0.293741	-2.297472
H	3.799781	-4.088770	-0.975568
H	-4.530069	1.176699	-1.520615
H	4.049513	-0.799957	1.249221
H	-3.364544	4.299904	0.622139
H	0.483534	-2.087663	-2.199304
H	-3.787570	3.222805	-0.723076
H	-2.069288	-1.058210	-3.625431
H	-2.449590	2.386475	-2.016517
H	4.204628	1.216502	-0.034295
H	-0.370165	-0.935685	-4.133319
H	4.267120	-3.461188	-3.359296
H	-2.921523	1.520886	-3.520765
H	0.318668	2.840050	-1.045371
H	2.446061	0.406442	-2.675879
H	5.285702	3.311450	-0.792882
H	3.579810	-1.196388	-4.193452
H	1.404308	4.938738	-1.822375
H	3.895630	5.193424	-1.698787
N	-1.225920	-2.051609	-0.970427
N	-3.139562	0.041920	-0.349744
P	1.402704	0.247933	0.078039
S	-1.127448	-1.173649	1.974557
S	-1.285265	2.230443	0.757387
S	-0.877260	0.706931	-2.383202
Ru	-0.896692	-0.003854	-0.154391

TABLE A3 Optimized coordinates of **2** (B3LYP)

C	3.433335	0.119184	4.317917
C	4.118403	-0.470413	3.255793
C	2.192551	0.716138	4.089062
C	0.560282	-3.509690	2.285438
C	1.624010	0.708546	2.814965
C	-1.852695	-3.963407	1.972080
C	2.301800	0.107929	1.740505
C	-0.698644	-3.040912	1.523451
C	2.929479	-2.163155	-0.655126
C	-0.384233	-3.167038	0.009275
C	3.642416	2.079455	-0.321356
C	3.566062	-3.017958	-1.559955
C	4.253632	3.246561	-0.771743
C	-3.378324	2.071369	2.622911
C	2.503247	-0.880418	-1.040720
C	2.261376	1.872599	-0.498927
C	3.783479	-2.613699	-2.877226
C	3.495840	4.234987	-1.407213
C	-3.446766	-1.713843	-0.203388
C	-3.297364	1.882669	1.101288
C	-3.784889	0.459572	0.771295
C	-2.542919	-2.585328	-1.061045
C	2.738083	-0.486817	-2.371765
C	-0.459692	-2.296436	-2.276499
C	1.510590	2.869004	-1.131952
C	3.365419	-1.342647	-3.278783
C	2.127811	4.042784	-1.580315
C	-4.103599	2.983895	0.400832
C	-0.945652	-1.199234	-3.234184
C	-3.648581	0.179699	-1.729165
C	-2.692976	1.027922	-2.569232
H	3.867602	0.120510	5.314570
H	5.092696	-0.925710	3.415618
H	1.655509	1.190368	4.906102
H	0.365145	-3.516243	3.362292
H	0.850769	-4.529700	1.988811
H	1.402861	-2.835071	2.113811
H	-2.031680	-3.834380	3.044031
H	-1.593073	-5.018191	1.798873
H	4.127939	-0.910372	1.162326
H	0.668396	1.194624	2.650310

H	2.775917	-2.503381	0.362730
H	4.246905	1.329540	0.177657
H	-2.799040	-3.768266	1.462143
H	3.894375	-3.999589	-1.227878
H	5.321152	3.386566	-0.621186
H	-2.744639	1.351955	3.148677
H	0.674112	-2.962951	-0.135581
H	-0.562573	-4.208179	-0.315434
H	-3.049234	3.074395	2.903585
H	-4.415196	1.935296	2.960636
H	-3.276283	-1.934981	0.847314
H	-3.573259	-0.165802	1.638139
H	-2.699275	-3.639548	-0.800364
H	4.279518	-3.277013	-3.580649
H	0.615459	-2.196600	-2.138729
H	3.971346	5.148916	-1.754465
H	-4.501853	-1.922798	-0.444618
H	-4.875513	0.469941	0.613335
H	-0.643499	-3.277413	-2.748688
H	2.437256	0.503282	-2.699911
H	-2.823061	-2.491639	-2.112374
H	-3.683508	3.968868	0.617925
H	0.438384	2.771464	-1.243904
H	3.538531	-1.008116	-4.298577
H	-5.138935	2.960593	0.767681
H	1.521199	4.809281	-2.055232
H	-4.120839	2.877989	-0.686254
H	-3.914407	-0.716655	-2.296415
H	-0.274251	-1.172903	-4.097334
H	-4.581367	0.739199	-1.589725
H	-1.952346	-1.387576	-3.617272
H	-2.621640	2.050110	-2.191433
H	-3.024577	1.044244	-3.613366
N	-1.090712	-2.239775	-0.928220
N	-3.141055	-0.265841	-0.379529
O	-0.744857	2.620358	1.788985
O	-1.525621	3.005022	-0.586576
P	1.510638	0.254964	0.065782
S	-1.047587	-1.259517	2.017778
S	-1.437260	2.049339	0.588805
S	-0.931176	0.504778	-2.474021
Ru	-0.896727	-0.109503	-0.145997

TABLE A4 Optimized coordinates of **2** (BP86)

C	3.404881	-0.131487	4.326814
C	4.092042	-0.664092	3.225934
C	2.159925	0.488065	4.131933
C	0.619685	-3.521032	2.196841
C	3.530994	-0.586148	1.938865
C	1.586491	0.556016	2.852983
C	-1.794343	-4.028478	1.872561
C	2.266203	0.010904	1.740045
C	-0.654609	-3.075587	1.439953
C	2.928568	-2.106410	-0.796474
C	-0.338201	-3.160018	-0.078854
C	3.591946	2.128063	-0.131256
C	3.573658	-2.897623	-1.763789
C	4.214799	3.317347	-0.532239
C	-3.386278	1.994191	2.674275
C	2.476469	-0.801354	-1.101837
C	2.219296	1.907890	-0.392844
C	3.771859	-2.406395	-3.063186
C	3.477172	4.310739	-1.199648
C	-3.417473	-1.743785	-0.244610
C	-3.314090	1.826534	1.147671
C	-3.775214	0.401642	0.793440
C	-2.508627	-2.574330	-1.139495
C	2.693850	-0.318581	-2.415199
C	-0.420949	-2.222629	-2.347787
C	1.486387	2.908291	-1.057291
C	3.328066	-1.111977	-3.384096
C	2.115136	4.103043	-1.454327
C	-4.11907	2.936409	0.455157
C	-0.921439	-1.097963	-3.266629
C	-3.644220	0.195125	-1.728279
C	-2.697878	1.093216	-2.527248
H	3.842851	-0.190220	5.330137
H	5.073556	-1.134079	3.359511
H	1.622214	0.921982	4.982578
H	0.423485	-3.549772	3.282383
H	0.943005	-4.535769	1.882350
H	1.446804	-2.810353	2.033760
H	-1.988592	-3.909895	2.952450
H	-1.507169	-5.084839	1.694164
H	4.100991	-0.980933	1.092207

H	0.627356	1.065184	2.708360
H	2.787904	-2.511956	0.210173
H	4.178507	1.370774	0.398474
H	-2.747745	-3.849427	1.348775
H	3.924549	-3.900518	-1.493926
H	5.278592	3.470462	-0.315763
H	-2.741801	1.262036	3.188512
H	0.728518	-2.941568	-0.223588
H	-0.514013	-4.201994	-0.436157
H	-3.053021	3.001846	2.969312
H	-4.428729	1.851512	3.021810
H	-3.216545	-1.986645	0.809847
H	-3.529524	-0.248348	1.648485
H	-2.646397	-3.650353	-0.916878
H	4.275190	-3.022358	-3.816872
H	0.663189	-2.115807	-2.202100
H	3.963256	5.243750	-1.508144
H	-4.483704	-1.958626	-0.475509
H	-4.877706	0.385682	0.644749
H	-0.599700	-3.201829	-2.848145
H	2.371673	0.695518	-2.675786
H	-2.789884	-2.441658	-2.197571
H	-3.692538	3.926760	0.680724
H	0.411122	2.793865	-1.219743
H	3.488763	-0.709321	-4.391071
H	-5.163305	2.913375	0.824860
H	1.521353	4.876649	-1.954473
H	-4.138362	2.838508	-0.642152
H	-3.885002	-0.699381	-2.328819
H	-0.246172	-1.023384	-4.135665
H	-4.600900	0.727667	-1.566979
H	-1.938217	-1.278662	-3.656089
H	-2.632829	2.107517	-2.097415
H	-3.015095	1.150658	-3.584157
N	-1.055682	-2.206275	-0.990612
N	-3.123660	-0.283119	-0.385301
O	-0.734063	2.546652	1.872135
O	-1.524052	3.027828	-0.509212
P	1.460526	0.253280	0.073405
S	-1.046200	-1.301819	1.965758
S	-1.426159	2.013917	0.636305
S	-0.919835	0.580177	-2.415530
Ru	-0.882241	-0.106574	-0.153694

TABLE A5 Optimized coordinates of **3** (B3LYP)

C	3.268532	-0.410516	4.400847
C	3.979679	-0.930304	3.318757
C	2.074586	0.275145	4.173747
C	0.560272	-3.600510	1.896396
C	3.493105	-0.773853	2.018642
C	1.576041	0.424596	2.878626
C	-1.859196	-4.036962	1.508318
C	2.277968	-0.108633	1.782973
C	-0.686883	-3.120990	1.131642
C	2.979710	-2.108153	-0.848635
C	-0.365801	-3.129115	-0.379512
C	3.738122	2.047923	0.046947
C	3.645248	-2.856469	-1.824159
C	4.393384	3.243216	-0.235848
C	-3.505760	1.981448	2.548684
C	2.588290	-0.779528	-1.089940
C	2.367092	1.893892	-0.233376
C	3.924998	-2.297594	-3.071220
C	3.690525	4.311480	-0.801657
C	-3.419611	-1.580311	-0.549635
C	-3.300670	1.906277	1.027882
C	-3.799046	0.532138	0.547460
C	-2.496141	-2.410005	-1.431283
C	2.886778	-0.229922	-2.351257
C	-0.365859	-2.042967	-2.561173
C	1.670488	2.968360	-0.795451
C	3.540899	-0.979889	-3.330124
C	2.332608	4.169981	-1.074367
C	-4.002351	3.092331	0.353360
C	-0.797213	-0.858292	-3.434244
C	-3.481462	0.429214	-1.946979
C	-2.476033	1.357824	-2.623524
H	3.648071	-0.530953	5.412310
H	4.920607	-1.450629	3.479471
H	1.519657	0.698205	5.006623
H	0.331852	-3.716483	2.960472
H	0.904388	-4.574228	1.517602
H	1.386660	-2.887934	1.818770
H	-2.096323	-3.938675	2.569622
H	-1.578729	-5.079616	1.305296
H	4.080921	-1.161275	1.194099
H	0.658981	0.984753	2.718452

H	2.776861	-2.569701	0.110783
H	4.299637	1.234878	0.495125
H	-2.779451	-3.823400	0.961755
H	3.946697	-3.876997	-1.602173
H	5.451715	3.342605	-0.008187
H	-2.992515	1.162803	3.058161
H	0.701180	-2.961060	-0.513153
H	-0.584181	-4.131353	-0.790121
H	-3.127243	2.928078	2.941665
H	-4.577928	1.911143	2.778946
H	-3.329159	-1.869480	0.499279
H	-3.668956	-0.164695	1.376758
H	-2.676718	-3.474775	-1.241110
H	4.443150	-2.878366	-3.829495
H	0.705383	-1.972626	-2.378781
H	4.200243	5.247206	-1.017260
H	-4.463351	-1.743171	-0.865293
H	-4.868773	0.593229	0.291858
H	-0.546655	-2.976136	-3.122158
H	2.617155	0.799218	-2.565919
H	-2.735811	-2.251856	-2.485524
H	-3.571763	4.040910	0.682970
H	0.604376	2.906734	-0.973486
H	3.762347	-0.525962	-4.292705
H	-5.064892	3.080053	0.631562
H	1.767923	4.997455	-1.495537
H	-3.934695	3.071680	-0.736772
H	-3.686034	-0.414091	-2.612152
H	-0.107903	-0.788256	-4.280901
H	-4.431118	0.966845	-1.835097
H	-1.801101	-0.981657	-3.849026
H	-2.397205	2.317604	-2.107124
H	-2.764204	1.524125	-3.667518
N	-1.039420	-2.100233	-1.231948
N	-3.077840	-0.125473	-0.604671
O	-2.506666	-1.433441	2.372882
O	-0.772301	2.424603	1.993653
O	-1.344439	3.096246	-0.382911
P	1.567289	0.237716	0.102378
S	-1.047491	-1.336220	1.821748
S	-1.398504	2.024499	0.690793
S	-0.739341	0.768194	-2.533919
Ru	-0.869835	-0.075719	-0.228630

TABLE A6 Optimized coordinates of **3** (BP86)

C	3.254140	-0.754292	4.357940
C	3.967111	-1.185998	3.228576
C	2.051109	-0.050822	4.190579
C	0.607514	-3.675172	1.707019
C	3.471211	-0.927933	1.939026
C	1.542152	0.199206	2.906366
C	-1.818448	-4.122435	1.298425
C	2.244210	-0.248837	1.763405
C	-0.647584	-3.189061	0.956162
C	2.972169	-2.022784	-1.016868
C	-0.330541	-3.107534	-0.551791
C	3.638332	2.107277	0.349926
C	3.653644	-2.684040	-2.053865
C	4.300133	3.321199	0.120434
C	-3.488150	1.861856	2.654548
C	2.559782	-0.675993	-1.153270
C	2.306616	1.918142	-0.086666
C	3.926256	-2.019415	-3.259448
C	3.644285	4.368980	-0.547945
C	-3.406363	-1.570650	-0.616400
C	-3.300039	1.843138	1.128186
C	-3.786331	0.487826	0.593431
C	-2.484284	-2.348364	-1.549989
C	2.851786	-0.019132	-2.372553
C	-0.356005	-1.898161	-2.676510
C	1.653818	2.974775	-0.749359
C	3.519951	-0.683468	-3.413428
C	2.321289	4.192244	-0.974732
C	-3.987832	3.062164	0.495451
C	-0.809998	-0.671909	-3.479102
C	-3.475849	0.519359	-1.913703
C	-2.476053	1.503455	-2.519152
H	3.643015	-0.953727	5.363381
H	4.920864	-1.714182	3.344864
H	1.497170	0.310462	5.064376
H	0.378445	-3.831613	2.775260
H	0.971773	-4.638183	1.294189
H	1.428571	-2.939444	1.654411
H	-2.061802	-4.058941	2.370797
H	-1.532231	-5.166171	1.061879
H	4.063661	-1.238829	1.073127
H	0.622603	0.785353	2.783312

H	2.775919	-2.565873	-0.087299
H	4.162342	1.307573	0.882638
H	-2.746682	-3.893601	0.751917
H	3.974707	-3.722641	-1.911558
H	5.330549	3.449423	0.472347
H	-2.974799	1.009762	3.127935
H	0.743508	-2.910538	-0.682022
H	-0.541097	-4.093204	-1.030562
H	-3.086394	2.794153	3.083073
H	-4.566911	1.798177	2.899896
H	-3.301483	-1.912233	0.429580
H	-3.632548	-0.255229	1.395664
H	-2.652879	-3.433622	-1.412756
H	4.457867	-2.534390	-4.067566
H	0.725306	-1.822191	-2.490730
H	4.160870	5.320100	-0.722701
H	-4.462819	-1.719623	-0.931259
H	-4.869135	0.542107	0.344703
H	-0.531025	-2.813721	-3.286198
H	2.565296	1.030305	-2.500975
H	-2.731785	-2.136973	-2.604227
H	-3.530710	4.000492	0.847801
H	0.601278	2.885572	-1.026107
H	3.737134	-0.146002	-4.343995
H	-5.056418	3.062970	0.787883
H	1.787596	5.008226	-1.475316
H	-3.935951	3.071904	-0.605389
H	-3.661272	-0.296697	-2.634003
H	-0.133286	-0.545093	-4.341105
H	-4.446675	1.032805	-1.770945
H	-1.833317	-0.772217	-3.878848
H	-2.385121	2.425042	-1.915934
H	-2.763927	1.757883	-3.555349
N	-1.023804	-2.030633	-1.340639
N	-3.063844	-0.107927	-0.597687
O	-2.490030	-1.565204	2.299841
O	-0.738851	2.276211	2.140732
O	-1.309418	3.130314	-0.201611
P	1.511951	0.227630	0.116538
S	-1.025852	-1.413132	1.738364
S	-1.363318	1.968714	0.795327
S	-0.733558	0.896568	-2.463978
Ru	-0.854866	-0.066105	-0.233391

TABLE A7 Optimized coordinates of **4** (B3LYP)

C	-3.660133	-0.283464	4.260329
C	-4.273253	0.423390	3.225840
C	-2.434854	-0.911090	4.033612
C	-0.171444	3.804330	1.886042
C	-3.662001	0.502292	1.972802
C	-1.811947	-0.825823	2.788674
C	2.255132	3.959018	1.392219
C	-2.420994	-0.113629	1.743679
C	0.977189	3.160368	1.094569
C	-2.837952	2.330425	-0.506321
C	0.583539	3.135569	-0.397882
C	-3.861111	-1.808804	-0.536604
C	-3.450190	3.270570	-1.340195
C	-4.542587	-2.937465	-0.982327
C	3.468541	-2.115533	2.497320
C	-2.538664	1.036301	-0.964996
C	-2.452868	-1.760336	-0.550838
C	-3.768979	2.940851	-2.658021
C	-3.831497	-4.050069	-1.443423
C	3.531607	1.385995	-0.668554
C	3.251527	-2.064843	0.977337
C	3.817843	-0.731225	0.455453
C	2.623724	2.261870	-1.521108
C	-2.873730	0.718657	-2.294863
C	0.436633	2.031509	-2.559658
C	-1.751161	-2.881178	-1.004276
C	-3.477670	1.659625	-3.131409
C	-2.440333	-4.017559	-1.446055
C	3.885289	-3.298231	0.320346
C	0.764835	0.818364	-3.437598
C	3.429658	-0.634244	-2.028893
C	2.348769	-1.486666	-2.686687
H	-4.136820	-0.346843	5.235357
H	-5.231917	0.910728	3.385658
H	-1.947730	-1.465237	4.831103
H	0.115950	3.942528	2.931138
H	-0.413918	4.788849	1.461862
H	-1.068403	3.183254	1.886060
H	2.512091	3.876520	2.450372
H	2.079492	5.018305	1.159089
H	-4.171670	1.039653	1.180888

H	-0.856818	-1.315400	2.634773
H	-2.608186	2.606689	0.516636
H	-4.434102	-0.963835	-0.169781
H	3.131402	3.635790	0.828428
H	-3.681539	4.259264	-0.952475
H	-5.629376	-2.951232	-0.961901
H	2.987154	-1.271996	2.997546
H	-0.496216	3.012925	-0.469546
H	0.828882	4.113507	-0.847833
H	3.062615	-3.041120	2.911736
H	4.544686	-2.076887	2.715923
H	3.513627	1.707366	0.370369
H	3.772100	-0.020515	1.277722
H	2.883092	3.314895	-1.358653
H	-4.247615	3.670193	-3.305854
H	-0.628768	2.027407	-2.339000
H	-4.362710	-4.934430	-1.786310
H	4.566679	1.475006	-1.036346
H	4.869739	-0.866725	0.159626
H	0.654790	2.949638	-3.131696
H	-2.677866	-0.278376	-2.676701
H	2.807717	2.071010	-2.580149
H	3.412594	-4.217082	0.675486
H	-0.668983	-2.907451	-0.986199
H	-3.732893	1.383745	-4.151502
H	4.950190	-3.333035	0.586754
H	-1.871038	-4.880068	-1.782412
H	3.802939	-3.294906	-0.768989
H	3.684094	0.190326	-2.700176
H	0.036468	0.776621	-4.252858
H	4.339239	-1.238552	-1.931214
H	1.754667	0.881799	-3.897310
H	2.232142	-2.450973	-2.187118
H	2.585390	-1.643106	-3.744963
N	1.159595	2.052280	-1.256775
N	3.095044	-0.044149	-0.678994
O	2.597950	1.321324	2.286476
O	0.728852	-2.542235	1.952100
O	1.246882	-3.140401	-0.450267
P	-1.612881	-0.206919	0.075847
S	1.178089	1.323421	1.763617
S	1.345473	-2.110175	0.660197
S	0.656955	-0.795445	-2.518224
Ru	0.883088	0.025326	-0.230239
O	0.142306	1.210764	2.829836

TABLE A8 Optimized coordinates of **4** (BP86)

C	-3.630911	-0.250566	4.276451
C	-4.225556	0.483275	3.239422
C	-2.413031	-0.910212	4.047799
C	-0.206015	3.785660	1.905374
C	-3.603816	0.558731	1.981545
C	-1.779060	-0.829461	2.799574
C	2.224980	3.975837	1.384583
C	-2.370265	-0.089050	1.752972
C	0.946098	3.174516	1.089843
C	-2.819080	2.319551	-0.552648
C	0.541548	3.141766	-0.398519
C	-3.828694	-1.805185	-0.454654
C	-3.453282	3.234367	-1.411966
C	-4.537153	-2.932650	-0.887945
C	3.503253	-2.116541	2.470121
C	-2.510832	1.007217	-0.979350
C	-2.413727	-1.771042	-0.510587
C	-3.783501	2.861695	-2.724155
C	-3.846265	-4.055519	-1.377437
C	3.506910	1.418829	-0.684259
C	3.285668	-2.046969	0.948995
C	3.821835	-0.699140	0.438768
C	2.586043	2.279921	-1.539931
C	-2.860476	0.645219	-2.303150
C	0.384008	2.025094	-2.560874
C	-1.730143	-2.901195	-0.991688
C	-3.484052	1.561847	-3.165248
C	-2.446866	-4.035215	-1.420006
C	3.910571	-3.272507	0.265160
C	0.718346	0.809859	-3.435186
C	3.408082	-0.608767	-2.054341
C	2.327252	-1.484029	-2.684626
H	-4.117734	-0.311275	5.256852
H	-5.181316	0.995994	3.399892
H	-1.939668	-1.488353	4.849137
H	0.097355	3.922783	2.955788
H	-0.483746	4.775920	1.492478
H	-1.093876	3.134433	1.916504
H	2.512161	3.857555	2.441226
H	2.034262	5.050161	1.191433
H	-4.102232	1.116410	1.182941

H	-0.827629	-1.346823	2.637436
H	-2.578004	2.629826	0.468738
H	-4.384664	-0.948256	-0.061255
H	3.096904	3.678035	0.782034
H	-3.693230	4.239703	-1.047071
H	-5.632095	-2.936503	-0.834523
H	3.024045	-1.266653	2.982010
H	-0.548569	3.012571	-0.468134
H	0.784854	4.125004	-0.864345
H	3.084908	-3.050408	2.877928
H	4.588218	-2.089810	2.692964
H	3.479834	1.739096	0.368308
H	3.750045	0.014606	1.273174
H	2.833238	3.348062	-1.388173
H	-4.279055	3.573677	-3.393548
H	-0.688576	2.009442	-2.324087
H	-4.399878	-4.940898	-1.711330
H	4.551445	1.514674	-1.053360
H	4.886487	-0.803434	0.136669
H	0.592481	2.955250	-3.136253
H	-2.658821	-0.371296	-2.657662
H	2.760240	2.078826	-2.609706
H	3.435704	-4.203942	0.612307
H	-0.636454	-2.935400	-0.996342
H	-3.749920	1.251179	-4.182449
H	4.987035	-3.314325	0.522628
H	-1.891170	-4.909268	-1.778604
H	3.818336	-3.251686	-0.832513
H	3.635655	0.229097	-2.736036
H	-0.021202	0.747784	-4.251574
H	4.340928	-1.196848	-1.963149
H	1.715648	0.872618	-3.903061
H	2.219852	-2.449256	-2.159298
H	2.540593	-1.654412	-3.755373
N	1.120861	2.049953	-1.256424
N	3.077187	-0.020539	-0.693357
O	2.615267	1.329982	2.268853
O	0.750259	-2.529308	1.965865
O	1.249524	-3.151747	-0.460009
P	-1.550286	-0.203890	0.082277
S	1.172968	1.309077	1.755084
S	1.347729	-2.095435	0.648510
S	0.626943	-0.796742	-2.476989
Ru	0.868239	0.027919	-0.230450
O	0.148649	1.188294	2.851738

Table A9. Crystal data and structure refinement for **8**.

Identification code	cag175lt	
Empirical formula	C62.75 H88.50 N5 O4 P2.50 Ru2 S6	
Formula weight	1448.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.7483(3) Å	$\alpha = 75.203(3)^\circ$.
	b = 14.4088(5) Å	$\beta = 80.610(3)^\circ$.
	c = 24.8048(7) Å	$\gamma = 81.507(3)^\circ$.
Volume	3302.85(19) Å ³	
Z	2	
Density (calculated)	1.457 Mg/m ³	
Absorption coefficient	0.757 mm ⁻¹	
F(000)	1507	
Crystal size	0.25 x 0.22 x 0.18 mm ³	
Theta range for data collection	3.25 to 29.10°.	
Index ranges	-13 ≤ h ≤ 12, -19 ≤ k ≤ 18, -31 ≤ l ≤ 32	
Reflections collected	66164	
Independent reflections	16098 [R(int) = 0.0279]	
Completeness to theta = 26.32°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.96524	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16098 / 0 / 709	
Goodness-of-fit on F ²	1.085	
Final R indices [I > 2σ(I)]	R1 = 0.0418, wR2 = 0.1244	
R indices (all data)	R1 = 0.0532, wR2 = 0.1279	
Largest diff. peak and hole	4.052 and -0.944 e.Å ⁻³	

Table A10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	6456(1)	4133(1)	3143(1)	11(1)
S(1)	4581(1)	4437(1)	2634(1)	16(1)
S(2)	8028(1)	3597(1)	2495(1)	15(1)
S(3)	8153(1)	4095(1)	3748(1)	15(1)
P(1)	5841(1)	2592(1)	3519(1)	11(1)
O(1)	7439(3)	3402(2)	2028(1)	26(1)
O(2)	9125(3)	2819(2)	2708(1)	23(1)
N(1)	6962(3)	5572(2)	2672(1)	14(1)
N(2)	5145(3)	5004(2)	3679(1)	15(1)
C(1)	6783(3)	6170(2)	3097(1)	16(1)
C(2)	5395(3)	6051(2)	3464(2)	17(1)
C(3)	3635(3)	4941(2)	3662(2)	17(1)
C(4)	3287(3)	5112(2)	3066(2)	18(1)
C(5)	5211(4)	5391(2)	2052(2)	20(1)
C(6)	6007(4)	6064(2)	2235(2)	18(1)
C(7)	8477(3)	5502(2)	2435(2)	17(1)
C(8)	9011(3)	4686(2)	2132(2)	18(1)
C(9)	5471(3)	4616(2)	4266(1)	17(1)
C(10)	7026(4)	4438(2)	4360(2)	18(1)
C(11)	10568(4)	4413(3)	2204(2)	25(1)
C(12)	8865(4)	4967(3)	1509(2)	26(1)
C(13)	7556(4)	5305(3)	4486(2)	23(1)
C(14)	7154(4)	3585(3)	4875(2)	24(1)
C(15)	4045(3)	2528(2)	3881(1)	14(1)
C(16)	3729(3)	2480(2)	4458(1)	17(1)
C(17)	2356(4)	2567(2)	4711(2)	21(1)
C(18)	1267(4)	2709(3)	4388(2)	23(1)
C(19)	1557(4)	2748(2)	3818(2)	22(1)
C(20)	2925(3)	2652(2)	3568(2)	17(1)
C(21)	6772(3)	1600(2)	3999(1)	14(1)
C(22)	6158(4)	748(2)	4246(2)	19(1)
C(23)	6887(4)	-48(2)	4560(2)	23(1)
C(24)	8251(4)	-2(3)	4640(2)	22(1)
C(25)	8869(4)	832(3)	4402(2)	21(1)
C(26)	8145(3)	1628(2)	4077(2)	17(1)
C(27)	5799(3)	1949(2)	2975(1)	17(1)
Ru(2)	2196(1)	9662(1)	2156(1)	11(1)
S(4)	2730(1)	10603(1)	2706(1)	14(1)
S(5)	2410(1)	8264(1)	2802(1)	14(1)
S(6)	1323(1)	9004(1)	1496(1)	16(1)
P(2)	4556(1)	9410(1)	1838(1)	13(1)
O(3)	3075(3)	8294(2)	3293(1)	22(1)
O(4)	2976(3)	7394(2)	2589(1)	22(1)
N(3)	62(3)	9856(2)	2583(1)	14(1)
N(4)	1439(3)	11037(2)	1616(1)	14(1)
C(28)	-799(3)	10425(2)	2140(2)	17(1)
C(29)	-91(3)	11293(2)	1796(2)	17(1)
C(30)	2210(3)	11824(2)	1669(1)	16(1)
C(31)	2254(3)	11825(2)	2282(2)	17(1)
C(32)	1251(3)	10449(3)	3258(1)	18(1)
C(33)	-102(3)	10406(2)	3038(2)	17(1)

C(34)	-449(3)	8875(2)	2794(2)	18(1)
C(35)	533(3)	8071(2)	3120(2)	19(1)
C(36)	1228(3)	10073(2)	893(1)	17(1)
C(37)	1715(3)	10956(2)	1019(1)	17(1)
C(38)	211(4)	7119(3)	3035(2)	28(1)
C(39)	335(4)	8017(3)	3753(2)	26(1)
C(40)	-253(4)	10277(3)	726(2)	23(1)
C(41)	2243(4)	9833(3)	391(2)	23(1)
C(42)	5372(3)	10496(2)	1434(1)	14(1)
C(43)	5775(3)	11115(2)	1709(2)	18(1)
C(44)	6305(4)	11978(3)	1412(2)	23(1)
C(45)	6406(4)	12218(3)	830(2)	26(1)
C(46)	5994(4)	11612(3)	551(2)	22(1)
C(47)	5501(3)	10756(2)	847(2)	18(1)
C(48)	5415(3)	8564(2)	1407(2)	18(1)
C(49)	6878(4)	8513(3)	1266(2)	24(1)
C(50)	7578(4)	7902(3)	939(2)	28(1)
C(51)	6856(4)	7342(3)	732(2)	27(1)
C(52)	5425(4)	7372(3)	874(2)	24(1)
C(53)	4702(4)	7972(2)	1217(2)	20(1)
C(54)	5596(3)	9008(3)	2425(2)	19(1)
N(200)	6416(4)	7939(3)	3928(2)	44(1)
C(200)	3994(5)	8816(3)	4229(2)	36(1)
C(201)	5339(5)	8321(3)	4056(2)	32(1)
P(3)	6377(2)	5709(2)	9577(1)	32(1)
C(500)	6160(9)	5883(7)	8853(4)	36(2)
C(300)	7602(3)	4600(2)	9683(2)	30(1)
C(305)	8496(4)	4441(3)	10087(2)	30(1)
C(304)	9434(4)	3611(3)	10174(2)	30(1)
C(303)	9478(4)	2939(3)	9856(2)	30(1)
C(302)	8584(4)	3098(3)	9452(2)	30(1)
C(301)	7646(4)	3929(3)	9366(2)	30(1)
C(400)	5001(4)	4997(3)	9999(2)	29(1)
C(404)	3615(5)	5141(4)	9681(2)	29(1)
C(403)	2419(6)	4729(5)	9975(3)	29(1)
C(402)	3560(5)	4400(4)	10796(2)	29(1)
C(401)	4718(4)	4793(3)	10520(2)	29(1)

Table A11. Bond lengths [Å] and angles [°] for **8**.

Ru(1)-N(1)	2.188(3)
Ru(1)-N(2)	2.190(3)
Ru(1)-S(2)	2.2384(8)
Ru(1)-P(1)	2.3045(8)
Ru(1)-S(1)	2.3163(8)
Ru(1)-S(3)	2.3940(8)
S(1)-C(5)	1.816(4)
S(1)-C(4)	1.848(3)
S(2)-O(1)	1.478(3)
S(2)-O(2)	1.485(3)
S(2)-C(8)	1.905(3)
S(3)-C(10)	1.853(4)
P(1)-C(27)	1.831(3)
P(1)-C(15)	1.836(3)
P(1)-C(21)	1.840(3)
N(1)-C(7)	1.497(4)
N(1)-C(1)	1.498(4)
N(1)-C(6)	1.511(4)
N(2)-C(9)	1.490(4)
N(2)-C(3)	1.496(4)
N(2)-C(2)	1.509(4)
C(1)-C(2)	1.509(5)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.522(5)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.521(5)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.537(5)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(12)	1.518(5)
C(8)-C(11)	1.539(5)
C(9)-C(10)	1.545(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(14)	1.538(5)
C(10)-C(13)	1.538(5)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600

C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.400(5)
C(15)-C(20)	1.405(5)
C(16)-C(17)	1.385(5)
C(16)-H(16)	0.9300
C(17)-C(18)	1.393(5)
C(17)-H(17)	0.9300
C(18)-C(19)	1.384(6)
C(18)-H(18)	0.9300
C(19)-C(20)	1.379(5)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(26)	1.390(5)
C(21)-C(22)	1.397(5)
C(22)-C(23)	1.382(5)
C(22)-H(22)	0.9300
C(23)-C(24)	1.390(5)
C(23)-H(23)	0.9300
C(24)-C(25)	1.374(5)
C(24)-H(24)	0.9300
C(25)-C(26)	1.393(5)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
Ru(2)-N(3)	2.188(3)
Ru(2)-N(4)	2.190(3)
Ru(2)-S(5)	2.2365(8)
Ru(2)-S(4)	2.3136(8)
Ru(2)-P(2)	2.3145(8)
Ru(2)-S(6)	2.4062(8)
S(4)-C(32)	1.816(3)
S(4)-C(31)	1.842(3)
S(5)-O(3)	1.482(3)
S(5)-O(4)	1.483(2)
S(5)-C(35)	1.901(3)
S(6)-C(36)	1.856(3)
P(2)-C(54)	1.834(3)
P(2)-C(42)	1.842(3)
P(2)-C(48)	1.843(3)
N(3)-C(28)	1.491(4)
N(3)-C(34)	1.504(4)
N(3)-C(33)	1.513(4)
N(4)-C(30)	1.492(4)
N(4)-C(37)	1.494(4)
N(4)-C(29)	1.505(4)
C(28)-C(29)	1.512(5)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-C(31)	1.528(5)

C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-C(33)	1.523(4)
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(34)-C(35)	1.537(5)
C(34)-H(34A)	0.9700
C(34)-H(34B)	0.9700
C(35)-C(38)	1.524(5)
C(35)-C(39)	1.532(5)
C(36)-C(40)	1.533(5)
C(36)-C(37)	1.540(5)
C(36)-C(41)	1.538(5)
C(37)-H(37A)	0.9700
C(37)-H(37B)	0.9700
C(38)-H(38A)	0.9600
C(38)-H(38B)	0.9600
C(38)-H(38C)	0.9600
C(39)-H(39A)	0.9600
C(39)-H(39B)	0.9600
C(39)-H(39C)	0.9600
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(41)-H(41A)	0.9600
C(41)-H(41B)	0.9600
C(41)-H(41C)	0.9600
C(42)-C(43)	1.385(5)
C(42)-C(47)	1.396(5)
C(43)-C(44)	1.398(5)
C(43)-H(43)	0.9300
C(44)-C(45)	1.385(6)
C(44)-H(44)	0.9300
C(45)-C(46)	1.379(5)
C(45)-H(45)	0.9300
C(46)-C(47)	1.375(5)
C(46)-H(46)	0.9300
C(47)-H(47)	0.9300
C(48)-C(53)	1.387(5)
C(48)-C(49)	1.407(5)
C(49)-C(50)	1.381(5)
C(49)-H(49)	0.9300
C(50)-C(51)	1.382(6)
C(50)-H(50)	0.9300
C(51)-C(52)	1.379(5)
C(51)-H(51)	0.9300
C(52)-C(53)	1.402(5)
C(52)-H(52)	0.9300
C(53)-H(53)	0.9300
C(54)-H(54A)	0.9600
C(54)-H(54B)	0.9600
C(54)-H(54C)	0.9600

N(200)-C(201)	1.148(6)
C(200)-C(201)	1.452(6)
C(200)-H(20A)	0.9600
C(200)-H(20B)	0.9600
C(200)-H(20C)	0.9600
P(3)-C(402)#1	0.968(7)
P(3)-C(401)#1	1.457(6)
P(3)-C(403)#1	1.690(6)
P(3)-C(400)	1.830(5)
P(3)-C(300)	1.836(4)
P(3)-C(500)	1.793(10)
P(3)-C(404)#1	1.932(5)
C(500)-C(402)#1	0.929(10)
C(500)-C(401)#1	1.772(10)
C(500)-H(50A)	0.9600
C(500)-H(50B)	0.9600
C(500)-H(50C)	0.9600
C(300)-C(305)	1.3873(16)
C(300)-C(301)	1.3873(16)
C(300)-C(403)#1	1.436(8)
C(300)-C(404)#1	1.895(7)
C(300)-C(402)#1	1.963(7)
C(305)-C(403)#1	1.373(8)
C(305)-C(304)	1.3871(16)
C(304)-C(303)	1.3873(15)
C(304)-H(304)	0.9300
C(303)-C(302)	1.3873(15)
C(303)-H(303)	0.9300
C(302)-C(301)	1.3873(16)
C(302)-H(302)	0.9300
C(301)-H(301)	0.9300
C(400)-C(401)	1.2439(14)
C(400)-C(401)#1	1.238(8)
C(400)-C(404)#1	1.637(8)
C(400)-C(404)	1.6332(19)
C(400)-P(3)#1	1.828(5)
C(404)-C(403)	1.3963(16)
C(404)-C(401)#1	1.629(10)
C(404)-C(300)#1	1.895(8)
C(404)-P(3)#1	1.932(6)
C(403)-C(305)#1	1.373(14)
C(403)-C(300)#1	1.436(8)
C(403)-P(3)#1	1.691(6)
C(402)-P(3)#1	0.968(6)
C(402)-C(500)#1	0.930(10)
C(402)-C(401)	1.3432(15)
C(402)-C(300)#1	1.963(7)
C(401)-P(3)#1	1.457(5)
C(401)-C(404)#1	1.629(7)
C(401)-C(500)#1	1.773(10)
N(1)-Ru(1)-N(2)	80.43(10)
N(1)-Ru(1)-S(2)	85.23(7)
N(2)-Ru(1)-S(2)	165.37(7)
N(1)-Ru(1)-P(1)	171.67(8)
N(2)-Ru(1)-P(1)	104.35(7)
S(2)-Ru(1)-P(1)	90.24(3)

N(1)-Ru(1)-S(1)	85.41(7)
N(2)-Ru(1)-S(1)	85.50(7)
S(2)-Ru(1)-S(1)	96.29(3)
P(1)-Ru(1)-S(1)	88.15(3)
N(1)-Ru(1)-S(3)	89.29(7)
N(2)-Ru(1)-S(3)	83.06(7)
S(2)-Ru(1)-S(3)	93.94(3)
P(1)-Ru(1)-S(3)	98.00(3)
S(1)-Ru(1)-S(3)	168.05(3)
C(5)-S(1)-C(4)	102.56(16)
C(5)-S(1)-Ru(1)	99.15(11)
C(4)-S(1)-Ru(1)	100.48(11)
O(1)-S(2)-O(2)	111.87(16)
O(1)-S(2)-C(8)	102.64(15)
O(2)-S(2)-C(8)	104.87(15)
O(1)-S(2)-Ru(1)	115.19(11)
O(2)-S(2)-Ru(1)	116.55(11)
C(8)-S(2)-Ru(1)	103.68(11)
C(10)-S(3)-Ru(1)	101.31(11)
C(27)-P(1)-C(15)	100.53(15)
C(27)-P(1)-C(21)	97.33(15)
C(15)-P(1)-C(21)	100.14(15)
C(27)-P(1)-Ru(1)	112.13(11)
C(15)-P(1)-Ru(1)	115.01(10)
C(21)-P(1)-Ru(1)	127.42(11)
C(7)-N(1)-C(1)	107.1(2)
C(7)-N(1)-C(6)	113.3(3)
C(1)-N(1)-C(6)	107.5(2)
C(7)-N(1)-Ru(1)	108.52(18)
C(1)-N(1)-Ru(1)	105.84(19)
C(6)-N(1)-Ru(1)	114.13(19)
C(9)-N(2)-C(3)	109.4(3)
C(9)-N(2)-C(2)	111.5(3)
C(3)-N(2)-C(2)	107.6(2)
C(9)-N(2)-Ru(1)	108.46(19)
C(3)-N(2)-Ru(1)	109.70(19)
C(2)-N(2)-Ru(1)	110.2(2)
N(1)-C(1)-C(2)	110.1(3)
N(1)-C(1)-H(1A)	109.6
C(2)-C(1)-H(1A)	109.6
N(1)-C(1)-H(1B)	109.6
C(2)-C(1)-H(1B)	109.6
H(1A)-C(1)-H(1B)	108.2
N(2)-C(2)-C(1)	112.0(3)
N(2)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2A)	109.2
N(2)-C(2)-H(2B)	109.2
C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
N(2)-C(3)-C(4)	112.6(3)
N(2)-C(3)-H(3A)	109.1
C(4)-C(3)-H(3A)	109.1
N(2)-C(3)-H(3B)	109.1
C(4)-C(3)-H(3B)	109.1
H(3A)-C(3)-H(3B)	107.8
C(3)-C(4)-S(1)	112.3(2)

C(3)-C(4)-H(4A)	109.1
S(1)-C(4)-H(4A)	109.1
C(3)-C(4)-H(4B)	109.1
S(1)-C(4)-H(4B)	109.1
H(4A)-C(4)-H(4B)	107.9
C(6)-C(5)-S(1)	112.7(2)
C(6)-C(5)-H(5A)	109.1
S(1)-C(5)-H(5A)	109.1
C(6)-C(5)-H(5B)	109.1
S(1)-C(5)-H(5B)	109.1
H(5A)-C(5)-H(5B)	107.8
N(1)-C(6)-C(5)	115.0(3)
N(1)-C(6)-H(6A)	108.5
C(5)-C(6)-H(6A)	108.5
N(1)-C(6)-H(6B)	108.5
C(5)-C(6)-H(6B)	108.5
H(6A)-C(6)-H(6B)	107.5
N(1)-C(7)-C(8)	116.6(3)
N(1)-C(7)-H(7A)	108.2
C(8)-C(7)-H(7A)	108.2
N(1)-C(7)-H(7B)	108.2
C(8)-C(7)-H(7B)	108.2
H(7A)-C(7)-H(7B)	107.3
C(12)-C(8)-C(7)	113.7(3)
C(12)-C(8)-C(11)	109.1(3)
C(7)-C(8)-C(11)	106.6(3)
C(12)-C(8)-S(2)	109.9(2)
C(7)-C(8)-S(2)	108.7(2)
C(11)-C(8)-S(2)	108.7(2)
N(2)-C(9)-C(10)	117.7(3)
N(2)-C(9)-H(9A)	107.9
C(10)-C(9)-H(9A)	107.9
N(2)-C(9)-H(9B)	107.9
C(10)-C(9)-H(9B)	107.9
H(9A)-C(9)-H(9B)	107.2
C(14)-C(10)-C(13)	107.7(3)
C(14)-C(10)-C(9)	106.7(3)
C(13)-C(10)-C(9)	113.5(3)
C(14)-C(10)-S(3)	108.2(2)
C(13)-C(10)-S(3)	109.6(2)
C(9)-C(10)-S(3)	111.0(2)
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5

C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(20)	117.9(3)
C(16)-C(15)-P(1)	121.6(2)
C(20)-C(15)-P(1)	119.9(3)
C(17)-C(16)-C(15)	121.0(3)
C(17)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
C(16)-C(17)-C(18)	119.8(3)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(19)-C(18)-C(17)	120.0(3)
C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(20)-C(19)-C(18)	120.1(3)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(15)	121.1(3)
C(19)-C(20)-H(20)	119.5
C(15)-C(20)-H(20)	119.5
C(26)-C(21)-C(22)	118.2(3)
C(26)-C(21)-P(1)	121.5(2)
C(22)-C(21)-P(1)	119.9(2)
C(23)-C(22)-C(21)	121.2(3)
C(23)-C(22)-H(22)	119.4
C(21)-C(22)-H(22)	119.4
C(22)-C(23)-C(24)	119.7(3)
C(22)-C(23)-H(23)	120.1
C(24)-C(23)-H(23)	120.1
C(25)-C(24)-C(23)	119.8(3)
C(25)-C(24)-H(24)	120.1
C(23)-C(24)-H(24)	120.1
C(24)-C(25)-C(26)	120.5(3)
C(24)-C(25)-H(25)	119.7
C(26)-C(25)-H(25)	119.7
C(21)-C(26)-C(25)	120.5(3)
C(21)-C(26)-H(26)	119.8
C(25)-C(26)-H(26)	119.8
P(1)-C(27)-H(27A)	109.5
P(1)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
P(1)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(3)-Ru(2)-N(4)	80.42(10)
N(3)-Ru(2)-S(5)	85.43(7)
N(4)-Ru(2)-S(5)	165.70(7)
N(3)-Ru(2)-S(4)	85.08(7)
N(4)-Ru(2)-S(4)	85.15(7)

S(5)-Ru(2)-S(4)	95.74(3)
N(3)-Ru(2)-P(2)	171.41(8)
N(4)-Ru(2)-P(2)	105.19(7)
S(5)-Ru(2)-P(2)	89.10(3)
S(4)-Ru(2)-P(2)	88.89(3)
N(3)-Ru(2)-S(6)	89.29(7)
N(4)-Ru(2)-S(6)	82.62(7)
S(5)-Ru(2)-S(6)	95.22(3)
S(4)-Ru(2)-S(6)	167.24(3)
P(2)-Ru(2)-S(6)	97.81(3)
C(32)-S(4)-C(31)	102.15(16)
C(32)-S(4)-Ru(2)	99.65(11)
C(31)-S(4)-Ru(2)	100.95(11)
O(3)-S(5)-O(4)	111.28(15)
O(3)-S(5)-C(35)	102.99(15)
O(4)-S(5)-C(35)	105.38(15)
O(3)-S(5)-Ru(2)	115.18(11)
O(4)-S(5)-Ru(2)	116.47(11)
C(35)-S(5)-Ru(2)	103.72(11)
C(36)-S(6)-Ru(2)	100.85(11)
C(54)-P(2)-C(42)	100.91(15)
C(54)-P(2)-C(48)	98.96(16)
C(42)-P(2)-C(48)	98.69(15)
C(54)-P(2)-Ru(2)	111.24(11)
C(42)-P(2)-Ru(2)	115.57(10)
C(48)-P(2)-Ru(2)	127.41(11)
C(28)-N(3)-C(34)	107.5(2)
C(28)-N(3)-C(33)	107.7(2)
C(34)-N(3)-C(33)	112.9(3)
C(28)-N(3)-Ru(2)	105.93(19)
C(34)-N(3)-Ru(2)	107.72(19)
C(33)-N(3)-Ru(2)	114.65(19)
C(30)-N(4)-C(37)	108.3(3)
C(30)-N(4)-C(29)	107.8(2)
C(37)-N(4)-C(29)	111.9(2)
C(30)-N(4)-Ru(2)	109.87(19)
C(37)-N(4)-Ru(2)	108.86(19)
C(29)-N(4)-Ru(2)	110.0(2)
N(3)-C(28)-C(29)	110.1(3)
N(3)-C(28)-H(28A)	109.6
C(29)-C(28)-H(28A)	109.6
N(3)-C(28)-H(28B)	109.6
C(29)-C(28)-H(28B)	109.6
H(28A)-C(28)-H(28B)	108.2
N(4)-C(29)-C(28)	112.4(3)
N(4)-C(29)-H(29A)	109.1
C(28)-C(29)-H(29A)	109.1
N(4)-C(29)-H(29B)	109.1
C(28)-C(29)-H(29B)	109.1
H(29A)-C(29)-H(29B)	107.9
N(4)-C(30)-C(31)	112.4(3)
N(4)-C(30)-H(30A)	109.1
C(31)-C(30)-H(30A)	109.1
N(4)-C(30)-H(30B)	109.1
C(31)-C(30)-H(30B)	109.1
H(30A)-C(30)-H(30B)	107.9

C(30)-C(31)-S(4)	111.8(2)
C(30)-C(31)-H(31A)	109.3
S(4)-C(31)-H(31A)	109.3
C(30)-C(31)-H(31B)	109.3
S(4)-C(31)-H(31B)	109.3
H(31A)-C(31)-H(31B)	107.9
C(33)-C(32)-S(4)	112.6(2)
C(33)-C(32)-H(32A)	109.1
S(4)-C(32)-H(32A)	109.1
C(33)-C(32)-H(32B)	109.1
S(4)-C(32)-H(32B)	109.1
H(32A)-C(32)-H(32B)	107.8
N(3)-C(33)-C(32)	114.8(3)
N(3)-C(33)-H(33A)	108.6
C(32)-C(33)-H(33A)	108.6
N(3)-C(33)-H(33B)	108.6
C(32)-C(33)-H(33B)	108.6
H(33A)-C(33)-H(33B)	107.5
N(3)-C(34)-C(35)	116.6(3)
N(3)-C(34)-H(34A)	108.1
C(35)-C(34)-H(34A)	108.1
N(3)-C(34)-H(34B)	108.1
C(35)-C(34)-H(34B)	108.1
H(34A)-C(34)-H(34B)	107.3
C(38)-C(35)-C(39)	108.5(3)
C(38)-C(35)-C(34)	106.9(3)
C(39)-C(35)-C(34)	113.5(3)
C(38)-C(35)-S(5)	108.8(2)
C(39)-C(35)-S(5)	110.5(2)
C(34)-C(35)-S(5)	108.5(2)
C(40)-C(36)-C(37)	112.6(3)
C(40)-C(36)-C(41)	108.0(3)
C(37)-C(36)-C(41)	106.5(3)
C(40)-C(36)-S(6)	109.7(2)
C(37)-C(36)-S(6)	111.7(2)
C(41)-C(36)-S(6)	108.1(2)
N(4)-C(37)-C(36)	116.7(3)
N(4)-C(37)-H(37A)	108.1
C(36)-C(37)-H(37A)	108.1
N(4)-C(37)-H(37B)	108.1
C(36)-C(37)-H(37B)	108.1
H(37A)-C(37)-H(37B)	107.3
C(35)-C(38)-H(38A)	109.5
C(35)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(35)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(35)-C(39)-H(39A)	109.5
C(35)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(35)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(36)-C(40)-H(40A)	109.5
C(36)-C(40)-H(40B)	109.5

H(40A)-C(40)-H(40B)	109.5
C(36)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(36)-C(41)-H(41A)	109.5
C(36)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(36)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(43)-C(42)-C(47)	118.4(3)
C(43)-C(42)-P(2)	120.3(3)
C(47)-C(42)-P(2)	121.1(2)
C(42)-C(43)-C(44)	121.3(3)
C(42)-C(43)-H(43)	119.3
C(44)-C(43)-H(43)	119.3
C(45)-C(44)-C(43)	118.8(3)
C(45)-C(44)-H(44)	120.6
C(43)-C(44)-H(44)	120.6
C(46)-C(45)-C(44)	120.4(3)
C(46)-C(45)-H(45)	119.8
C(44)-C(45)-H(45)	119.8
C(47)-C(46)-C(45)	120.4(3)
C(47)-C(46)-H(46)	119.8
C(45)-C(46)-H(46)	119.8
C(46)-C(47)-C(42)	120.7(3)
C(46)-C(47)-H(47)	119.6
C(42)-C(47)-H(47)	119.6
C(53)-C(48)-C(49)	118.1(3)
C(53)-C(48)-P(2)	123.7(3)
C(49)-C(48)-P(2)	118.2(3)
C(50)-C(49)-C(48)	120.8(4)
C(50)-C(49)-H(49)	119.6
C(48)-C(49)-H(49)	119.6
C(49)-C(50)-C(51)	120.8(4)
C(49)-C(50)-H(50)	119.6
C(51)-C(50)-H(50)	119.6
C(52)-C(51)-C(50)	119.0(3)
C(52)-C(51)-H(51)	120.5
C(50)-C(51)-H(51)	120.5
C(51)-C(52)-C(53)	120.9(4)
C(51)-C(52)-H(52)	119.6
C(53)-C(52)-H(52)	119.6
C(48)-C(53)-C(52)	120.3(3)
C(48)-C(53)-H(53)	119.8
C(52)-C(53)-H(53)	119.8
P(2)-C(54)-H(54A)	109.5
P(2)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
P(2)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(201)-C(200)-H(20A)	109.5
C(201)-C(200)-H(20B)	109.5
H(20A)-C(200)-H(20B)	109.5
C(201)-C(200)-H(20C)	109.5

H(20A)-C(200)-H(20C)	109.5
H(20B)-C(200)-H(20C)	109.5
N(200)-C(201)-C(200)	178.4(5)
C(402)#1-P(3)-C(401)#1	63.6(3)
C(402)#1-P(3)-C(403)#1	125.5(4)
C(401)#1-P(3)-C(403)#1	127.4(3)
C(402)#1-P(3)-C(400)	104.9(4)
C(401)#1-P(3)-C(400)	42.4(3)
C(403)#1-P(3)-C(400)	96.0(2)
C(402)#1-P(3)-C(300)	82.6(3)
C(401)#1-P(3)-C(300)	92.2(2)
C(403)#1-P(3)-C(300)	47.8(2)
C(400)-P(3)-C(300)	88.36(19)
C(402)#1-P(3)-C(500)	18.7(4)
C(401)#1-P(3)-C(500)	65.1(3)
C(403)#1-P(3)-C(500)	141.2(4)
C(400)-P(3)-C(500)	107.3(4)
C(300)-P(3)-C(500)	101.2(3)
C(402)#1-P(3)-C(404)#1	133.5(4)
C(401)#1-P(3)-C(404)#1	89.1(2)
C(403)#1-P(3)-C(404)#1	44.72(14)
C(400)-P(3)-C(404)#1	51.5(2)
C(300)-P(3)-C(404)#1	60.33(18)
C(500)-P(3)-C(404)#1	148.7(3)
C(402)#1-C(500)-C(401)#1	48.1(5)
C(402)#1-C(500)-P(3)	19.5(5)
C(401)#1-C(500)-P(3)	48.2(3)
C(402)#1-C(500)-H(50A)	109.5
C(401)#1-C(500)-H(50A)	91.6
P(3)-C(500)-H(50A)	90.1
C(402)#1-C(500)-H(50B)	109.5
C(401)#1-C(500)-H(50B)	74.7
P(3)-C(500)-H(50B)	120.5
H(50A)-C(500)-H(50B)	109.5
C(402)#1-C(500)-H(50C)	109.5
C(401)#1-C(500)-H(50C)	154.7
P(3)-C(500)-H(50C)	115.7
H(50A)-C(500)-H(50C)	109.5
H(50B)-C(500)-H(50C)	109.5
C(305)-C(300)-C(301)	120.0
C(305)-C(300)-C(403)#1	58.2(4)
C(301)-C(300)-C(403)#1	178.1(4)
C(305)-C(300)-P(3)	118.9(2)
C(301)-C(300)-P(3)	121.1(2)
C(403)#1-C(300)-P(3)	60.8(3)
C(305)-C(300)-C(404)#1	77.2(2)
C(301)-C(300)-C(404)#1	132.6(2)
C(403)#1-C(300)-C(404)#1	47.1(2)
P(3)-C(300)-C(404)#1	62.36(18)
C(305)-C(300)-C(402)#1	143.9(4)
C(301)-C(300)-C(402)#1	94.1(4)
C(403)#1-C(300)-C(402)#1	87.8(3)
P(3)-C(300)-C(402)#1	29.3(2)
C(404)#1-C(300)-C(402)#1	88.5(3)
C(403)#1-C(305)-C(304)	177.2(4)
C(403)#1-C(305)-C(300)	62.7(4)

C(304)-C(305)-C(300)	120.0
C(305)-C(304)-C(303)	120.0
C(305)-C(304)-H(304)	120.0
C(303)-C(304)-H(304)	120.0
C(302)-C(303)-C(304)	120.0
C(302)-C(303)-H(303)	120.0
C(304)-C(303)-H(303)	120.0
C(301)-C(302)-C(303)	120.0
C(301)-C(302)-H(302)	120.0
C(303)-C(302)-H(302)	120.0
C(302)-C(301)-C(300)	120.0
C(302)-C(301)-H(301)	120.0
C(300)-C(301)-H(301)	120.0
C(401)-C(400)-C(401)#1	179.6(5)
C(401)-C(400)-C(404)#1	67.3(3)
C(401)#1-C(400)-C(404)#1	112.6(5)
C(401)-C(400)-C(404)	112.5
C(401)#1-C(400)-C(404)	67.5(4)
C(404)#1-C(400)-C(404)	179.6(3)
C(401)-C(400)-P(3)	127.2(2)
C(401)#1-C(400)-P(3)	52.5(4)
C(404)#1-C(400)-P(3)	67.5(3)
C(404)-C(400)-P(3)	112.50(19)
C(401)-C(400)-P(3)#1	52.54(18)
C(401)#1-C(400)-P(3)#1	127.7(5)
C(404)#1-C(400)-P(3)#1	112.4(3)
C(404)-C(400)-P(3)#1	67.60(18)
P(3)-C(400)-P(3)#1	179.7(3)
C(403)-C(404)-C(401)#1	156.9(3)
C(403)-C(404)-C(400)	119.1
C(401)#1-C(404)-C(400)	44.6(3)
C(403)-C(404)-C(300)#1	48.9(3)
C(401)#1-C(404)-C(300)#1	132.9(6)
C(400)-C(404)-C(300)#1	92.6(2)
C(403)-C(404)-P(3)#1	58.42(16)
C(401)#1-C(404)-P(3)#1	101.5(4)
C(400)-C(404)-P(3)#1	61.01(16)
C(300)#1-C(404)-P(3)#1	57.31(19)
C(305)#1-C(403)-C(404)	97.8(7)
C(305)#1-C(403)-C(300)#1	59.2(5)
C(404)-C(403)-C(300)#1	84.0(3)
C(305)#1-C(403)-P(3)#1	130.5(7)
C(404)-C(403)-P(3)#1	76.85(19)
C(300)#1-C(403)-P(3)#1	71.4(3)
P(3)#1-C(402)-C(500)#1	141.8(9)
P(3)#1-C(402)-C(401)	76.3(3)
C(500)#1-C(402)-C(401)	100.9(7)
P(3)#1-C(402)-C(300)#1	68.1(4)
C(500)#1-C(402)-C(300)#1	149.7(8)
C(401)-C(402)-C(300)#1	90.5(2)
C(400)-C(401)-C(402)	123.7
C(400)-C(401)-P(3)#1	84.8(2)
C(402)-C(401)-P(3)#1	40.2(2)
C(400)-C(401)-C(404)#1	67.9(3)
C(402)-C(401)-C(404)#1	157.4(3)
P(3)#1-C(401)-C(404)#1	137.9(4)

C(400)-C(401)-C(500)#1	150.6(4)
C(402)-C(401)-C(500)#1	31.0(3)
P(3)#1-C(401)-C(500)#1	66.6(4)
C(404)#1-C(401)-C(500)#1	130.2(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Table A12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8** The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	10(1)	9(1)	12(1)	-2(1)	-1(1)	0(1)
S(1)	15(1)	14(1)	18(1)	-1(1)	-5(1)	-1(1)
S(2)	16(1)	14(1)	16(1)	-5(1)	3(1)	-3(1)
S(3)	13(1)	16(1)	17(1)	-5(1)	-3(1)	0(1)
P(1)	10(1)	10(1)	13(1)	-2(1)	-1(1)	0(1)
O(1)	33(2)	31(1)	20(1)	-11(1)	2(1)	-14(1)
O(2)	19(1)	14(1)	31(2)	-3(1)	6(1)	2(1)
N(1)	14(1)	12(1)	14(1)	-1(1)	-1(1)	-1(1)
N(2)	12(1)	12(1)	19(2)	-5(1)	0(1)	-1(1)
C(1)	17(2)	11(2)	20(2)	-4(1)	-3(1)	-2(1)
C(2)	17(2)	11(2)	24(2)	-6(1)	-3(1)	0(1)
C(3)	12(2)	14(2)	23(2)	-6(1)	1(1)	0(1)
C(4)	11(2)	14(2)	28(2)	-3(1)	-4(1)	0(1)
C(5)	21(2)	20(2)	17(2)	1(1)	-5(1)	-3(1)
C(6)	19(2)	15(2)	18(2)	2(1)	-4(1)	0(1)
C(7)	14(2)	13(2)	21(2)	-1(1)	1(1)	-3(1)
C(8)	18(2)	16(2)	18(2)	-3(1)	3(1)	-5(1)
C(9)	18(2)	16(2)	16(2)	-7(1)	2(1)	-1(1)
C(10)	20(2)	19(2)	17(2)	-7(1)	-3(1)	0(1)
C(11)	16(2)	20(2)	36(2)	-5(2)	4(2)	-4(1)
C(12)	31(2)	25(2)	19(2)	-2(2)	5(2)	-7(2)
C(13)	22(2)	26(2)	23(2)	-12(2)	-3(1)	-5(1)
C(14)	27(2)	24(2)	18(2)	-6(1)	-4(1)	2(1)
C(15)	12(2)	10(1)	18(2)	0(1)	0(1)	-2(1)
C(16)	16(2)	13(2)	19(2)	0(1)	-1(1)	-1(1)
C(17)	18(2)	17(2)	22(2)	-1(1)	5(1)	0(1)
C(18)	14(2)	19(2)	33(2)	-4(2)	5(1)	-1(1)
C(19)	14(2)	17(2)	33(2)	-3(1)	-5(1)	-2(1)
C(20)	17(2)	15(2)	20(2)	-4(1)	-2(1)	-4(1)
C(21)	15(2)	12(1)	16(2)	-4(1)	-2(1)	0(1)
C(22)	17(2)	16(2)	24(2)	0(1)	-4(1)	-4(1)
C(23)	28(2)	14(2)	26(2)	2(1)	-6(2)	-5(1)
C(24)	27(2)	19(2)	20(2)	-2(1)	-10(1)	5(1)
C(25)	16(2)	23(2)	24(2)	-6(1)	-7(1)	3(1)
C(26)	16(2)	16(2)	19(2)	-4(1)	-2(1)	-2(1)
C(27)	18(2)	15(2)	19(2)	-7(1)	-1(1)	-2(1)
Ru(2)	10(1)	11(1)	13(1)	-3(1)	-3(1)	1(1)
S(4)	13(1)	15(1)	16(1)	-6(1)	-3(1)	0(1)
S(5)	12(1)	13(1)	16(1)	-2(1)	-2(1)	-1(1)
S(6)	17(1)	17(1)	18(1)	-6(1)	-6(1)	-1(1)
P(2)	12(1)	12(1)	14(1)	-2(1)	-2(1)	1(1)
O(3)	20(1)	28(1)	18(1)	0(1)	-6(1)	-5(1)
O(4)	20(1)	14(1)	27(1)	-3(1)	0(1)	0(1)
N(3)	11(1)	16(1)	17(2)	-5(1)	-2(1)	0(1)
N(4)	12(1)	13(1)	18(2)	-4(1)	-4(1)	1(1)
C(28)	12(2)	19(2)	20(2)	-6(1)	-4(1)	2(1)
C(29)	12(2)	17(2)	22(2)	-4(1)	-5(1)	4(1)
C(30)	16(2)	13(2)	20(2)	-4(1)	-4(1)	0(1)
C(31)	16(2)	13(2)	22(2)	-6(1)	-4(1)	0(1)
C(32)	16(2)	23(2)	16(2)	-7(1)	0(1)	-3(1)
C(33)	13(2)	20(2)	18(2)	-7(1)	-1(1)	1(1)

C(34)	13(2)	18(2)	22(2)	-4(1)	-2(1)	-3(1)
C(35)	15(2)	18(2)	23(2)	-2(1)	-2(1)	-4(1)
C(36)	18(2)	19(2)	15(2)	-5(1)	-6(1)	2(1)
C(37)	16(2)	16(2)	18(2)	-2(1)	-5(1)	0(1)
C(38)	20(2)	20(2)	43(2)	-4(2)	-6(2)	-5(1)
C(39)	20(2)	33(2)	21(2)	2(2)	1(1)	-3(2)
C(40)	21(2)	27(2)	20(2)	-4(1)	-9(1)	-1(1)
C(41)	24(2)	27(2)	17(2)	-7(1)	-5(1)	1(1)
C(42)	10(1)	15(2)	16(2)	-3(1)	-1(1)	2(1)
C(43)	15(2)	20(2)	18(2)	-5(1)	-2(1)	0(1)
C(44)	20(2)	20(2)	30(2)	-7(2)	-1(1)	-7(1)
C(45)	26(2)	21(2)	28(2)	-2(2)	1(2)	-8(1)
C(46)	24(2)	22(2)	18(2)	-3(1)	0(1)	-1(1)
C(47)	18(2)	19(2)	17(2)	-6(1)	-3(1)	0(1)
C(48)	19(2)	13(2)	18(2)	-2(1)	0(1)	1(1)
C(49)	19(2)	18(2)	33(2)	-9(2)	6(2)	-2(1)
C(50)	22(2)	21(2)	37(2)	-7(2)	10(2)	1(1)
C(51)	35(2)	16(2)	25(2)	-5(2)	6(2)	4(2)
C(52)	30(2)	20(2)	22(2)	-8(1)	-6(2)	4(1)
C(53)	20(2)	19(2)	18(2)	-4(1)	-4(1)	3(1)
C(54)	14(2)	22(2)	18(2)	1(1)	-2(1)	-1(1)
N(200)	45(2)	44(2)	50(3)	-20(2)	-16(2)	-3(2)
C(200)	41(2)	36(2)	35(2)	-13(2)	-16(2)	-1(2)
C(201)	42(2)	31(2)	31(2)	-9(2)	-17(2)	-6(2)
P(3)	31(1)	22(1)	41(1)	-9(1)	-1(1)	-3(1)

Table A13. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **8**

	x	y	z	U(eq)
H(1A)	6825	6844	2905	19
H(1B)	7536	5970	3328	19
H(2A)	5370	6335	3781	20
H(2B)	4650	6396	3250	20
H(3A)	3066	5416	3843	20
H(3B)	3399	4307	3874	20
H(4A)	3255	5797	2889	22
H(4B)	2368	4918	3081	22
H(5A)	5820	5103	1774	24
H(5B)	4421	5764	1876	24
H(6A)	6562	6416	1906	22
H(6B)	5335	6533	2385	22
H(7A)	9025	5422	2740	20
H(7B)	8657	6111	2173	20
H(9A)	5073	4009	4415	20
H(9B)	4993	5060	4489	20
H(11A)	10950	3908	2016	37
H(11B)	10661	4191	2597	37
H(11C)	11064	4968	2045	37
H(12A)	9434	5475	1323	39
H(12B)	7905	5186	1461	39
H(12C)	9165	4416	1351	39
H(13A)	7047	5430	4830	34
H(13B)	7417	5864	4184	34
H(13C)	8535	5161	4523	34
H(14A)	8077	3506	4980	35
H(14B)	6985	3006	4785	35
H(14C)	6478	3711	5183	35
H(16)	4453	2388	4675	20
H(17)	2161	2531	5095	25
H(18)	344	2777	4555	28
H(19)	829	2839	3603	26
H(20)	3110	2670	3186	21
H(22)	5242	715	4197	23
H(23)	6465	-611	4718	28
H(24)	8745	-533	4852	27
H(25)	9778	865	4460	25
H(26)	8582	2182	3910	21
H(27A)	5317	1387	3136	25
H(27B)	6739	1756	2825	25
H(27C)	5320	2366	2679	25
H(28A)	-1717	10636	2314	20
H(28B)	-919	10021	1896	20
H(29A)	-553	11579	1465	21
H(29B)	-192	11771	2017	21
H(30A)	1761	12442	1481	19
H(30B)	3159	11746	1482	19
H(31A)	1344	12080	2440	20
H(31B)	2930	12246	2297	20
H(32A)	1454	9858	3539	21
H(32B)	1126	10982	3441	21

H(33A)	-756	10109	3350	21
H(33B)	-507	11061	2891	21
H(34A)	-641	8669	2473	21
H(34B)	-1330	8941	3035	21
H(37A)	2714	10947	899	20
H(37B)	1263	11534	790	20
H(38A)	777	6594	3247	42
H(38B)	414	7119	2643	42
H(38C)	-760	7045	3161	42
H(39A)	460	8630	3812	40
H(39B)	1011	7528	3929	40
H(39C)	-590	7859	3913	40
H(40A)	-273	10786	390	34
H(40B)	-898	10470	1024	34
H(40C)	-514	9704	659	34
H(41A)	1938	9314	279	34
H(41B)	3165	9642	498	34
H(41C)	2260	10393	82	34
H(43)	5692	10953	2100	22
H(44)	6585	12384	1601	28
H(45)	6753	12791	626	31
H(46)	6050	11784	161	27
H(47)	5250	10344	654	21
H(49)	7379	8896	1395	29
H(50)	8547	7867	857	34
H(51)	7328	6951	499	33
H(52)	4933	6989	742	28
H(53)	3740	7972	1317	23
H(54A)	6571	9027	2283	28
H(54B)	5434	8359	2621	28
H(54C)	5328	9427	2678	28
H(20A)	3958	8872	4609	54
H(20B)	3260	8454	4209	54
H(20C)	3873	9448	3985	54
H(50A)	5519	6450	8874	54
H(50B)	5708	5433	8736	54
H(50C)	6964	6059	8585	54
H(304)	10033	3504	10444	37
H(303)	10106	2382	9914	37
H(302)	8613	2647	9240	37
H(301)	7047	4035	9095	37

Table A14. Torsion angles [°] for **8**.

N(1)-Ru(1)-S(1)-C(5)	20.09(14)
N(2)-Ru(1)-S(1)-C(5)	100.83(14)
S(2)-Ru(1)-S(1)-C(5)	-64.59(12)
P(1)-Ru(1)-S(1)-C(5)	-154.62(12)
S(3)-Ru(1)-S(1)-C(5)	84.07(19)
N(1)-Ru(1)-S(1)-C(4)	-84.61(13)
N(2)-Ru(1)-S(1)-C(4)	-3.88(13)
S(2)-Ru(1)-S(1)-C(4)	-169.29(11)
P(1)-Ru(1)-S(1)-C(4)	100.67(11)
S(3)-Ru(1)-S(1)-C(4)	-20.63(19)
N(1)-Ru(1)-S(2)-O(1)	-96.58(14)
N(2)-Ru(1)-S(2)-O(1)	-108.0(3)
P(1)-Ru(1)-S(2)-O(1)	76.43(12)
S(1)-Ru(1)-S(2)-O(1)	-11.74(13)
S(3)-Ru(1)-S(2)-O(1)	174.46(12)
N(1)-Ru(1)-S(2)-O(2)	129.38(14)
N(2)-Ru(1)-S(2)-O(2)	117.9(3)
P(1)-Ru(1)-S(2)-O(2)	-57.62(12)
S(1)-Ru(1)-S(2)-O(2)	-145.78(12)
S(3)-Ru(1)-S(2)-O(2)	40.42(12)
N(1)-Ru(1)-S(2)-C(8)	14.74(13)
N(2)-Ru(1)-S(2)-C(8)	3.3(3)
P(1)-Ru(1)-S(2)-C(8)	-172.26(12)
S(1)-Ru(1)-S(2)-C(8)	99.58(12)
S(3)-Ru(1)-S(2)-C(8)	-74.22(12)
N(1)-Ru(1)-S(3)-C(10)	98.88(13)
N(2)-Ru(1)-S(3)-C(10)	18.44(13)
S(2)-Ru(1)-S(3)-C(10)	-175.94(11)
P(1)-Ru(1)-S(3)-C(10)	-85.15(11)
S(1)-Ru(1)-S(3)-C(10)	35.3(2)
N(1)-Ru(1)-P(1)-C(27)	17.8(5)
N(2)-Ru(1)-P(1)-C(27)	142.04(14)
S(2)-Ru(1)-P(1)-C(27)	-39.12(12)
S(1)-Ru(1)-P(1)-C(27)	57.17(12)
S(3)-Ru(1)-P(1)-C(27)	-133.12(12)
N(1)-Ru(1)-P(1)-C(15)	-96.2(5)
N(2)-Ru(1)-P(1)-C(15)	27.99(14)
S(2)-Ru(1)-P(1)-C(15)	-153.16(12)
S(1)-Ru(1)-P(1)-C(15)	-56.88(12)
S(3)-Ru(1)-P(1)-C(15)	112.83(12)
N(1)-Ru(1)-P(1)-C(21)	136.8(5)
N(2)-Ru(1)-P(1)-C(21)	-98.98(15)
S(2)-Ru(1)-P(1)-C(21)	79.87(14)
S(1)-Ru(1)-P(1)-C(21)	176.15(14)
S(3)-Ru(1)-P(1)-C(21)	-14.14(14)
N(2)-Ru(1)-N(1)-C(7)	143.2(2)
S(2)-Ru(1)-N(1)-C(7)	-33.9(2)
P(1)-Ru(1)-N(1)-C(7)	-91.1(5)
S(1)-Ru(1)-N(1)-C(7)	-130.6(2)
S(3)-Ru(1)-N(1)-C(7)	60.1(2)
N(2)-Ru(1)-N(1)-C(1)	28.57(19)
S(2)-Ru(1)-N(1)-C(1)	-148.52(18)
P(1)-Ru(1)-N(1)-C(1)	154.2(4)
S(1)-Ru(1)-N(1)-C(1)	114.77(18)

S(3)-Ru(1)-N(1)-C(1)	-54.51(18)
N(2)-Ru(1)-N(1)-C(6)	-89.4(2)
S(2)-Ru(1)-N(1)-C(6)	93.5(2)
P(1)-Ru(1)-N(1)-C(6)	36.2(6)
S(1)-Ru(1)-N(1)-C(6)	-3.2(2)
S(3)-Ru(1)-N(1)-C(6)	-172.5(2)
N(1)-Ru(1)-N(2)-C(9)	-126.8(2)
S(2)-Ru(1)-N(2)-C(9)	-115.3(3)
P(1)-Ru(1)-N(2)-C(9)	60.13(19)
S(1)-Ru(1)-N(2)-C(9)	147.06(19)
S(3)-Ru(1)-N(2)-C(9)	-36.39(18)
N(1)-Ru(1)-N(2)-C(3)	113.7(2)
S(2)-Ru(1)-N(2)-C(3)	125.3(3)
P(1)-Ru(1)-N(2)-C(3)	-59.3(2)
S(1)-Ru(1)-N(2)-C(3)	27.64(19)
S(3)-Ru(1)-N(2)-C(3)	-155.8(2)
N(1)-Ru(1)-N(2)-C(2)	-4.5(2)
S(2)-Ru(1)-N(2)-C(2)	7.0(4)
P(1)-Ru(1)-N(2)-C(2)	-177.54(18)
S(1)-Ru(1)-N(2)-C(2)	-90.6(2)
S(3)-Ru(1)-N(2)-C(2)	85.9(2)
C(7)-N(1)-C(1)-C(2)	-164.5(3)
C(6)-N(1)-C(1)-C(2)	73.4(3)
Ru(1)-N(1)-C(1)-C(2)	-48.9(3)
C(9)-N(2)-C(2)-C(1)	99.5(3)
C(3)-N(2)-C(2)-C(1)	-140.6(3)
Ru(1)-N(2)-C(2)-C(1)	-21.0(3)
N(1)-C(1)-C(2)-N(2)	47.7(4)
C(9)-N(2)-C(3)-C(4)	-167.3(3)
C(2)-N(2)-C(3)-C(4)	71.4(3)
Ru(1)-N(2)-C(3)-C(4)	-48.5(3)
N(2)-C(3)-C(4)-S(1)	45.7(3)
C(5)-S(1)-C(4)-C(3)	-121.7(2)
Ru(1)-S(1)-C(4)-C(3)	-19.8(2)
C(4)-S(1)-C(5)-C(6)	65.7(3)
Ru(1)-S(1)-C(5)-C(6)	-37.3(3)
C(7)-N(1)-C(6)-C(5)	104.7(3)
C(1)-N(1)-C(6)-C(5)	-137.3(3)
Ru(1)-N(1)-C(6)-C(5)	-20.2(4)
S(1)-C(5)-C(6)-N(1)	40.1(4)
C(1)-N(1)-C(7)-C(8)	161.7(3)
C(6)-N(1)-C(7)-C(8)	-79.9(3)
Ru(1)-N(1)-C(7)-C(8)	47.9(3)
N(1)-C(7)-C(8)-C(12)	88.7(4)
N(1)-C(7)-C(8)-C(11)	-151.0(3)
N(1)-C(7)-C(8)-S(2)	-34.1(3)
O(1)-S(2)-C(8)-C(12)	-0.3(3)
O(2)-S(2)-C(8)-C(12)	116.7(3)
Ru(1)-S(2)-C(8)-C(12)	-120.5(2)
O(1)-S(2)-C(8)-C(7)	124.8(2)
O(2)-S(2)-C(8)-C(7)	-118.2(2)
Ru(1)-S(2)-C(8)-C(7)	4.5(2)
O(1)-S(2)-C(8)-C(11)	-119.6(3)
O(2)-S(2)-C(8)-C(11)	-2.6(3)
Ru(1)-S(2)-C(8)-C(11)	120.1(2)
C(3)-N(2)-C(9)-C(10)	169.0(3)

C(2)-N(2)-C(9)-C(10)	-72.2(3)
Ru(1)-N(2)-C(9)-C(10)	49.3(3)
N(2)-C(9)-C(10)-C(14)	-149.4(3)
N(2)-C(9)-C(10)-C(13)	92.2(4)
N(2)-C(9)-C(10)-S(3)	-31.7(4)
Ru(1)-S(3)-C(10)-C(14)	116.9(2)
Ru(1)-S(3)-C(10)-C(13)	-126.0(2)
Ru(1)-S(3)-C(10)-C(9)	0.1(2)
C(27)-P(1)-C(15)-C(16)	148.2(3)
C(21)-P(1)-C(15)-C(16)	48.7(3)
Ru(1)-P(1)-C(15)-C(16)	-91.2(3)
C(27)-P(1)-C(15)-C(20)	-40.0(3)
C(21)-P(1)-C(15)-C(20)	-139.5(3)
Ru(1)-P(1)-C(15)-C(20)	80.6(3)
C(20)-C(15)-C(16)-C(17)	-1.0(5)
P(1)-C(15)-C(16)-C(17)	170.9(2)
C(15)-C(16)-C(17)-C(18)	-0.2(5)
C(16)-C(17)-C(18)-C(19)	0.9(5)
C(17)-C(18)-C(19)-C(20)	-0.4(5)
C(18)-C(19)-C(20)-C(15)	-0.9(5)
C(16)-C(15)-C(20)-C(19)	1.6(5)
P(1)-C(15)-C(20)-C(19)	-170.5(3)
C(27)-P(1)-C(21)-C(26)	109.5(3)
C(15)-P(1)-C(21)-C(26)	-148.3(3)
Ru(1)-P(1)-C(21)-C(26)	-15.7(3)
C(27)-P(1)-C(21)-C(22)	-63.1(3)
C(15)-P(1)-C(21)-C(22)	39.0(3)
Ru(1)-P(1)-C(21)-C(22)	171.7(2)
C(26)-C(21)-C(22)-C(23)	0.3(5)
P(1)-C(21)-C(22)-C(23)	173.2(3)
C(21)-C(22)-C(23)-C(24)	0.6(6)
C(22)-C(23)-C(24)-C(25)	-0.3(6)
C(23)-C(24)-C(25)-C(26)	-0.9(6)
C(22)-C(21)-C(26)-C(25)	-1.5(5)
P(1)-C(21)-C(26)-C(25)	-174.2(3)
C(24)-C(25)-C(26)-C(21)	1.8(5)
N(3)-Ru(2)-S(4)-C(32)	20.25(14)
N(4)-Ru(2)-S(4)-C(32)	101.02(14)
S(5)-Ru(2)-S(4)-C(32)	-64.65(12)
P(2)-Ru(2)-S(4)-C(32)	-153.63(12)
S(6)-Ru(2)-S(4)-C(32)	84.40(18)
N(3)-Ru(2)-S(4)-C(31)	-84.25(13)
N(4)-Ru(2)-S(4)-C(31)	-3.48(13)
S(5)-Ru(2)-S(4)-C(31)	-169.15(11)
P(2)-Ru(2)-S(4)-C(31)	101.87(11)
S(6)-Ru(2)-S(4)-C(31)	-20.11(19)
N(3)-Ru(2)-S(5)-O(3)	-96.84(14)
N(4)-Ru(2)-S(5)-O(3)	-105.1(3)
S(4)-Ru(2)-S(5)-O(3)	-12.26(12)
P(2)-Ru(2)-S(5)-O(3)	76.53(12)
S(6)-Ru(2)-S(5)-O(3)	174.29(12)
N(3)-Ru(2)-S(5)-O(4)	130.14(14)
N(4)-Ru(2)-S(5)-O(4)	121.9(3)
S(4)-Ru(2)-S(5)-O(4)	-145.27(12)
P(2)-Ru(2)-S(5)-O(4)	-56.48(12)
S(6)-Ru(2)-S(5)-O(4)	41.28(12)

N(3)-Ru(2)-S(5)-C(35)	14.89(14)
N(4)-Ru(2)-S(5)-C(35)	6.6(3)
S(4)-Ru(2)-S(5)-C(35)	99.48(12)
P(2)-Ru(2)-S(5)-C(35)	-171.73(12)
S(6)-Ru(2)-S(5)-C(35)	-73.97(12)
N(3)-Ru(2)-S(6)-C(36)	99.33(13)
N(4)-Ru(2)-S(6)-C(36)	18.89(13)
S(5)-Ru(2)-S(6)-C(36)	-175.33(11)
S(4)-Ru(2)-S(6)-C(36)	35.60(19)
P(2)-Ru(2)-S(6)-C(36)	-85.53(11)
N(3)-Ru(2)-P(2)-C(54)	5.2(5)
N(4)-Ru(2)-P(2)-C(54)	135.28(14)
S(5)-Ru(2)-P(2)-C(54)	-45.14(13)
S(4)-Ru(2)-P(2)-C(54)	50.62(13)
S(6)-Ru(2)-P(2)-C(54)	-140.29(13)
N(3)-Ru(2)-P(2)-C(42)	-109.1(5)
N(4)-Ru(2)-P(2)-C(42)	21.01(14)
S(5)-Ru(2)-P(2)-C(42)	-159.42(12)
S(4)-Ru(2)-P(2)-C(42)	-63.66(12)
S(6)-Ru(2)-P(2)-C(42)	105.44(12)
N(3)-Ru(2)-P(2)-C(48)	125.7(5)
N(4)-Ru(2)-P(2)-C(48)	-104.21(16)
S(5)-Ru(2)-P(2)-C(48)	75.37(14)
S(4)-Ru(2)-P(2)-C(48)	171.12(14)
S(6)-Ru(2)-P(2)-C(48)	-19.78(14)
N(4)-Ru(2)-N(3)-C(28)	28.91(19)
S(5)-Ru(2)-N(3)-C(28)	-149.02(19)
S(4)-Ru(2)-N(3)-C(28)	114.80(19)
P(2)-Ru(2)-N(3)-C(28)	160.4(4)
S(6)-Ru(2)-N(3)-C(28)	-53.73(18)
N(4)-Ru(2)-N(3)-C(34)	143.7(2)
S(5)-Ru(2)-N(3)-C(34)	-34.19(19)
S(4)-Ru(2)-N(3)-C(34)	-130.4(2)
P(2)-Ru(2)-N(3)-C(34)	-84.8(5)
S(6)-Ru(2)-N(3)-C(34)	61.10(19)
N(4)-Ru(2)-N(3)-C(33)	-89.7(2)
S(5)-Ru(2)-N(3)-C(33)	92.3(2)
S(4)-Ru(2)-N(3)-C(33)	-3.8(2)
P(2)-Ru(2)-N(3)-C(33)	41.8(6)
S(6)-Ru(2)-N(3)-C(33)	-172.4(2)
N(3)-Ru(2)-N(4)-C(30)	113.5(2)
S(5)-Ru(2)-N(4)-C(30)	121.9(3)
S(4)-Ru(2)-N(4)-C(30)	27.7(2)
P(2)-Ru(2)-N(4)-C(30)	-59.8(2)
S(6)-Ru(2)-N(4)-C(30)	-155.9(2)
N(3)-Ru(2)-N(4)-C(37)	-128.0(2)
S(5)-Ru(2)-N(4)-C(37)	-119.6(3)
S(4)-Ru(2)-N(4)-C(37)	146.22(19)
P(2)-Ru(2)-N(4)-C(37)	58.7(2)
S(6)-Ru(2)-N(4)-C(37)	-37.44(18)
N(3)-Ru(2)-N(4)-C(29)	-5.0(2)
S(5)-Ru(2)-N(4)-C(29)	3.3(4)
S(4)-Ru(2)-N(4)-C(29)	-90.9(2)
P(2)-Ru(2)-N(4)-C(29)	-178.39(18)
S(6)-Ru(2)-N(4)-C(29)	85.5(2)
C(34)-N(3)-C(28)-C(29)	-163.7(3)

C(33)-N(3)-C(28)-C(29)	74.4(3)
Ru(2)-N(3)-C(28)-C(29)	-48.7(3)
C(30)-N(4)-C(29)-C(28)	-140.1(3)
C(37)-N(4)-C(29)-C(28)	100.9(3)
Ru(2)-N(4)-C(29)-C(28)	-20.2(3)
N(3)-C(28)-C(29)-N(4)	47.1(4)
C(37)-N(4)-C(30)-C(31)	-167.8(3)
C(29)-N(4)-C(30)-C(31)	70.9(3)
Ru(2)-N(4)-C(30)-C(31)	-49.0(3)
N(4)-C(30)-C(31)-S(4)	46.3(3)
C(32)-S(4)-C(31)-C(30)	-122.9(2)
Ru(2)-S(4)-C(31)-C(30)	-20.4(2)
C(31)-S(4)-C(32)-C(33)	66.6(3)
Ru(2)-S(4)-C(32)-C(33)	-36.9(2)
C(28)-N(3)-C(33)-C(32)	-136.8(3)
C(34)-N(3)-C(33)-C(32)	104.7(3)
Ru(2)-N(3)-C(33)-C(32)	-19.1(4)
S(4)-C(32)-C(33)-N(3)	38.9(4)
C(28)-N(3)-C(34)-C(35)	162.5(3)
C(33)-N(3)-C(34)-C(35)	-78.8(3)
Ru(2)-N(3)-C(34)-C(35)	48.8(3)
N(3)-C(34)-C(35)-C(38)	-152.2(3)
N(3)-C(34)-C(35)-C(39)	88.2(4)
N(3)-C(34)-C(35)-S(5)	-35.1(4)
O(3)-S(5)-C(35)-C(38)	-118.8(3)
O(4)-S(5)-C(35)-C(38)	-2.0(3)
Ru(2)-S(5)-C(35)-C(38)	120.9(2)
O(3)-S(5)-C(35)-C(39)	0.3(3)
O(4)-S(5)-C(35)-C(39)	117.0(3)
Ru(2)-S(5)-C(35)-C(39)	-120.1(2)
O(3)-S(5)-C(35)-C(34)	125.3(2)
O(4)-S(5)-C(35)-C(34)	-118.0(2)
Ru(2)-S(5)-C(35)-C(34)	4.9(3)
Ru(2)-S(6)-C(36)-C(40)	-125.5(2)
Ru(2)-S(6)-C(36)-C(37)	0.1(2)
Ru(2)-S(6)-C(36)-C(41)	117.0(2)
C(30)-N(4)-C(37)-C(36)	169.7(3)
C(29)-N(4)-C(37)-C(36)	-71.6(3)
Ru(2)-N(4)-C(37)-C(36)	50.2(3)
C(40)-C(36)-C(37)-N(4)	92.0(3)
C(41)-C(36)-C(37)-N(4)	-149.8(3)
S(6)-C(36)-C(37)-N(4)	-31.9(3)
C(54)-P(2)-C(42)-C(43)	-39.6(3)
C(48)-P(2)-C(42)-C(43)	-140.6(3)
Ru(2)-P(2)-C(42)-C(43)	80.4(3)
C(54)-P(2)-C(42)-C(47)	145.3(3)
C(48)-P(2)-C(42)-C(47)	44.3(3)
Ru(2)-P(2)-C(42)-C(47)	-94.6(3)
C(47)-C(42)-C(43)-C(44)	-0.2(5)
P(2)-C(42)-C(43)-C(44)	-175.4(3)
C(42)-C(43)-C(44)-C(45)	0.9(5)
C(43)-C(44)-C(45)-C(46)	-0.2(5)
C(44)-C(45)-C(46)-C(47)	-1.1(6)
C(45)-C(46)-C(47)-C(42)	1.8(5)
C(43)-C(42)-C(47)-C(46)	-1.1(5)
P(2)-C(42)-C(47)-C(46)	174.1(3)

C(54)-P(2)-C(48)-C(53)	126.3(3)
C(42)-P(2)-C(48)-C(53)	-131.1(3)
Ru(2)-P(2)-C(48)-C(53)	0.7(4)
C(54)-P(2)-C(48)-C(49)	-53.4(3)
C(42)-P(2)-C(48)-C(49)	49.2(3)
Ru(2)-P(2)-C(48)-C(49)	-179.0(2)
C(53)-C(48)-C(49)-C(50)	1.1(5)
P(2)-C(48)-C(49)-C(50)	-179.2(3)
C(48)-C(49)-C(50)-C(51)	1.5(6)
C(49)-C(50)-C(51)-C(52)	-2.6(6)
C(50)-C(51)-C(52)-C(53)	1.1(6)
C(49)-C(48)-C(53)-C(52)	-2.5(5)
P(2)-C(48)-C(53)-C(52)	177.7(3)
C(51)-C(52)-C(53)-C(48)	1.5(5)
C(401)#1-P(3)-C(500)-C(402)#1	-80.7(14)
C(403)#1-P(3)-C(500)-C(402)#1	38.8(15)
C(400)-P(3)-C(500)-C(402)#1	-85.3(13)
C(300)-P(3)-C(500)-C(402)#1	6.5(14)
C(404)#1-P(3)-C(500)-C(402)#1	-43.3(16)
C(402)#1-P(3)-C(500)-C(401)#1	80.7(14)
C(403)#1-P(3)-C(500)-C(401)#1	119.5(5)
C(400)-P(3)-C(500)-C(401)#1	-4.6(4)
C(300)-P(3)-C(500)-C(401)#1	87.2(3)
C(404)#1-P(3)-C(500)-C(401)#1	37.4(7)
C(402)#1-P(3)-C(300)-C(305)	154.3(5)
C(401)#1-P(3)-C(300)-C(305)	-142.7(3)
C(403)#1-P(3)-C(300)-C(305)	-0.9(3)
C(400)-P(3)-C(300)-C(305)	-100.4(2)
C(500)-P(3)-C(300)-C(305)	152.2(3)
C(404)#1-P(3)-C(300)-C(305)	-54.92(19)
C(402)#1-P(3)-C(300)-C(301)	-25.5(4)
C(401)#1-P(3)-C(300)-C(301)	37.5(2)
C(403)#1-P(3)-C(300)-C(301)	179.3(4)
C(400)-P(3)-C(300)-C(301)	79.7(2)
C(500)-P(3)-C(300)-C(301)	-27.6(4)
C(404)#1-P(3)-C(300)-C(301)	125.3(2)
C(402)#1-P(3)-C(300)-C(403)#1	155.2(5)
C(401)#1-P(3)-C(300)-C(403)#1	-141.8(4)
C(400)-P(3)-C(300)-C(403)#1	-99.6(3)
C(500)-P(3)-C(300)-C(403)#1	153.1(4)
C(404)#1-P(3)-C(300)-C(403)#1	-54.0(2)
C(402)#1-P(3)-C(300)-C(404)#1	-150.7(5)
C(401)#1-P(3)-C(300)-C(404)#1	-87.8(2)
C(403)#1-P(3)-C(300)-C(404)#1	54.0(2)
C(400)-P(3)-C(300)-C(404)#1	-45.5(3)
C(500)-P(3)-C(300)-C(404)#1	-152.8(3)
C(401)#1-P(3)-C(300)-C(402)#1	63.0(3)
C(403)#1-P(3)-C(300)-C(402)#1	-155.2(5)
C(400)-P(3)-C(300)-C(402)#1	105.2(4)
C(500)-P(3)-C(300)-C(402)#1	-2.1(5)
C(404)#1-P(3)-C(300)-C(402)#1	150.7(5)
C(301)-C(300)-C(305)-C(403)#1	-179.3(4)
P(3)-C(300)-C(305)-C(403)#1	0.9(3)
C(404)#1-C(300)-C(305)-C(403)#1	-47.1(2)
C(402)#1-C(300)-C(305)-C(403)#1	22.0(4)
C(301)-C(300)-C(305)-C(304)	0.0

C(403)#1-C(300)-C(305)-C(304)	179.3(4)
P(3)-C(300)-C(305)-C(304)	-179.83(17)
C(404)#1-C(300)-C(305)-C(304)	132.1(2)
C(402)#1-C(300)-C(305)-C(304)	-158.8(4)
C(403)#1-C(305)-C(304)-C(303)	166(7)
C(300)-C(305)-C(304)-C(303)	0.0
C(305)-C(304)-C(303)-C(302)	0.0
C(304)-C(303)-C(302)-C(301)	0.0
C(303)-C(302)-C(301)-C(300)	0.0
C(305)-C(300)-C(301)-C(302)	0.0
C(403)#1-C(300)-C(301)-C(302)	-19(10)
P(3)-C(300)-C(301)-C(302)	179.83(17)
C(404)#1-C(300)-C(301)-C(302)	-100.6(3)
C(402)#1-C(300)-C(301)-C(302)	167.7(3)
C(402)#1-P(3)-C(400)-C(401)	167.3(4)
C(401)#1-P(3)-C(400)-C(401)	-179.6(5)
C(403)#1-P(3)-C(400)-C(401)	38.08(17)
C(300)-P(3)-C(400)-C(401)	85.4(2)
C(500)-P(3)-C(400)-C(401)	-173.4(3)
C(404)#1-P(3)-C(400)-C(401)	32.96(18)
C(402)#1-P(3)-C(400)-C(401)#1	-13.1(2)
C(403)#1-P(3)-C(400)-C(401)#1	-142.3(5)
C(300)-P(3)-C(400)-C(401)#1	-95.0(4)
C(500)-P(3)-C(400)-C(401)#1	6.2(5)
C(404)#1-P(3)-C(400)-C(401)#1	-147.4(6)
C(402)#1-P(3)-C(400)-C(404)#1	134.3(4)
C(401)#1-P(3)-C(400)-C(404)#1	147.4(6)
C(403)#1-P(3)-C(400)-C(404)#1	5.11(16)
C(300)-P(3)-C(400)-C(404)#1	52.4(3)
C(500)-P(3)-C(400)-C(404)#1	153.7(4)
C(402)#1-P(3)-C(400)-C(404)	-46.1(3)
C(401)#1-P(3)-C(400)-C(404)	-32.9(4)
C(403)#1-P(3)-C(400)-C(404)	-175.29(18)
C(300)-P(3)-C(400)-C(404)	-128.00(16)
C(500)-P(3)-C(400)-C(404)	-26.7(3)
C(404)#1-P(3)-C(400)-C(404)	179.6(3)
C(402)#1-P(3)-C(400)-P(3)#1	-152(69)
C(401)#1-P(3)-C(400)-P(3)#1	-139(69)
C(403)#1-P(3)-C(400)-P(3)#1	78(69)
C(300)-P(3)-C(400)-P(3)#1	126(100)
C(500)-P(3)-C(400)-P(3)#1	-133(69)
C(404)#1-P(3)-C(400)-P(3)#1	73(69)
C(401)-C(400)-C(404)-C(403)	-21.3
C(401)#1-C(400)-C(404)-C(403)	159.1(5)
C(404)#1-C(400)-C(404)-C(403)	-83(71)
P(3)-C(400)-C(404)-C(403)	-173.01(19)
P(3)#1-C(400)-C(404)-C(403)	6.64(18)
C(401)-C(400)-C(404)-C(401)#1	179.5(5)
C(404)#1-C(400)-C(404)-C(401)#1	118(71)
P(3)-C(400)-C(404)-C(401)#1	27.8(4)
P(3)#1-C(400)-C(404)-C(401)#1	-152.5(6)
C(401)-C(400)-C(404)-C(300)#1	22.0(2)
C(401)#1-C(400)-C(404)-C(300)#1	-157.6(7)
C(404)#1-C(400)-C(404)-C(300)#1	-40(71)
P(3)-C(400)-C(404)-C(300)#1	-129.7(4)
P(3)#1-C(400)-C(404)-C(300)#1	49.94(19)

C(401)-C(400)-C(404)-P(3)#1	-27.95(18)
C(401)#1-C(400)-C(404)-P(3)#1	152.5(6)
C(404)#1-C(400)-C(404)-P(3)#1	-90(71)
P(3)-C(400)-C(404)-P(3)#1	-179.6(3)
C(401)#1-C(404)-C(403)-C(305)#1	162.6(15)
C(400)-C(404)-C(403)-C(305)#1	123.1(6)
C(300)#1-C(404)-C(403)-C(305)#1	57.7(5)
P(3)#1-C(404)-C(403)-C(305)#1	129.9(7)
C(401)#1-C(404)-C(403)-C(300)#1	104.9(11)
C(400)-C(404)-C(403)-C(300)#1	65.4(3)
P(3)#1-C(404)-C(403)-C(300)#1	72.2(3)
C(401)#1-C(404)-C(403)-P(3)#1	32.7(9)
C(400)-C(404)-C(403)-P(3)#1	-6.81(18)
C(300)#1-C(404)-C(403)-P(3)#1	-72.2(3)
C(401)#1-C(400)-C(401)-C(402)	120(54)
C(404)#1-C(400)-C(401)-C(402)	-158.0(3)
C(404)-C(400)-C(401)-C(402)	22.4
P(3)-C(400)-C(401)-C(402)	169.03(18)
P(3)#1-C(400)-C(401)-C(402)	-10.7(2)
C(401)#1-C(400)-C(401)-P(3)#1	130(54)
C(404)#1-C(400)-C(401)-P(3)#1	-147.3(4)
C(404)-C(400)-C(401)-P(3)#1	33.1(2)
P(3)-C(400)-C(401)-P(3)#1	179.7(3)
C(401)#1-C(400)-C(401)-C(404)#1	-82(54)
C(404)-C(400)-C(401)-C(404)#1	-179.6(3)
P(3)-C(400)-C(401)-C(404)#1	-33.0(2)
P(3)#1-C(400)-C(401)-C(404)#1	147.3(4)
C(401)#1-C(400)-C(401)-C(500)#1	143(54)
C(404)#1-C(400)-C(401)-C(500)#1	-134.3(8)
C(404)-C(400)-C(401)-C(500)#1	46.0(7)
P(3)-C(400)-C(401)-C(500)#1	-167.4(7)
P(3)#1-C(400)-C(401)-C(500)#1	12.9(6)
P(3)#1-C(402)-C(401)-C(400)	16.6(3)
C(500)#1-C(402)-C(401)-C(400)	157.6(7)
C(300)#1-C(402)-C(401)-C(400)	-50.6(3)
C(500)#1-C(402)-C(401)-P(3)#1	140.9(9)
C(300)#1-C(402)-C(401)-P(3)#1	-67.3(4)
P(3)#1-C(402)-C(401)-C(404)#1	-98.6(8)
C(500)#1-C(402)-C(401)-C(404)#1	42.4(9)
C(300)#1-C(402)-C(401)-C(404)#1	-165.9(9)
P(3)#1-C(402)-C(401)-C(500)#1	-140.9(9)
C(300)#1-C(402)-C(401)-C(500)#1	151.8(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Table A15. Crystal data and structure refinement for **9**

Identification code	cag174lt	
Empirical formula	C27 H41 N2 O3 P Ru S3	
Formula weight	669.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.7767(3) Å	$\alpha = 89.823(3)^\circ$.
	b = 15.8615(5) Å	$\beta = 79.435(3)^\circ$.
	c = 21.4533(7) Å	$\gamma = 76.449(3)^\circ$.
Volume	2851.70(16) Å ³	
Z	4	
Density (calculated)	1.560 Mg/m ³	
Absorption coefficient	0.858 mm ⁻¹	
F(000)	1392	
Crystal size	0.38 x 0.20 x 0.15 mm ³	
Theta range for data collection	3.21 to 29.09°	
Index ranges	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21, -28 ≤ l ≤ 28	
Reflections collected	63219	
Independent reflections	14094 [R(int) = 0.0252]	
Completeness to theta = 26.32°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.918	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14094 / 0 / 677	
Goodness-of-fit on F ²	1.051	
Final R indices [I > 2σ(I)]	R1 = 0.0225, wR2 = 0.0571	
R indices (all data)	R1 = 0.0289, wR2 = 0.0584	
Largest diff. peak and hole	1.093 and -0.660 e.Å ⁻³	

Table A16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	5047(1)	1460(1)	1552(1)	8(1)
Ru(2)	3968(1)	2767(1)	5690(1)	8(1)
S(1)	6052(1)	192(1)	897(1)	13(1)
S(2)	2601(1)	1200(1)	1841(1)	11(1)
S(3)	4497(1)	2756(1)	2170(1)	15(1)
S(4)	3913(1)	3830(1)	4926(1)	12(1)
S(5)	6650(1)	2381(1)	5498(1)	11(1)
S(6)	3560(1)	1749(1)	6469(1)	12(1)
P(1)	4270(1)	2210(1)	684(1)	11(1)
P(2)	3958(1)	3810(1)	6453(1)	10(1)
O(1)	2330(2)	497(1)	1449(1)	17(1)
O(2)	1206(1)	1950(1)	1947(1)	17(1)
O(3)	4226(2)	2672(1)	2886(1)	30(1)
O(4)	7396(1)	2979(1)	5079(1)	16(1)
O(5)	7492(1)	2138(1)	6032(1)	16(1)
O(6)	4012(2)	792(1)	6247(1)	31(1)
N(1)	5638(2)	613(1)	2315(1)	12(1)
N(2)	7552(2)	1493(1)	1466(1)	13(1)
N(3)	4201(2)	1874(1)	4892(1)	12(1)
N(4)	1454(2)	2929(1)	5664(1)	12(1)
C(1)	6884(2)	950(1)	2560(1)	15(1)
C(2)	8200(2)	1042(1)	2018(1)	16(1)
C(3)	8543(2)	1028(1)	869(1)	16(1)
C(4)	8199(2)	150(1)	758(1)	17(1)
C(5)	5887(2)	-603(1)	1500(1)	17(1)
C(6)	6299(2)	-333(1)	2116(1)	16(1)
C(7)	4214(2)	748(1)	2844(1)	14(1)
C(8)	2632(2)	721(1)	2654(1)	14(1)
C(9)	7689(2)	2417(1)	1451(1)	14(1)
C(10)	6503(2)	3054(1)	1947(1)	16(1)
C(11)	1318(2)	1301(1)	3137(1)	21(1)
C(12)	2328(2)	-190(1)	2649(1)	21(1)
C(13)	7158(2)	3167(1)	2546(1)	22(1)
C(14)	6117(2)	3937(1)	1642(1)	22(1)
C(15)	5917(2)	2177(1)	11(1)	13(1)
C(16)	6799(2)	2814(1)	-67(1)	17(1)
C(17)	8154(2)	2713(1)	-533(1)	23(1)
C(18)	8660(2)	1977(1)	-936(1)	22(1)
C(19)	7794(2)	1346(1)	-871(1)	18(1)
C(20)	6443(2)	1443(1)	-405(1)	14(1)
C(21)	3079(2)	3339(1)	724(1)	15(1)
C(22)	1861(2)	3605(1)	1249(1)	18(1)
C(23)	797(2)	4413(1)	1268(1)	22(1)
C(24)	939(2)	4963(1)	770(1)	27(1)
C(25)	2145(3)	4708(1)	250(1)	30(1)
C(26)	3205(2)	3900(1)	222(1)	23(1)
C(27)	2939(2)	1720(1)	313(1)	16(1)
C(28)	2720(2)	1540(1)	5025(1)	15(1)
C(29)	1256(2)	2278(1)	5192(1)	15(1)
C(30)	757(2)	3816(1)	5455(1)	14(1)
C(31)	1793(2)	4072(1)	4870(1)	16(1)

C(32)	4799(2)	3136(1)	4220(1)	16(1)
C(33)	4293(2)	2282(1)	4252(1)	16(1)
C(34)	5577(2)	1118(1)	4908(1)	14(1)
C(35)	7139(2)	1333(1)	4994(1)	15(1)
C(36)	558(2)	2829(1)	6313(1)	14(1)
C(37)	1299(2)	2046(1)	6674(1)	15(1)
C(38)	7992(2)	606(1)	5365(1)	20(1)
C(39)	8236(2)	1414(1)	4368(1)	22(1)
C(40)	850(2)	2316(1)	7381(1)	24(1)
C(41)	678(2)	1244(1)	6570(1)	22(1)
C(42)	4193(2)	3529(1)	7269(1)	14(1)
C(43)	3425(2)	4058(1)	7805(1)	20(1)
C(44)	3723(3)	3822(1)	8403(1)	28(1)
C(45)	4833(3)	3065(1)	8469(1)	29(1)
C(46)	5640(2)	2548(1)	7942(1)	22(1)
C(47)	5323(2)	2768(1)	7342(1)	16(1)
C(48)	2245(2)	4758(1)	6557(1)	13(1)
C(49)	832(2)	4785(1)	6990(1)	15(1)
C(50)	-489(2)	5480(1)	7019(1)	18(1)
C(51)	-419(2)	6159(1)	6617(1)	18(1)
C(52)	967(2)	6142(1)	6180(1)	16(1)
C(53)	2288(2)	5446(1)	6150(1)	14(1)
C(54)	5632(2)	4332(1)	6248(1)	15(1)

Table A17. Bond lengths [Å] and angles [°] for **9**

Ru(1)-N(1)	2.1746(13)
Ru(1)-N(2)	2.1852(14)
Ru(1)-S(2)	2.2562(4)
Ru(1)-P(1)	2.3276(4)
Ru(1)-S(1)	2.3508(4)
Ru(1)-S(3)	2.3532(4)
Ru(2)-N(4)	2.1720(14)
Ru(2)-N(3)	2.1743(13)
Ru(2)-S(5)	2.2481(4)
Ru(2)-P(2)	2.3279(4)
Ru(2)-S(4)	2.3455(4)
Ru(2)-S(6)	2.3596(4)
S(1)-C(5)	1.8154(17)
S(1)-C(4)	1.8378(18)
S(2)-O(2)	1.4767(12)
S(2)-O(1)	1.4862(12)
S(2)-C(8)	1.9022(16)
S(3)-O(3)	1.5197(14)
S(3)-C(10)	1.9057(18)
S(4)-C(32)	1.8138(17)
S(4)-C(31)	1.8359(17)
S(5)-O(5)	1.4779(12)
S(5)-O(4)	1.4856(12)
S(5)-C(35)	1.9028(16)
S(6)-O(6)	1.5303(15)
S(6)-C(37)	1.8961(17)
P(1)-C(27)	1.8362(17)
P(1)-C(15)	1.8377(17)
P(1)-C(21)	1.8438(17)
P(2)-C(54)	1.8353(17)
P(2)-C(48)	1.8419(17)
P(2)-C(42)	1.8422(16)
N(1)-C(1)	1.498(2)
N(1)-C(7)	1.500(2)
N(1)-C(6)	1.509(2)
N(2)-C(3)	1.495(2)
N(2)-C(9)	1.499(2)
N(2)-C(2)	1.511(2)
N(3)-C(34)	1.495(2)
N(3)-C(28)	1.496(2)
N(3)-C(33)	1.511(2)
N(4)-C(36)	1.496(2)
N(4)-C(30)	1.500(2)
N(4)-C(29)	1.509(2)
C(1)-C(2)	1.515(2)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.522(2)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700

C(5)-C(6)	1.520(2)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.528(2)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(11)	1.524(2)
C(8)-C(12)	1.530(2)
C(9)-C(10)	1.531(2)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(13)	1.529(2)
C(10)-C(14)	1.535(2)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.402(2)
C(15)-C(20)	1.402(2)
C(16)-C(17)	1.384(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.389(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.384(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.383(2)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(22)	1.392(2)
C(21)-C(26)	1.401(2)
C(22)-C(23)	1.393(2)
C(22)-H(22)	0.9300
C(23)-C(24)	1.385(3)
C(23)-H(23)	0.9300
C(24)-C(25)	1.377(3)
C(24)-H(24)	0.9300
C(25)-C(26)	1.390(3)
C(25)-H(25)	0.9300
C(26)-H(26)	0.9300
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-C(29)	1.509(2)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-H(29A)	0.9700

C(29)-H(29B)	0.9700
C(30)-C(31)	1.523(2)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-C(33)	1.519(2)
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700
C(34)-C(35)	1.531(2)
C(34)-H(34A)	0.9700
C(34)-H(34B)	0.9700
C(35)-C(39)	1.525(2)
C(35)-C(38)	1.528(2)
C(36)-C(37)	1.538(2)
C(36)-H(36A)	0.9700
C(36)-H(36B)	0.9700
C(37)-C(41)	1.527(2)
C(37)-C(40)	1.532(3)
C(38)-H(38A)	0.9600
C(38)-H(38B)	0.9600
C(38)-H(38C)	0.9600
C(39)-H(39A)	0.9600
C(39)-H(39B)	0.9600
C(39)-H(39C)	0.9600
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(41)-H(41A)	0.9600
C(41)-H(41B)	0.9600
C(41)-H(41C)	0.9600
C(42)-C(43)	1.392(2)
C(42)-C(47)	1.400(2)
C(43)-C(44)	1.388(2)
C(43)-H(43)	0.9300
C(44)-C(45)	1.383(3)
C(44)-H(44)	0.9300
C(45)-C(46)	1.377(3)
C(45)-H(45)	0.9300
C(46)-C(47)	1.391(2)
C(46)-H(46)	0.9300
C(47)-H(47)	0.9300
C(48)-C(49)	1.399(2)
C(48)-C(53)	1.400(2)
C(49)-C(50)	1.392(2)
C(49)-H(49)	0.9300
C(50)-C(51)	1.384(2)
C(50)-H(50)	0.9300
C(51)-C(52)	1.388(3)
C(51)-H(51)	0.9300
C(52)-C(53)	1.393(2)
C(52)-H(52)	0.9300
C(53)-H(53)	0.9300
C(54)-H(54A)	0.9600

C(54)-H(54B)	0.9600
C(54)-H(54C)	0.9600
N(1)-Ru(1)-N(2)	81.18(5)
N(1)-Ru(1)-S(2)	84.24(4)
N(2)-Ru(1)-S(2)	165.43(4)
N(1)-Ru(1)-P(1)	171.82(4)
N(2)-Ru(1)-P(1)	103.90(4)
S(2)-Ru(1)-P(1)	90.574(15)
N(1)-Ru(1)-S(1)	84.81(4)
N(2)-Ru(1)-S(1)	84.73(4)
S(2)-Ru(1)-S(1)	93.868(15)
P(1)-Ru(1)-S(1)	89.248(15)
N(1)-Ru(1)-S(3)	95.06(4)
N(2)-Ru(1)-S(3)	85.50(4)
S(2)-Ru(1)-S(3)	95.939(15)
P(1)-Ru(1)-S(3)	91.759(15)
S(1)-Ru(1)-S(3)	170.130(16)
N(4)-Ru(2)-N(3)	81.28(5)
N(4)-Ru(2)-S(5)	165.44(4)
N(3)-Ru(2)-S(5)	84.19(4)
N(4)-Ru(2)-P(2)	103.33(4)
N(3)-Ru(2)-P(2)	172.24(4)
S(5)-Ru(2)-P(2)	91.022(15)
N(4)-Ru(2)-S(4)	85.31(4)
N(3)-Ru(2)-S(4)	84.89(4)
S(5)-Ru(2)-S(4)	92.599(15)
P(2)-Ru(2)-S(4)	89.247(15)
N(4)-Ru(2)-S(6)	85.22(4)
N(3)-Ru(2)-S(6)	94.79(4)
S(5)-Ru(2)-S(6)	96.861(15)
P(2)-Ru(2)-S(6)	91.830(15)
S(4)-Ru(2)-S(6)	170.457(15)
C(5)-S(1)-C(4)	101.62(8)
C(5)-S(1)-Ru(1)	98.65(6)
C(4)-S(1)-Ru(1)	100.45(6)
O(2)-S(2)-O(1)	111.32(7)
O(2)-S(2)-C(8)	104.44(7)
O(1)-S(2)-C(8)	103.75(7)
O(2)-S(2)-Ru(1)	118.15(5)
O(1)-S(2)-Ru(1)	113.47(5)
C(8)-S(2)-Ru(1)	103.87(5)
O(3)-S(3)-C(10)	105.58(8)
O(3)-S(3)-Ru(1)	116.47(6)
C(10)-S(3)-Ru(1)	99.61(5)
C(32)-S(4)-C(31)	101.03(8)
C(32)-S(4)-Ru(2)	99.25(6)
C(31)-S(4)-Ru(2)	100.07(5)
O(5)-S(5)-O(4)	110.96(7)
O(5)-S(5)-C(35)	103.79(7)
O(4)-S(5)-C(35)	103.95(7)
O(5)-S(5)-Ru(2)	119.21(5)
O(4)-S(5)-Ru(2)	113.35(5)
C(35)-S(5)-Ru(2)	103.55(5)
O(6)-S(6)-C(37)	105.17(8)
O(6)-S(6)-Ru(2)	116.99(6)
C(37)-S(6)-Ru(2)	99.78(5)

C(27)-P(1)-C(15)	101.04(8)
C(27)-P(1)-C(21)	96.99(8)
C(15)-P(1)-C(21)	103.98(8)
C(27)-P(1)-Ru(1)	112.72(6)
C(15)-P(1)-Ru(1)	113.92(5)
C(21)-P(1)-Ru(1)	124.65(5)
C(54)-P(2)-C(48)	101.18(8)
C(54)-P(2)-C(42)	98.32(8)
C(48)-P(2)-C(42)	104.05(7)
C(54)-P(2)-Ru(2)	112.68(6)
C(48)-P(2)-Ru(2)	115.39(5)
C(42)-P(2)-Ru(2)	122.07(5)
C(1)-N(1)-C(7)	106.76(12)
C(1)-N(1)-C(6)	109.03(13)
C(7)-N(1)-C(6)	112.07(13)
C(1)-N(1)-Ru(1)	104.39(9)
C(7)-N(1)-Ru(1)	109.16(9)
C(6)-N(1)-Ru(1)	114.86(10)
C(3)-N(2)-C(9)	108.06(12)
C(3)-N(2)-C(2)	107.61(13)
C(9)-N(2)-C(2)	111.05(12)
C(3)-N(2)-Ru(1)	111.44(10)
C(9)-N(2)-Ru(1)	109.33(10)
C(2)-N(2)-Ru(1)	109.35(10)
C(34)-N(3)-C(28)	107.02(12)
C(34)-N(3)-C(33)	112.42(13)
C(28)-N(3)-C(33)	108.34(12)
C(34)-N(3)-Ru(2)	109.02(9)
C(28)-N(3)-Ru(2)	104.66(10)
C(33)-N(3)-Ru(2)	114.81(10)
C(36)-N(4)-C(30)	107.80(13)
C(36)-N(4)-C(29)	111.16(12)
C(30)-N(4)-C(29)	107.47(12)
C(36)-N(4)-Ru(2)	109.76(9)
C(30)-N(4)-Ru(2)	110.81(10)
C(29)-N(4)-Ru(2)	109.80(10)
N(1)-C(1)-C(2)	110.35(13)
N(1)-C(1)-H(1A)	109.6
C(2)-C(1)-H(1A)	109.6
N(1)-C(1)-H(1B)	109.6
C(2)-C(1)-H(1B)	109.6
H(1A)-C(1)-H(1B)	108.1
N(2)-C(2)-C(1)	112.23(13)
N(2)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2A)	109.2
N(2)-C(2)-H(2B)	109.2
C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
N(2)-C(3)-C(4)	112.65(14)
N(2)-C(3)-H(3A)	109.1
C(4)-C(3)-H(3A)	109.1
N(2)-C(3)-H(3B)	109.1
C(4)-C(3)-H(3B)	109.1
H(3A)-C(3)-H(3B)	107.8
C(3)-C(4)-S(1)	112.69(12)
C(3)-C(4)-H(4A)	109.1

S(1)-C(4)-H(4A)	109.1
C(3)-C(4)-H(4B)	109.1
S(1)-C(4)-H(4B)	109.1
H(4A)-C(4)-H(4B)	107.8
C(6)-C(5)-S(1)	112.20(11)
C(6)-C(5)-H(5A)	109.2
S(1)-C(5)-H(5A)	109.2
C(6)-C(5)-H(5B)	109.2
S(1)-C(5)-H(5B)	109.2
H(5A)-C(5)-H(5B)	107.9
N(1)-C(6)-C(5)	114.79(13)
N(1)-C(6)-H(6A)	108.6
C(5)-C(6)-H(6A)	108.6
N(1)-C(6)-H(6B)	108.6
C(5)-C(6)-H(6B)	108.6
H(6A)-C(6)-H(6B)	107.5
N(1)-C(7)-C(8)	116.12(13)
N(1)-C(7)-H(7A)	108.3
C(8)-C(7)-H(7A)	108.3
N(1)-C(7)-H(7B)	108.3
C(8)-C(7)-H(7B)	108.3
H(7A)-C(7)-H(7B)	107.4
C(11)-C(8)-C(7)	106.72(14)
C(11)-C(8)-C(12)	108.87(14)
C(7)-C(8)-C(12)	113.59(14)
C(11)-C(8)-S(2)	108.64(12)
C(7)-C(8)-S(2)	108.38(11)
C(12)-C(8)-S(2)	110.47(11)
N(2)-C(9)-C(10)	116.58(13)
N(2)-C(9)-H(9A)	108.1
C(10)-C(9)-H(9A)	108.1
N(2)-C(9)-H(9B)	108.1
C(10)-C(9)-H(9B)	108.1
H(9A)-C(9)-H(9B)	107.3
C(13)-C(10)-C(9)	113.00(15)
C(13)-C(10)-C(14)	108.73(14)
C(9)-C(10)-C(14)	107.60(14)
C(13)-C(10)-S(3)	109.77(12)
C(9)-C(10)-S(3)	112.77(11)
C(14)-C(10)-S(3)	104.53(12)
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5

H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(20)	117.74(16)
C(16)-C(15)-P(1)	122.53(13)
C(20)-C(15)-P(1)	119.32(13)
C(17)-C(16)-C(15)	120.89(16)
C(17)-C(16)-H(16)	119.6
C(15)-C(16)-H(16)	119.6
C(16)-C(17)-C(18)	120.36(17)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(19)-C(18)-C(17)	119.58(17)
C(19)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
C(20)-C(19)-C(18)	120.25(16)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	121.17(16)
C(19)-C(20)-H(20)	119.4
C(15)-C(20)-H(20)	119.4
C(22)-C(21)-C(26)	118.57(16)
C(22)-C(21)-P(1)	117.66(13)
C(26)-C(21)-P(1)	123.24(13)
C(21)-C(22)-C(23)	120.24(16)
C(21)-C(22)-H(22)	119.9
C(23)-C(22)-H(22)	119.9
C(24)-C(23)-C(22)	120.63(18)
C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7
C(25)-C(24)-C(23)	119.59(17)
C(25)-C(24)-H(24)	120.2
C(23)-C(24)-H(24)	120.2
C(24)-C(25)-C(26)	120.35(18)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(25)-C(26)-C(21)	120.61(18)
C(25)-C(26)-H(26)	119.7
C(21)-C(26)-H(26)	119.7
P(1)-C(27)-H(27A)	109.5
P(1)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
P(1)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(3)-C(28)-C(29)	110.86(13)
N(3)-C(28)-H(28A)	109.5
C(29)-C(28)-H(28A)	109.5
N(3)-C(28)-H(28B)	109.5
C(29)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	108.1

C(28)-C(29)-N(4)	112.23(13)
C(28)-C(29)-H(29A)	109.2
N(4)-C(29)-H(29A)	109.2
C(28)-C(29)-H(29B)	109.2
N(4)-C(29)-H(29B)	109.2
H(29A)-C(29)-H(29B)	107.9
N(4)-C(30)-C(31)	112.58(14)
N(4)-C(30)-H(30A)	109.1
C(31)-C(30)-H(30A)	109.1
N(4)-C(30)-H(30B)	109.1
C(31)-C(30)-H(30B)	109.1
H(30A)-C(30)-H(30B)	107.8
C(30)-C(31)-S(4)	112.56(11)
C(30)-C(31)-H(31A)	109.1
S(4)-C(31)-H(31A)	109.1
C(30)-C(31)-H(31B)	109.1
S(4)-C(31)-H(31B)	109.1
H(31A)-C(31)-H(31B)	107.8
C(33)-C(32)-S(4)	112.37(12)
C(33)-C(32)-H(32A)	109.1
S(4)-C(32)-H(32A)	109.1
C(33)-C(32)-H(32B)	109.1
S(4)-C(32)-H(32B)	109.1
H(32A)-C(32)-H(32B)	107.9
N(3)-C(33)-C(32)	115.29(13)
N(3)-C(33)-H(33A)	108.5
C(32)-C(33)-H(33A)	108.5
N(3)-C(33)-H(33B)	108.5
C(32)-C(33)-H(33B)	108.5
H(33A)-C(33)-H(33B)	107.5
N(3)-C(34)-C(35)	116.24(13)
N(3)-C(34)-H(34A)	108.2
C(35)-C(34)-H(34A)	108.2
N(3)-C(34)-H(34B)	108.2
C(35)-C(34)-H(34B)	108.2
H(34A)-C(34)-H(34B)	107.4
C(39)-C(35)-C(38)	109.34(15)
C(39)-C(35)-C(34)	113.41(14)
C(38)-C(35)-C(34)	107.30(14)
C(39)-C(35)-S(5)	110.17(11)
C(38)-C(35)-S(5)	107.67(11)
C(34)-C(35)-S(5)	108.76(11)
N(4)-C(36)-C(37)	116.20(13)
N(4)-C(36)-H(36A)	108.2
C(37)-C(36)-H(36A)	108.2
N(4)-C(36)-H(36B)	108.2
C(37)-C(36)-H(36B)	108.2
H(36A)-C(36)-H(36B)	107.4
C(41)-C(37)-C(40)	108.60(15)
C(41)-C(37)-C(36)	112.81(14)
C(40)-C(37)-C(36)	106.90(14)
C(41)-C(37)-S(6)	109.20(12)
C(40)-C(37)-S(6)	106.54(12)
C(36)-C(37)-S(6)	112.50(11)
C(35)-C(38)-H(38A)	109.5
C(35)-C(38)-H(38B)	109.5

H(38A)-C(38)-H(38B)	109.5
C(35)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(35)-C(39)-H(39A)	109.5
C(35)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(35)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(37)-C(40)-H(40A)	109.5
C(37)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(37)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(37)-C(41)-H(41A)	109.5
C(37)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(37)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(43)-C(42)-C(47)	118.55(15)
C(43)-C(42)-P(2)	124.20(13)
C(47)-C(42)-P(2)	117.02(13)
C(44)-C(43)-C(42)	120.86(16)
C(44)-C(43)-H(43)	119.6
C(42)-C(43)-H(43)	119.6
C(45)-C(44)-C(43)	120.04(17)
C(45)-C(44)-H(44)	120.0
C(43)-C(44)-H(44)	120.0
C(46)-C(45)-C(44)	119.81(17)
C(46)-C(45)-H(45)	120.1
C(44)-C(45)-H(45)	120.1
C(45)-C(46)-C(47)	120.66(17)
C(45)-C(46)-H(46)	119.7
C(47)-C(46)-H(46)	119.7
C(46)-C(47)-C(42)	120.04(16)
C(46)-C(47)-H(47)	120.0
C(42)-C(47)-H(47)	120.0
C(49)-C(48)-C(53)	118.08(15)
C(49)-C(48)-P(2)	122.46(12)
C(53)-C(48)-P(2)	119.18(13)
C(50)-C(49)-C(48)	120.96(16)
C(50)-C(49)-H(49)	119.5
C(48)-C(49)-H(49)	119.5
C(51)-C(50)-C(49)	120.15(17)
C(51)-C(50)-H(50)	119.9
C(49)-C(50)-H(50)	119.9
C(50)-C(51)-C(52)	119.81(16)
C(50)-C(51)-H(51)	120.1
C(52)-C(51)-H(51)	120.1
C(51)-C(52)-C(53)	120.09(16)
C(51)-C(52)-H(52)	120.0
C(53)-C(52)-H(52)	120.0
C(52)-C(53)-C(48)	120.90(16)

C(52)-C(53)-H(53)	119.6
C(48)-C(53)-H(53)	119.6
P(2)-C(54)-H(54A)	109.5
P(2)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
P(2)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table A18. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for. **9** The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	8(1)	10(1)	8(1)	1(1)	-2(1)	-2(1)
Ru(2)	7(1)	9(1)	8(1)	1(1)	-2(1)	-2(1)
S(1)	14(1)	12(1)	13(1)	-1(1)	-1(1)	-2(1)
S(2)	10(1)	13(1)	12(1)	1(1)	-2(1)	-4(1)
S(3)	14(1)	16(1)	14(1)	-4(1)	0(1)	-6(1)
S(4)	14(1)	13(1)	10(1)	3(1)	-3(1)	-6(1)
S(5)	8(1)	12(1)	12(1)	-1(1)	-1(1)	-3(1)
S(6)	10(1)	13(1)	14(1)	5(1)	-2(1)	-3(1)
P(1)	13(1)	11(1)	9(1)	0(1)	-3(1)	-2(1)
P(2)	11(1)	10(1)	9(1)	0(1)	-2(1)	-2(1)
O(1)	19(1)	19(1)	16(1)	0(1)	-5(1)	-10(1)
O(2)	9(1)	18(1)	22(1)	3(1)	-2(1)	-1(1)
O(3)	32(1)	36(1)	23(1)	-1(1)	-4(1)	-9(1)
O(4)	14(1)	17(1)	17(1)	0(1)	1(1)	-6(1)
O(5)	12(1)	19(1)	17(1)	-1(1)	-5(1)	-1(1)
O(6)	31(1)	26(1)	36(1)	5(1)	-6(1)	-6(1)
N(1)	11(1)	14(1)	12(1)	3(1)	-3(1)	-3(1)
N(2)	10(1)	17(1)	11(1)	0(1)	-2(1)	-3(1)
N(3)	13(1)	13(1)	11(1)	0(1)	-3(1)	-5(1)
N(4)	10(1)	13(1)	14(1)	4(1)	-4(1)	-3(1)
C(1)	14(1)	20(1)	13(1)	3(1)	-6(1)	-5(1)
C(2)	11(1)	22(1)	16(1)	4(1)	-6(1)	-3(1)
C(3)	10(1)	20(1)	16(1)	0(1)	1(1)	-3(1)
C(4)	11(1)	18(1)	19(1)	-3(1)	2(1)	0(1)
C(5)	20(1)	10(1)	18(1)	2(1)	-1(1)	-3(1)
C(6)	16(1)	15(1)	17(1)	4(1)	-3(1)	-1(1)
C(7)	14(1)	17(1)	10(1)	3(1)	-2(1)	-5(1)
C(8)	14(1)	18(1)	11(1)	3(1)	-1(1)	-6(1)
C(9)	13(1)	18(1)	14(1)	2(1)	-2(1)	-8(1)
C(10)	17(1)	19(1)	15(1)	-1(1)	-2(1)	-10(1)
C(11)	15(1)	32(1)	14(1)	0(1)	2(1)	-6(1)
C(12)	26(1)	23(1)	18(1)	7(1)	-4(1)	-14(1)
C(13)	24(1)	28(1)	18(1)	-4(1)	-4(1)	-15(1)
C(14)	26(1)	18(1)	23(1)	-2(1)	-1(1)	-10(1)
C(15)	16(1)	15(1)	9(1)	3(1)	-4(1)	-3(1)
C(16)	24(1)	16(1)	13(1)	2(1)	-5(1)	-6(1)
C(17)	27(1)	24(1)	21(1)	6(1)	-3(1)	-13(1)
C(18)	20(1)	29(1)	15(1)	4(1)	2(1)	-6(1)
C(19)	20(1)	20(1)	13(1)	0(1)	-3(1)	0(1)
C(20)	17(1)	15(1)	12(1)	2(1)	-5(1)	-5(1)
C(21)	18(1)	13(1)	15(1)	0(1)	-7(1)	-2(1)
C(22)	18(1)	18(1)	16(1)	1(1)	-4(1)	-3(1)
C(23)	20(1)	20(1)	22(1)	-2(1)	-2(1)	0(1)
C(24)	29(1)	16(1)	32(1)	1(1)	-7(1)	4(1)
C(25)	39(1)	21(1)	24(1)	8(1)	-4(1)	3(1)
C(26)	30(1)	20(1)	15(1)	2(1)	-1(1)	3(1)
C(27)	16(1)	20(1)	13(1)	1(1)	-6(1)	-4(1)
C(28)	16(1)	16(1)	16(1)	0(1)	-6(1)	-8(1)
C(29)	14(1)	16(1)	18(1)	3(1)	-8(1)	-7(1)
C(30)	12(1)	12(1)	18(1)	5(1)	-6(1)	-1(1)
C(31)	16(1)	16(1)	18(1)	7(1)	-9(1)	-5(1)

C(32)	20(1)	19(1)	9(1)	1(1)	0(1)	-7(1)
C(33)	22(1)	19(1)	9(1)	0(1)	-4(1)	-7(1)
C(34)	15(1)	12(1)	15(1)	-3(1)	-2(1)	-3(1)
C(35)	12(1)	14(1)	16(1)	-4(1)	0(1)	-2(1)
C(36)	10(1)	16(1)	16(1)	6(1)	-2(1)	-3(1)
C(37)	10(1)	18(1)	18(1)	7(1)	-1(1)	-3(1)
C(38)	15(1)	14(1)	30(1)	-3(1)	-4(1)	0(1)
C(39)	18(1)	22(1)	22(1)	-9(1)	6(1)	-7(1)
C(40)	18(1)	29(1)	18(1)	10(1)	3(1)	1(1)
C(41)	14(1)	21(1)	33(1)	14(1)	-5(1)	-8(1)
C(42)	18(1)	13(1)	12(1)	1(1)	-5(1)	-5(1)
C(43)	26(1)	16(1)	16(1)	-2(1)	-8(1)	2(1)
C(44)	42(1)	24(1)	13(1)	-4(1)	-6(1)	3(1)
C(45)	48(1)	24(1)	14(1)	2(1)	-14(1)	-1(1)
C(46)	31(1)	16(1)	19(1)	2(1)	-13(1)	0(1)
C(47)	20(1)	15(1)	14(1)	0(1)	-6(1)	-3(1)
C(48)	15(1)	12(1)	11(1)	-2(1)	-4(1)	-2(1)
C(49)	18(1)	15(1)	13(1)	1(1)	-3(1)	-3(1)
C(50)	15(1)	22(1)	14(1)	-4(1)	-2(1)	-1(1)
C(51)	19(1)	15(1)	19(1)	-4(1)	-9(1)	3(1)
C(52)	21(1)	12(1)	18(1)	1(1)	-9(1)	-3(1)
C(53)	15(1)	14(1)	12(1)	-1(1)	-4(1)	-5(1)
C(54)	14(1)	14(1)	18(1)	1(1)	-4(1)	-5(1)

Table A19. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **9**.

	x	y	z	U(eq)
H(1A)	7331	553	2861	18
H(1B)	6401	1509	2779	18
H(2A)	8872	1371	2169	19
H(2B)	8857	471	1873	19
H(3A)	9663	946	890	19
H(3B)	8339	1386	512	19
H(4A)	8699	-262	1038	21
H(4B)	8669	-58	324	21
H(5A)	4805	-681	1584	20
H(5B)	6598	-1156	1343	20
H(6A)	5901	-681	2452	20
H(6B)	7451	-463	2070	20
H(7A)	4087	1307	3056	16
H(7B)	4436	307	3151	16
H(9A)	7565	2627	1034	17
H(9B)	8759	2427	1503	17
H(11A)	296	1259	3059	31
H(11B)	1407	1892	3099	31
H(11C)	1425	1119	3557	31
H(12A)	2211	-393	3073	31
H(12B)	3212	-577	2382	31
H(12C)	1370	-172	2488	31
H(13A)	7357	2624	2752	33
H(13B)	6393	3596	2830	33
H(13C)	8136	3352	2434	33
H(14A)	7091	4103	1476	33
H(14B)	5464	4365	1956	33
H(14C)	5555	3894	1304	33
H(16)	6470	3310	199	21
H(17)	8727	3140	-578	27
H(18)	9575	1908	-1247	26
H(19)	8122	855	-1143	22
H(20)	5873	1013	-365	17
H(22)	1757	3241	1587	21
H(23)	-16	4584	1620	26
H(24)	224	5501	786	32
H(25)	2251	5079	-84	36
H(26)	4004	3730	-135	28
H(27A)	2844	1967	-91	24
H(27B)	1905	1830	583	24
H(27C)	3372	1104	254	24
H(28A)	2774	1151	5374	18
H(28B)	2645	1215	4654	18
H(29A)	348	2045	5368	18
H(29B)	1036	2569	4808	18
H(30A)	626	4237	5800	17
H(30B)	-292	3832	5364	17
H(31A)	1425	4688	4813	19
H(31B)	1673	3763	4499	19
H(32A)	4489	3438	3852	19

H(32B)	5952	3018	4166	19
H(33A)	3254	2377	4133	19
H(33B)	5041	1872	3941	19
H(34A)	5780	775	4514	17
H(34B)	5264	758	5251	17
H(36A)	-507	2786	6276	17
H(36B)	447	3352	6567	17
H(38A)	8251	68	5122	30
H(38B)	7307	558	5761	30
H(38C)	8955	736	5446	30
H(39A)	8558	865	4136	32
H(39B)	9162	1582	4453	32
H(39C)	7678	1845	4122	32
H(40A)	-286	2529	7497	36
H(40B)	1363	2765	7463	36
H(40C)	1191	1824	7626	36
H(41A)	1125	787	6825	33
H(41B)	982	1056	6131	33
H(41C)	-464	1386	6690	33
H(43)	2702	4578	7762	24
H(44)	3177	4172	8758	33
H(45)	5034	2905	8869	34
H(46)	6405	2046	7986	27
H(47)	5862	2409	6990	20
H(49)	773	4331	7263	19
H(50)	-1421	5488	7309	21
H(51)	-1298	6626	6639	21
H(52)	1014	6595	5906	20
H(53)	3212	5439	5855	16
H(54A)	5454	4835	6524	23
H(54B)	5714	4503	5816	23
H(54C)	6604	3931	6297	23

Table A20. Torsion angles [°] for **9**.

N(1)-Ru(1)-S(1)-C(5)	20.23(7)
N(2)-Ru(1)-S(1)-C(5)	101.82(7)
S(2)-Ru(1)-S(1)-C(5)	-63.62(6)
P(1)-Ru(1)-S(1)-C(5)	-154.15(6)
S(3)-Ru(1)-S(1)-C(5)	109.91(10)
N(1)-Ru(1)-S(1)-C(4)	-83.38(7)
N(2)-Ru(1)-S(1)-C(4)	-1.79(7)
S(2)-Ru(1)-S(1)-C(4)	-167.23(6)
P(1)-Ru(1)-S(1)-C(4)	102.24(6)
S(3)-Ru(1)-S(1)-C(4)	6.30(11)
N(1)-Ru(1)-S(2)-O(2)	130.33(7)
N(2)-Ru(1)-S(2)-O(2)	130.78(16)
P(1)-Ru(1)-S(2)-O(2)	-56.01(6)
S(1)-Ru(1)-S(2)-O(2)	-145.29(6)
S(3)-Ru(1)-S(2)-O(2)	35.82(6)
N(1)-Ru(1)-S(2)-O(1)	-96.69(6)
N(2)-Ru(1)-S(2)-O(1)	-96.24(16)
P(1)-Ru(1)-S(2)-O(1)	76.98(6)
S(1)-Ru(1)-S(2)-O(1)	-12.31(6)
S(3)-Ru(1)-S(2)-O(1)	168.81(5)
N(1)-Ru(1)-S(2)-C(8)	15.28(6)
N(2)-Ru(1)-S(2)-C(8)	15.73(16)
P(1)-Ru(1)-S(2)-C(8)	-171.06(5)
S(1)-Ru(1)-S(2)-C(8)	99.66(5)
S(3)-Ru(1)-S(2)-C(8)	-79.23(5)
N(1)-Ru(1)-S(3)-O(3)	-16.46(8)
N(2)-Ru(1)-S(3)-O(3)	-97.18(8)
S(2)-Ru(1)-S(3)-O(3)	68.26(7)
P(1)-Ru(1)-S(3)-O(3)	159.02(7)
S(1)-Ru(1)-S(3)-O(3)	-105.25(11)
N(1)-Ru(1)-S(3)-C(10)	96.41(7)
N(2)-Ru(1)-S(3)-C(10)	15.69(7)
S(2)-Ru(1)-S(3)-C(10)	-178.87(6)
P(1)-Ru(1)-S(3)-C(10)	-88.11(6)
S(1)-Ru(1)-S(3)-C(10)	7.62(11)
N(4)-Ru(2)-S(4)-C(32)	-101.09(7)
N(3)-Ru(2)-S(4)-C(32)	-19.45(7)
S(5)-Ru(2)-S(4)-C(32)	64.47(6)
P(2)-Ru(2)-S(4)-C(32)	155.46(6)
S(6)-Ru(2)-S(4)-C(32)	-107.97(10)
N(4)-Ru(2)-S(4)-C(31)	1.95(7)
N(3)-Ru(2)-S(4)-C(31)	83.60(7)
S(5)-Ru(2)-S(4)-C(31)	167.52(6)
P(2)-Ru(2)-S(4)-C(31)	-101.49(6)
S(6)-Ru(2)-S(4)-C(31)	-4.92(11)
N(4)-Ru(2)-S(5)-O(5)	-135.68(15)
N(3)-Ru(2)-S(5)-O(5)	-132.39(7)
P(2)-Ru(2)-S(5)-O(5)	53.72(6)
S(4)-Ru(2)-S(5)-O(5)	143.01(6)
S(6)-Ru(2)-S(5)-O(5)	-38.25(6)
N(4)-Ru(2)-S(5)-O(4)	90.86(15)
N(3)-Ru(2)-S(5)-O(4)	94.15(6)
P(2)-Ru(2)-S(5)-O(4)	-79.74(5)
S(4)-Ru(2)-S(5)-O(4)	9.55(5)

S(6)-Ru(2)-S(5)-O(4)	-171.71(5)
N(4)-Ru(2)-S(5)-C(35)	-21.11(16)
N(3)-Ru(2)-S(5)-C(35)	-17.83(7)
P(2)-Ru(2)-S(5)-C(35)	168.29(6)
S(4)-Ru(2)-S(5)-C(35)	-102.42(6)
S(6)-Ru(2)-S(5)-C(35)	76.32(6)
N(4)-Ru(2)-S(6)-O(6)	97.13(8)
N(3)-Ru(2)-S(6)-O(6)	16.32(8)
S(5)-Ru(2)-S(6)-O(6)	-68.39(7)
P(2)-Ru(2)-S(6)-O(6)	-159.64(7)
S(4)-Ru(2)-S(6)-O(6)	104.00(11)
N(4)-Ru(2)-S(6)-C(37)	-15.56(7)
N(3)-Ru(2)-S(6)-C(37)	-96.37(7)
S(5)-Ru(2)-S(6)-C(37)	178.92(6)
P(2)-Ru(2)-S(6)-C(37)	87.67(6)
S(4)-Ru(2)-S(6)-C(37)	-8.69(11)
N(1)-Ru(1)-P(1)-C(27)	13.1(3)
N(2)-Ru(1)-P(1)-C(27)	140.85(7)
S(2)-Ru(1)-P(1)-C(27)	-37.40(6)
S(1)-Ru(1)-P(1)-C(27)	56.47(6)
S(3)-Ru(1)-P(1)-C(27)	-133.36(6)
N(1)-Ru(1)-P(1)-C(15)	-101.2(3)
N(2)-Ru(1)-P(1)-C(15)	26.46(7)
S(2)-Ru(1)-P(1)-C(15)	-151.78(6)
S(1)-Ru(1)-P(1)-C(15)	-57.92(6)
S(3)-Ru(1)-P(1)-C(15)	112.26(6)
N(1)-Ru(1)-P(1)-C(21)	129.9(3)
N(2)-Ru(1)-P(1)-C(21)	-102.42(8)
S(2)-Ru(1)-P(1)-C(21)	79.34(7)
S(1)-Ru(1)-P(1)-C(21)	173.20(7)
S(3)-Ru(1)-P(1)-C(21)	-16.62(7)
N(4)-Ru(2)-P(2)-C(54)	-142.21(7)
N(3)-Ru(2)-P(2)-C(54)	-16.4(3)
S(5)-Ru(2)-P(2)-C(54)	35.37(6)
S(4)-Ru(2)-P(2)-C(54)	-57.21(6)
S(6)-Ru(2)-P(2)-C(54)	132.27(6)
N(4)-Ru(2)-P(2)-C(48)	-26.68(7)
N(3)-Ru(2)-P(2)-C(48)	99.2(3)
S(5)-Ru(2)-P(2)-C(48)	150.91(6)
S(4)-Ru(2)-P(2)-C(48)	58.32(6)
S(6)-Ru(2)-P(2)-C(48)	-112.20(6)
N(4)-Ru(2)-P(2)-C(42)	101.24(8)
N(3)-Ru(2)-P(2)-C(42)	-132.9(3)
S(5)-Ru(2)-P(2)-C(42)	-81.17(7)
S(4)-Ru(2)-P(2)-C(42)	-173.76(7)
S(6)-Ru(2)-P(2)-C(42)	15.73(7)
N(2)-Ru(1)-N(1)-C(1)	31.39(10)
S(2)-Ru(1)-N(1)-C(1)	-148.72(10)
P(1)-Ru(1)-N(1)-C(1)	160.4(2)
S(1)-Ru(1)-N(1)-C(1)	116.85(10)
S(3)-Ru(1)-N(1)-C(1)	-53.24(10)
N(2)-Ru(1)-N(1)-C(7)	145.24(10)
S(2)-Ru(1)-N(1)-C(7)	-34.87(9)
P(1)-Ru(1)-N(1)-C(7)	-85.8(3)
S(1)-Ru(1)-N(1)-C(7)	-129.30(10)
S(3)-Ru(1)-N(1)-C(7)	60.61(10)

N(2)-Ru(1)-N(1)-C(6)	-87.94(11)
S(2)-Ru(1)-N(1)-C(6)	91.95(11)
P(1)-Ru(1)-N(1)-C(6)	41.1(3)
S(1)-Ru(1)-N(1)-C(6)	-2.48(10)
S(3)-Ru(1)-N(1)-C(6)	-172.57(10)
N(1)-Ru(1)-N(2)-C(3)	110.80(11)
S(2)-Ru(1)-N(2)-C(3)	110.35(15)
P(1)-Ru(1)-N(2)-C(3)	-62.66(10)
S(1)-Ru(1)-N(2)-C(3)	25.26(10)
S(3)-Ru(1)-N(2)-C(3)	-153.36(10)
N(1)-Ru(1)-N(2)-C(9)	-129.81(10)
S(2)-Ru(1)-N(2)-C(9)	-130.26(13)
P(1)-Ru(1)-N(2)-C(9)	56.73(10)
S(1)-Ru(1)-N(2)-C(9)	144.64(10)
S(3)-Ru(1)-N(2)-C(9)	-33.97(9)
N(1)-Ru(1)-N(2)-C(2)	-8.03(10)
S(2)-Ru(1)-N(2)-C(2)	-8.5(2)
P(1)-Ru(1)-N(2)-C(2)	178.51(9)
S(1)-Ru(1)-N(2)-C(2)	-93.58(10)
S(3)-Ru(1)-N(2)-C(2)	87.81(10)
N(4)-Ru(2)-N(3)-C(34)	-144.38(10)
S(5)-Ru(2)-N(3)-C(34)	36.46(9)
P(2)-Ru(2)-N(3)-C(34)	88.5(3)
S(4)-Ru(2)-N(3)-C(34)	129.60(10)
S(6)-Ru(2)-N(3)-C(34)	-59.97(10)
N(4)-Ru(2)-N(3)-C(28)	-30.16(10)
S(5)-Ru(2)-N(3)-C(28)	150.68(9)
P(2)-Ru(2)-N(3)-C(28)	-157.2(2)
S(4)-Ru(2)-N(3)-C(28)	-116.18(9)
S(6)-Ru(2)-N(3)-C(28)	54.25(9)
N(4)-Ru(2)-N(3)-C(33)	88.48(11)
S(5)-Ru(2)-N(3)-C(33)	-90.68(11)
P(2)-Ru(2)-N(3)-C(33)	-38.6(3)
S(4)-Ru(2)-N(3)-C(33)	2.46(11)
S(6)-Ru(2)-N(3)-C(33)	172.89(11)
N(3)-Ru(2)-N(4)-C(36)	129.85(10)
S(5)-Ru(2)-N(4)-C(36)	133.16(13)
P(2)-Ru(2)-N(4)-C(36)	-56.50(10)
S(4)-Ru(2)-N(4)-C(36)	-144.61(10)
S(6)-Ru(2)-N(4)-C(36)	34.25(9)
N(3)-Ru(2)-N(4)-C(30)	-111.20(11)
S(5)-Ru(2)-N(4)-C(30)	-107.90(15)
P(2)-Ru(2)-N(4)-C(30)	62.44(10)
S(4)-Ru(2)-N(4)-C(30)	-25.66(10)
S(6)-Ru(2)-N(4)-C(30)	153.19(10)
N(3)-Ru(2)-N(4)-C(29)	7.37(10)
S(5)-Ru(2)-N(4)-C(29)	10.7(2)
P(2)-Ru(2)-N(4)-C(29)	-178.99(9)
S(4)-Ru(2)-N(4)-C(29)	92.91(9)
S(6)-Ru(2)-N(4)-C(29)	-88.23(9)
C(7)-N(1)-C(1)-C(2)	-166.28(13)
C(6)-N(1)-C(1)-C(2)	72.46(16)
Ru(1)-N(1)-C(1)-C(2)	-50.74(14)
C(3)-N(2)-C(2)-C(1)	-138.76(14)
C(9)-N(2)-C(2)-C(1)	103.16(16)
Ru(1)-N(2)-C(2)-C(1)	-17.57(16)

N(1)-C(1)-C(2)-N(2)	46.96(18)
C(9)-N(2)-C(3)-C(4)	-166.60(13)
C(2)-N(2)-C(3)-C(4)	73.40(17)
Ru(1)-N(2)-C(3)-C(4)	-46.47(16)
N(2)-C(3)-C(4)-S(1)	45.15(18)
C(5)-S(1)-C(4)-C(3)	-122.59(13)
Ru(1)-S(1)-C(4)-C(3)	-21.40(13)
C(4)-S(1)-C(5)-C(6)	64.50(14)
Ru(1)-S(1)-C(5)-C(6)	-38.13(13)
C(1)-N(1)-C(6)-C(5)	-138.55(15)
C(7)-N(1)-C(6)-C(5)	103.48(16)
Ru(1)-N(1)-C(6)-C(5)	-21.84(18)
S(1)-C(5)-C(6)-N(1)	41.89(18)
C(1)-N(1)-C(7)-C(8)	161.69(13)
C(6)-N(1)-C(7)-C(8)	-79.00(17)
Ru(1)-N(1)-C(7)-C(8)	49.40(15)
N(1)-C(7)-C(8)-C(11)	-151.28(14)
N(1)-C(7)-C(8)-C(12)	88.74(17)
N(1)-C(7)-C(8)-S(2)	-34.44(17)
O(2)-S(2)-C(8)-C(11)	-4.35(13)
O(1)-S(2)-C(8)-C(11)	-121.06(12)
Ru(1)-S(2)-C(8)-C(11)	120.07(11)
O(2)-S(2)-C(8)-C(7)	-119.95(11)
O(1)-S(2)-C(8)-C(7)	123.34(11)
Ru(1)-S(2)-C(8)-C(7)	4.48(12)
O(2)-S(2)-C(8)-C(12)	115.01(12)
O(1)-S(2)-C(8)-C(12)	-1.70(14)
Ru(1)-S(2)-C(8)-C(12)	-120.56(11)
C(3)-N(2)-C(9)-C(10)	167.60(14)
C(2)-N(2)-C(9)-C(10)	-74.59(17)
Ru(1)-N(2)-C(9)-C(10)	46.15(16)
N(2)-C(9)-C(10)-C(13)	93.74(17)
N(2)-C(9)-C(10)-C(14)	-146.22(14)
N(2)-C(9)-C(10)-S(3)	-31.48(18)
O(3)-S(3)-C(10)-C(13)	-3.30(14)
Ru(1)-S(3)-C(10)-C(13)	-124.40(12)
O(3)-S(3)-C(10)-C(9)	123.65(12)
Ru(1)-S(3)-C(10)-C(9)	2.55(12)
O(3)-S(3)-C(10)-C(14)	-119.76(12)
Ru(1)-S(3)-C(10)-C(14)	119.14(10)
C(27)-P(1)-C(15)-C(16)	147.15(14)
C(21)-P(1)-C(15)-C(16)	46.99(16)
Ru(1)-P(1)-C(15)-C(16)	-91.71(14)
C(27)-P(1)-C(15)-C(20)	-40.35(15)
C(21)-P(1)-C(15)-C(20)	-140.50(13)
Ru(1)-P(1)-C(15)-C(20)	80.79(13)
C(20)-C(15)-C(16)-C(17)	-0.7(2)
P(1)-C(15)-C(16)-C(17)	171.87(14)
C(15)-C(16)-C(17)-C(18)	0.2(3)
C(16)-C(17)-C(18)-C(19)	0.5(3)
C(17)-C(18)-C(19)-C(20)	-0.7(3)
C(18)-C(19)-C(20)-C(15)	0.2(3)
C(16)-C(15)-C(20)-C(19)	0.6(2)
P(1)-C(15)-C(20)-C(19)	-172.29(13)
C(27)-P(1)-C(21)-C(22)	85.85(14)
C(15)-P(1)-C(21)-C(22)	-170.89(13)

Ru(1)-P(1)-C(21)-C(22)	-38.06(16)
C(27)-P(1)-C(21)-C(26)	-85.68(16)
C(15)-P(1)-C(21)-C(26)	17.58(17)
Ru(1)-P(1)-C(21)-C(26)	150.41(13)
C(26)-C(21)-C(22)-C(23)	-0.1(3)
P(1)-C(21)-C(22)-C(23)	-172.04(14)
C(21)-C(22)-C(23)-C(24)	-0.2(3)
C(22)-C(23)-C(24)-C(25)	-0.1(3)
C(23)-C(24)-C(25)-C(26)	0.7(3)
C(24)-C(25)-C(26)-C(21)	-1.1(3)
C(22)-C(21)-C(26)-C(25)	0.7(3)
P(1)-C(21)-C(26)-C(25)	172.20(16)
C(34)-N(3)-C(28)-C(29)	164.86(13)
C(33)-N(3)-C(28)-C(29)	-73.70(16)
Ru(2)-N(3)-C(28)-C(29)	49.24(14)
N(3)-C(28)-C(29)-N(4)	-45.93(18)
C(36)-N(4)-C(29)-C(28)	-104.06(15)
C(30)-N(4)-C(29)-C(28)	138.20(14)
Ru(2)-N(4)-C(29)-C(28)	17.59(16)
C(36)-N(4)-C(30)-C(31)	167.28(13)
C(29)-N(4)-C(30)-C(31)	-72.82(16)
Ru(2)-N(4)-C(30)-C(31)	47.16(15)
N(4)-C(30)-C(31)-S(4)	-45.90(17)
C(32)-S(4)-C(31)-C(30)	123.22(12)
Ru(2)-S(4)-C(31)-C(30)	21.63(12)
C(31)-S(4)-C(32)-C(33)	-65.76(14)
Ru(2)-S(4)-C(32)-C(33)	36.49(13)
C(34)-N(3)-C(33)-C(32)	-104.52(16)
C(28)-N(3)-C(33)-C(32)	137.42(15)
Ru(2)-N(3)-C(33)-C(32)	20.87(18)
S(4)-C(32)-C(33)-N(3)	-40.01(19)
C(28)-N(3)-C(34)-C(35)	-161.35(14)
C(33)-N(3)-C(34)-C(35)	79.82(17)
Ru(2)-N(3)-C(34)-C(35)	-48.67(16)
N(3)-C(34)-C(35)-C(39)	-91.32(17)
N(3)-C(34)-C(35)-C(38)	147.83(14)
N(3)-C(34)-C(35)-S(5)	31.62(17)
O(5)-S(5)-C(35)-C(39)	-110.90(13)
O(4)-S(5)-C(35)-C(39)	5.24(14)
Ru(2)-S(5)-C(35)-C(39)	123.92(11)
O(5)-S(5)-C(35)-C(38)	8.26(13)
O(4)-S(5)-C(35)-C(38)	124.40(12)
Ru(2)-S(5)-C(35)-C(38)	-116.92(11)
O(5)-S(5)-C(35)-C(34)	124.22(12)
O(4)-S(5)-C(35)-C(34)	-119.63(12)
Ru(2)-S(5)-C(35)-C(34)	-0.95(12)
C(30)-N(4)-C(36)-C(37)	-167.53(13)
C(29)-N(4)-C(36)-C(37)	74.93(17)
Ru(2)-N(4)-C(36)-C(37)	-46.75(16)
N(4)-C(36)-C(37)-C(41)	-92.18(18)
N(4)-C(36)-C(37)-C(40)	148.51(15)
N(4)-C(36)-C(37)-S(6)	31.90(18)
O(6)-S(6)-C(37)-C(41)	1.50(14)
Ru(2)-S(6)-C(37)-C(41)	123.09(11)
O(6)-S(6)-C(37)-C(40)	118.61(12)
Ru(2)-S(6)-C(37)-C(40)	-119.79(11)

O(6)-S(6)-C(37)-C(36)	-124.57(12)
Ru(2)-S(6)-C(37)-C(36)	-2.97(12)
C(54)-P(2)-C(42)-C(43)	91.90(16)
C(48)-P(2)-C(42)-C(43)	-11.91(17)
Ru(2)-P(2)-C(42)-C(43)	-144.64(13)
C(54)-P(2)-C(42)-C(47)	-82.47(14)
C(48)-P(2)-C(42)-C(47)	173.73(13)
Ru(2)-P(2)-C(42)-C(47)	41.00(16)
C(47)-C(42)-C(43)-C(44)	-2.5(3)
P(2)-C(42)-C(43)-C(44)	-176.77(15)
C(42)-C(43)-C(44)-C(45)	2.1(3)
C(43)-C(44)-C(45)-C(46)	0.0(3)
C(44)-C(45)-C(46)-C(47)	-1.6(3)
C(45)-C(46)-C(47)-C(42)	1.1(3)
C(43)-C(42)-C(47)-C(46)	0.9(3)
P(2)-C(42)-C(47)-C(46)	175.61(14)
C(54)-P(2)-C(48)-C(49)	-148.02(14)
C(42)-P(2)-C(48)-C(49)	-46.39(15)
Ru(2)-P(2)-C(48)-C(49)	90.05(14)
C(54)-P(2)-C(48)-C(53)	38.25(14)
C(42)-P(2)-C(48)-C(53)	139.88(13)
Ru(2)-P(2)-C(48)-C(53)	-83.68(13)
C(53)-C(48)-C(49)-C(50)	-0.6(2)
P(2)-C(48)-C(49)-C(50)	-174.43(13)
C(48)-C(49)-C(50)-C(51)	0.0(3)
C(49)-C(50)-C(51)-C(52)	0.6(2)
C(50)-C(51)-C(52)-C(53)	-0.5(2)
C(51)-C(52)-C(53)-C(48)	-0.2(2)
C(49)-C(48)-C(53)-C(52)	0.7(2)
P(2)-C(48)-C(53)-C(52)	174.74(12)

Symmetry transformations used to generate equivalent atoms:

Table A21. Crystal data and structure refinement for **10**

Identification code	cag148p1bar	
Empirical formula	C18 H22 I N2 O P Ru S3	
Formula weight	637.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3441(10) Å	$\alpha = 111.689(2)^\circ$.
	b = 11.7392(13) Å	$\beta = 107.581(2)^\circ$.
	c = 12.4768(14) Å	$\gamma = 91.071(2)^\circ$.
Volume	1070.8(2) Å ³	
Z	2	
Density (calculated)	1.977 Mg/m ³	
Absorption coefficient	2.553 mm ⁻¹	
F(000)	624	
Crystal size	0.39 x 0.11 x 0.04 mm ³	
Crystal color, habit	orange plate	
Theta range for data collection	2.59 to 28.03°	
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 14, -16 ≤ l ≤ 16	
Reflections collected	9488	
Independent reflections	4842 [R(int) = 0.0136]	
Completeness to theta = 28.03°	93.5 %	
Absorption correction	SADABS	
Max. and min. transmission	0.905 and 0.436	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4842 / 0 / 223	
Goodness-of-fit on F ²	1.052	
Final R indices [I > 2σ(I)]	R1 = 0.0202, wR2 = 0.0484	
R indices (all data)	R1 = 0.0210, wR2 = 0.0490	
Largest diff. peak and hole	0.765 and -0.502 e.Å ⁻³	

Table A22. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	5448(1)	244(1)	6262(1)	10(1)
S(1)	8078(1)	-598(1)	6314(1)	14(1)
S(2)	2970(1)	1013(1)	6590(1)	14(1)
S(3)	5500(1)	1633(1)	5357(1)	12(1)
N(1)	5599(2)	-359(2)	7704(2)	13(1)
N(2)	6862(2)	1914(2)	7800(2)	14(1)
C(1)	7958(2)	-1613(2)	7142(2)	15(1)
C(2)	6300(2)	-1567(2)	7452(2)	14(1)
C(5)	3850(2)	-594(2)	7751(2)	15(1)
C(6)	2887(3)	495(2)	7794(2)	16(1)
C(3)	6655(3)	621(2)	8935(2)	16(1)
C(4)	7826(3)	1516(2)	8802(2)	16(1)
C(7)	5730(3)	2833(2)	8293(2)	17(1)
C(8)	3903(3)	2636(2)	7458(2)	16(1)
C(9)	8210(3)	2492(2)	7489(2)	17(1)
C(10)	7664(2)	2535(2)	6206(2)	13(1)
C(11)	7432(3)	3852(2)	6272(2)	18(1)
C(12)	8982(3)	2048(2)	5595(2)	18(1)
C(13)	9545(3)	-1280(2)	8280(2)	18(1)
C(14)	7913(3)	-2964(2)	6301(2)	19(1)
O(1)	6588(2)	2871(1)	1301(2)	25(1)
I	7521(1)	6441(1)	9581(1)	20(1)
C(15)	7706(3)	4024(2)	1975(2)	25(1)
C(16)	7751(3)	4583(2)	3283(2)	32(1)

Table A23. Bond lengths [Å] and angles [°] for **10**

Ru(1)-N(1)	2.1351(16)
Ru(1)-N(2)	2.1639(16)
Ru(1)-S(3)#1	2.2899(5)
Ru(1)-S(3)	2.3068(5)
Ru(1)-S(2)	2.3589(5)
Ru(1)-S(1)	2.4170(5)
Ru(1)-Ru(1)#1	2.8349(4)
S(1)-C(1)	1.862(2)
S(2)-C(8)	1.821(2)
S(2)-C(6)	1.834(2)
S(3)-C(10)	1.857(2)
S(3)-Ru(1)#1	2.2898(5)
N(1)-C(5)	1.503(2)
N(1)-C(2)	1.505(2)
N(1)-C(3)	1.516(2)
N(2)-C(4)	1.506(2)
N(2)-C(9)	1.518(3)
N(2)-C(7)	1.527(3)
C(1)-C(13)	1.535(3)
C(1)-C(14)	1.537(3)
C(1)-C(2)	1.542(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(5)-C(6)	1.515(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(3)-C(4)	1.508(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(7)-C(8)	1.520(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.547(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(12)	1.525(3)
C(10)-C(11)	1.537(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800

C(14)-H(14C)	0.9800
O(1)-C(15)	1.431(3)
O(1)-H(1)	0.8400
C(15)-C(16)	1.505(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
N(1)-Ru(1)-N(2)	81.21(6)
N(1)-Ru(1)-S(3)#1	98.67(5)
N(2)-Ru(1)-S(3)#1	168.08(5)
N(1)-Ru(1)-S(3)	157.24(5)
N(2)-Ru(1)-S(3)	77.46(5)
S(3)#1-Ru(1)-S(3)	103.842(18)
N(1)-Ru(1)-S(2)	85.19(4)
N(2)-Ru(1)-S(2)	86.77(5)
S(3)#1-Ru(1)-S(2)	105.113(18)
S(3)-Ru(1)-S(2)	85.762(17)
N(1)-Ru(1)-S(1)	83.30(4)
N(2)-Ru(1)-S(1)	89.19(5)
S(3)#1-Ru(1)-S(1)	78.981(17)
S(3)-Ru(1)-S(1)	104.111(17)
S(2)-Ru(1)-S(1)	168.268(18)
N(1)-Ru(1)-Ru(1)#1	150.70(4)
N(2)-Ru(1)-Ru(1)#1	127.86(4)
S(3)#1-Ru(1)-Ru(1)#1	52.189(13)
S(3)-Ru(1)-Ru(1)#1	51.653(13)
S(2)-Ru(1)-Ru(1)#1	98.653(14)
S(1)-Ru(1)-Ru(1)#1	92.522(14)
C(1)-S(1)-Ru(1)	100.16(6)
C(8)-S(2)-C(6)	102.41(10)
C(8)-S(2)-Ru(1)	97.28(7)
C(6)-S(2)-Ru(1)	99.64(6)
C(10)-S(3)-Ru(1)#1	131.26(6)
C(10)-S(3)-Ru(1)	102.94(6)
Ru(1)#1-S(3)-Ru(1)	76.157(18)
C(5)-N(1)-C(2)	107.14(14)
C(5)-N(1)-C(3)	107.45(15)
C(2)-N(1)-C(3)	111.54(15)
C(5)-N(1)-Ru(1)	109.83(11)
C(2)-N(1)-Ru(1)	109.61(12)
C(3)-N(1)-Ru(1)	111.16(12)
C(4)-N(2)-C(9)	105.44(15)
C(4)-N(2)-C(7)	107.85(15)
C(9)-N(2)-C(7)	112.80(15)
C(4)-N(2)-Ru(1)	106.49(11)
C(9)-N(2)-Ru(1)	110.37(12)
C(7)-N(2)-Ru(1)	113.35(12)
C(13)-C(1)-C(14)	107.30(16)
C(13)-C(1)-C(2)	112.33(17)
C(14)-C(1)-C(2)	106.35(16)
C(13)-C(1)-S(1)	110.55(14)
C(14)-C(1)-S(1)	108.95(14)
C(2)-C(1)-S(1)	111.15(13)
N(1)-C(2)-C(1)	116.50(15)

N(1)-C(2)-H(2A)	108.2
C(1)-C(2)-H(2A)	108.2
N(1)-C(2)-H(2B)	108.2
C(1)-C(2)-H(2B)	108.2
H(2A)-C(2)-H(2B)	107.3
N(1)-C(5)-C(6)	112.44(16)
N(1)-C(5)-H(5A)	109.1
C(6)-C(5)-H(5A)	109.1
N(1)-C(5)-H(5B)	109.1
C(6)-C(5)-H(5B)	109.1
H(5A)-C(5)-H(5B)	107.8
C(5)-C(6)-S(2)	110.65(14)
C(5)-C(6)-H(6A)	109.5
S(2)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
S(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	108.1
C(4)-C(3)-N(1)	111.57(16)
C(4)-C(3)-H(3A)	109.3
N(1)-C(3)-H(3A)	109.3
C(4)-C(3)-H(3B)	109.3
N(1)-C(3)-H(3B)	109.3
H(3A)-C(3)-H(3B)	108.0
N(2)-C(4)-C(3)	109.63(16)
N(2)-C(4)-H(4A)	109.7
C(3)-C(4)-H(4A)	109.7
N(2)-C(4)-H(4B)	109.7
C(3)-C(4)-H(4B)	109.7
H(4A)-C(4)-H(4B)	108.2
C(8)-C(7)-N(2)	116.33(16)
C(8)-C(7)-H(7A)	108.2
N(2)-C(7)-H(7A)	108.2
C(8)-C(7)-H(7B)	108.2
N(2)-C(7)-H(7B)	108.2
H(7A)-C(7)-H(7B)	107.4
C(7)-C(8)-S(2)	114.06(14)
C(7)-C(8)-H(8A)	108.7
S(2)-C(8)-H(8A)	108.7
C(7)-C(8)-H(8B)	108.7
S(2)-C(8)-H(8B)	108.7
H(8A)-C(8)-H(8B)	107.6
N(2)-C(9)-C(10)	116.45(16)
N(2)-C(9)-H(9A)	108.2
C(10)-C(9)-H(9A)	108.2
N(2)-C(9)-H(9B)	108.2
C(10)-C(9)-H(9B)	108.2
H(9A)-C(9)-H(9B)	107.3
C(12)-C(10)-C(11)	110.25(16)
C(12)-C(10)-C(9)	109.54(16)
C(11)-C(10)-C(9)	111.66(16)
C(12)-C(10)-S(3)	114.11(13)
C(11)-C(10)-S(3)	104.35(13)
C(9)-C(10)-S(3)	106.83(13)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5

C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(1)-C(13)-H(13A)	109.5
C(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(1)-C(14)-H(14A)	109.5
C(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(15)-O(1)-H(1)	109.5
O(1)-C(15)-C(16)	111.57(19)
O(1)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15A)	109.3
O(1)-C(15)-H(15B)	109.3
C(16)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Table A24. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **10** The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	10(1)	10(1)	10(1)	4(1)	3(1)	1(1)
S(1)	12(1)	15(1)	15(1)	8(1)	4(1)	3(1)
S(2)	14(1)	14(1)	15(1)	7(1)	6(1)	4(1)
S(3)	12(1)	11(1)	12(1)	5(1)	3(1)	2(1)
N(1)	13(1)	12(1)	13(1)	5(1)	3(1)	2(1)
N(2)	16(1)	11(1)	13(1)	5(1)	4(1)	1(1)
C(1)	15(1)	15(1)	17(1)	9(1)	4(1)	4(1)
C(2)	15(1)	12(1)	17(1)	8(1)	5(1)	3(1)
C(5)	15(1)	16(1)	17(1)	8(1)	6(1)	1(1)
C(6)	17(1)	18(1)	18(1)	10(1)	8(1)	5(1)
C(3)	19(1)	14(1)	12(1)	5(1)	2(1)	1(1)
C(4)	17(1)	16(1)	11(1)	6(1)	0(1)	0(1)
C(7)	22(1)	12(1)	15(1)	4(1)	7(1)	3(1)
C(8)	20(1)	14(1)	16(1)	6(1)	9(1)	5(1)
C(9)	17(1)	16(1)	16(1)	8(1)	2(1)	-3(1)
C(10)	14(1)	12(1)	14(1)	5(1)	3(1)	0(1)
C(11)	20(1)	12(1)	20(1)	7(1)	4(1)	0(1)
C(12)	13(1)	20(1)	20(1)	7(1)	5(1)	2(1)
C(13)	15(1)	22(1)	20(1)	12(1)	3(1)	3(1)
C(14)	20(1)	15(1)	23(1)	8(1)	8(1)	6(1)
O(1)	28(1)	19(1)	25(1)	6(1)	6(1)	3(1)
I	23(1)	17(1)	18(1)	6(1)	6(1)	0(1)
C(15)	29(1)	19(1)	25(1)	7(1)	9(1)	1(1)
C(16)	34(1)	28(1)	27(1)	4(1)	10(1)	3(1)

Table A25. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **10**

	x	y	z	U(eq)
H(2A)	5420	-2223	6762	17
H(2B)	6500	-1772	8179	17
H(5A)	3946	-769	8484	18
H(5B)	3199	-1336	7021	18
H(6A)	3390	1187	8603	19
H(6B)	1688	250	7684	19
H(3A)	5889	1084	9354	19
H(3B)	7337	214	9449	19
H(4A)	8289	2250	9582	19
H(4B)	8789	1113	8602	19
H(7A)	5713	2802	9072	20
H(7B)	6260	3678	8483	20
H(8A)	3863	3034	6878	19
H(8B)	3203	3054	7961	19
H(9A)	9186	2027	7568	20
H(9B)	8615	3351	8107	20
H(11A)	8522	4399	6738	27
H(11B)	6597	4159	6679	27
H(11C)	7030	3837	5443	27
H(12A)	8684	2139	4811	28
H(12B)	9003	1171	5454	28
H(12C)	10105	2522	6126	28
H(13A)	9431	-1789	8730	28
H(13B)	9665	-401	8807	28
H(13C)	10553	-1435	8029	28
H(14A)	8960	-3046	6094	29
H(14B)	6932	-3200	5551	29
H(14C)	7818	-3508	6723	29
H(1)	5583	3008	1069	38
H(15A)	7323	4610	1581	30
H(15B)	8866	3888	1956	30
H(16A)	6605	4727	3304	48
H(16B)	8521	5371	3716	48
H(16C)	8155	4013	3680	48

Table A26. Torsion angles [°] for **10**

N(1)-Ru(1)-S(1)-C(1)	18.43(8)
N(2)-Ru(1)-S(1)-C(1)	99.67(8)
S(3)#1-Ru(1)-S(1)-C(1)	-81.80(7)
S(3)-Ru(1)-S(1)-C(1)	176.53(7)
S(2)-Ru(1)-S(1)-C(1)	29.84(11)
Ru(1)#1-Ru(1)-S(1)-C(1)	-132.47(7)
N(1)-Ru(1)-S(2)-C(8)	101.78(8)
N(2)-Ru(1)-S(2)-C(8)	20.35(8)
S(3)#1-Ru(1)-S(2)-C(8)	-160.51(7)
S(3)-Ru(1)-S(2)-C(8)	-57.31(7)
S(1)-Ru(1)-S(2)-C(8)	90.41(11)
Ru(1)#1-Ru(1)-S(2)-C(8)	-107.47(7)
N(1)-Ru(1)-S(2)-C(6)	-2.19(8)
N(2)-Ru(1)-S(2)-C(6)	-83.63(8)
S(3)#1-Ru(1)-S(2)-C(6)	95.51(7)
S(3)-Ru(1)-S(2)-C(6)	-161.28(7)
S(1)-Ru(1)-S(2)-C(6)	-13.56(12)
Ru(1)#1-Ru(1)-S(2)-C(6)	148.55(7)
N(1)-Ru(1)-S(3)-C(10)	58.84(13)
N(2)-Ru(1)-S(3)-C(10)	38.02(8)
S(3)#1-Ru(1)-S(3)-C(10)	-129.81(7)
S(2)-Ru(1)-S(3)-C(10)	125.65(7)
S(1)-Ru(1)-S(3)-C(10)	-47.92(7)
Ru(1)#1-Ru(1)-S(3)-C(10)	-129.81(7)
N(1)-Ru(1)-S(3)-Ru(1)#1	-171.35(11)
N(2)-Ru(1)-S(3)-Ru(1)#1	167.83(5)
S(3)#1-Ru(1)-S(3)-Ru(1)#1	0.0
S(2)-Ru(1)-S(3)-Ru(1)#1	-104.536(17)
S(1)-Ru(1)-S(3)-Ru(1)#1	81.893(17)
N(2)-Ru(1)-N(1)-C(5)	115.06(12)
S(3)#1-Ru(1)-N(1)-C(5)	-76.99(11)
S(3)-Ru(1)-N(1)-C(5)	94.51(15)
S(2)-Ru(1)-N(1)-C(5)	27.59(11)
S(1)-Ru(1)-N(1)-C(5)	-154.72(12)
Ru(1)#1-Ru(1)-N(1)-C(5)	-71.54(15)
N(2)-Ru(1)-N(1)-C(2)	-127.49(12)
S(3)#1-Ru(1)-N(1)-C(2)	40.46(12)
S(3)-Ru(1)-N(1)-C(2)	-148.04(10)
S(2)-Ru(1)-N(1)-C(2)	145.04(11)
S(1)-Ru(1)-N(1)-C(2)	-37.27(11)
Ru(1)#1-Ru(1)-N(1)-C(2)	45.91(17)
N(2)-Ru(1)-N(1)-C(3)	-3.72(12)
S(3)#1-Ru(1)-N(1)-C(3)	164.23(11)
S(3)-Ru(1)-N(1)-C(3)	-24.3(2)
S(2)-Ru(1)-N(1)-C(3)	-91.19(12)
S(1)-Ru(1)-N(1)-C(3)	86.50(12)
Ru(1)#1-Ru(1)-N(1)-C(3)	169.68(9)
N(1)-Ru(1)-N(2)-C(4)	27.35(12)
S(3)#1-Ru(1)-N(2)-C(4)	-63.0(3)
S(3)-Ru(1)-N(2)-C(4)	-160.65(12)
S(2)-Ru(1)-N(2)-C(4)	112.98(12)
S(1)-Ru(1)-N(2)-C(4)	-56.00(11)
Ru(1)#1-Ru(1)-N(2)-C(4)	-148.57(10)
N(1)-Ru(1)-N(2)-C(9)	141.31(13)

S(3)#1-Ru(1)-N(2)-C(9)	51.0(3)
S(3)-Ru(1)-N(2)-C(9)	-46.69(11)
S(2)-Ru(1)-N(2)-C(9)	-133.06(12)
S(1)-Ru(1)-N(2)-C(9)	57.96(12)
Ru(1)#1-Ru(1)-N(2)-C(9)	-34.61(14)
N(1)-Ru(1)-N(2)-C(7)	-91.07(13)
S(3)#1-Ru(1)-N(2)-C(7)	178.58(16)
S(3)-Ru(1)-N(2)-C(7)	80.93(12)
S(2)-Ru(1)-N(2)-C(7)	-5.44(12)
S(1)-Ru(1)-N(2)-C(7)	-174.42(12)
Ru(1)#1-Ru(1)-N(2)-C(7)	93.01(13)
Ru(1)-S(1)-C(1)-C(13)	-124.37(13)
Ru(1)-S(1)-C(1)-C(14)	117.95(13)
Ru(1)-S(1)-C(1)-C(2)	1.08(14)
C(5)-N(1)-C(2)-C(1)	169.79(16)
C(3)-N(1)-C(2)-C(1)	-72.9(2)
Ru(1)-N(1)-C(2)-C(1)	50.67(19)
C(13)-C(1)-C(2)-N(1)	92.3(2)
C(14)-C(1)-C(2)-N(1)	-150.63(16)
S(1)-C(1)-C(2)-N(1)	-32.2(2)
C(2)-N(1)-C(5)-C(6)	-170.67(16)
C(3)-N(1)-C(5)-C(6)	69.3(2)
Ru(1)-N(1)-C(5)-C(6)	-51.70(18)
N(1)-C(5)-C(6)-S(2)	49.7(2)
C(8)-S(2)-C(6)-C(5)	-122.89(15)
Ru(1)-S(2)-C(6)-C(5)	-23.16(15)
C(5)-N(1)-C(3)-C(4)	-141.45(16)
C(2)-N(1)-C(3)-C(4)	101.41(18)
Ru(1)-N(1)-C(3)-C(4)	-21.25(19)
C(9)-N(2)-C(4)-C(3)	-164.18(16)
C(7)-N(2)-C(4)-C(3)	75.08(19)
Ru(1)-N(2)-C(4)-C(3)	-46.90(17)
N(1)-C(3)-C(4)-N(2)	45.9(2)
C(4)-N(2)-C(7)-C(8)	-134.22(17)
C(9)-N(2)-C(7)-C(8)	109.75(19)
Ru(1)-N(2)-C(7)-C(8)	-16.6(2)
N(2)-C(7)-C(8)-S(2)	37.5(2)
C(6)-S(2)-C(8)-C(7)	65.94(16)
Ru(1)-S(2)-C(8)-C(7)	-35.65(15)
C(4)-N(2)-C(9)-C(10)	157.61(16)
C(7)-N(2)-C(9)-C(10)	-84.9(2)
Ru(1)-N(2)-C(9)-C(10)	42.98(19)
N(2)-C(9)-C(10)-C(12)	-131.53(17)
N(2)-C(9)-C(10)-C(11)	106.04(19)
N(2)-C(9)-C(10)-S(3)	-7.5(2)
Ru(1)#1-S(3)-C(10)-C(12)	11.38(18)
Ru(1)-S(3)-C(10)-C(12)	94.19(14)
Ru(1)#1-S(3)-C(10)-C(11)	131.77(11)
Ru(1)-S(3)-C(10)-C(11)	-145.41(11)
Ru(1)#1-S(3)-C(10)-C(9)	-109.83(13)
Ru(1)-S(3)-C(10)-C(9)	-27.02(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Table A27. Crystal data and structure refinement for **11**

Identification code	cag177lt	
Empirical formula	C ₁₆ H ₂₈ N ₂ O ₂ Ru S ₃	
Formula weight	477.65	
Temperature	100.0 K	
Wavelength	0.7107 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.2404(2) Å	α = 90°.
	b = 20.7973(4) Å	β = 94.916(2)°.
	c = 10.6722(3) Å	γ = 90°.
Volume	2043.40(8) Å ³	
Z	4	
Density (calculated)	1.553 Mg/m ³	
Absorption coefficient	1.085 mm ⁻¹	
F(000)	984	
Theta range for data collection	3.42 to 29.01°	
Crystal color, habit	yellow plate	
Crystal size	0.23 x 0.18 x 0.05 mm ³	
Theta range for data collection	3.42 to 29.01°	
Index ranges	-12 ≤ h ≤ 11, -28 ≤ k ≤ 23, -13 ≤ l ≤ 7	
Reflections collected	11721	
Independent reflections	4763 [R(int) = 0.0278]	
Completeness to theta = 29.0°	87.5 %	
Completeness to theta = 26.3°	99.4%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.958 and 0.803	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4763 / 3 / 223	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R1 = 0.0280, wR2 = 0.0615	
R indices (all data)	R1 = 0.0384, wR2 = 0.0667	
Largest diff. peak and hole	0.610 and -0.436 e.Å ⁻³	

Table A28. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **11** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	8555(1)	2214(1)	5854(1)	9(1)
S(2)	8749(1)	3080(1)	4411(1)	13(1)
S(3)	7274(1)	1336(1)	4840(1)	13(1)
S(1)	10914(1)	1845(1)	5283(1)	13(1)
O(1)	5702(2)	2767(1)	6400(2)	18(1)
N(2)	9752(2)	2840(1)	7125(2)	10(1)
N(1)	8912(2)	1515(1)	7313(2)	11(1)
C(15)	6809(3)	2539(1)	6218(2)	12(1)
C(4)	9322(3)	2597(1)	8368(2)	12(1)
C(7)	7490(2)	1199(1)	7495(2)	13(1)
C(5)	11383(2)	2799(1)	7110(2)	13(1)
C(3)	9510(3)	1871(1)	8483(2)	13(1)
C(11)	9205(3)	3514(1)	6916(2)	14(1)
C(1)	11351(3)	1261(1)	6545(2)	15(1)
C(12)	9094(3)	3752(1)	5547(2)	14(1)
C(14)	10460(3)	4122(1)	5256(3)	17(1)
C(13)	7803(3)	4219(1)	5378(3)	19(1)
C(2)	9960(3)	1005(1)	7011(2)	14(1)
C(9)	5045(3)	1082(1)	6337(3)	18(1)
C(10)	6823(3)	208(1)	6111(3)	19(1)
C(6)	11896(3)	2551(1)	5886(2)	15(1)
C(8)	6663(3)	937(1)	6265(2)	14(1)
C(20)	9639(8)	744(3)	2476(7)	31(2)
O(20)	8272(5)	336(2)	2748(5)	36(1)
C(30)	9267(8)	683(3)	2126(6)	26(2)
O(30A)	8919(11)	327(4)	3274(9)	25(2)
O(30B)	9472(8)	421(3)	3643(7)	14(2)

Table A29. Bond lengths [Å] and angles [°] for **11**

Ru(1)-C(15)	1.822(2)
Ru(1)-N(2)	2.1215(19)
Ru(1)-N(1)	2.1354(19)
Ru(1)-S(2)	2.3854(6)
Ru(1)-S(3)	2.3854(6)
Ru(1)-S(1)	2.4379(6)
S(2)-C(12)	1.861(2)
S(3)-C(8)	1.861(3)
S(1)-C(6)	1.815(2)
S(1)-C(1)	1.832(3)
O(1)-C(15)	1.158(3)
N(2)-C(11)	1.500(3)
N(2)-C(4)	1.504(3)
N(2)-C(5)	1.512(3)
N(1)-C(2)	1.490(3)
N(1)-C(7)	1.496(3)
N(1)-C(3)	1.515(3)
C(4)-C(3)	1.522(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(7)-C(8)	1.559(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(5)-C(6)	1.517(3)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(11)-C(12)	1.538(3)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(1)-C(2)	1.515(3)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(12)-C(14)	1.532(3)
C(12)-C(13)	1.537(3)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(9)-C(8)	1.534(3)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(8)	1.535(3)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700

C(20)-O(20)	1.569(8)
C(30)-O(30A)	1.490(10)
C(30)-O(30B)	1.703(9)
C(15)-Ru(1)-N(2)	93.36(9)
C(15)-Ru(1)-N(1)	100.43(9)
N(2)-Ru(1)-N(1)	84.94(7)
C(15)-Ru(1)-S(2)	88.57(8)
N(2)-Ru(1)-S(2)	83.46(5)
N(1)-Ru(1)-S(2)	165.71(5)
C(15)-Ru(1)-S(3)	88.10(7)
N(2)-Ru(1)-S(3)	166.21(5)
N(1)-Ru(1)-S(3)	81.31(5)
S(2)-Ru(1)-S(3)	110.30(2)
C(15)-Ru(1)-S(1)	176.13(8)
N(2)-Ru(1)-S(1)	85.70(5)
N(1)-Ru(1)-S(1)	83.23(5)
S(2)-Ru(1)-S(1)	87.59(2)
S(3)-Ru(1)-S(1)	93.71(2)
C(12)-S(2)-Ru(1)	99.49(8)
C(8)-S(3)-Ru(1)	98.26(8)
C(6)-S(1)-C(1)	101.72(12)
C(6)-S(1)-Ru(1)	94.99(8)
C(1)-S(1)-Ru(1)	99.80(8)
C(11)-N(2)-C(4)	109.56(18)
C(11)-N(2)-C(5)	112.03(17)
C(4)-N(2)-C(5)	109.23(18)
C(11)-N(2)-Ru(1)	109.11(14)
C(4)-N(2)-Ru(1)	101.24(13)
C(5)-N(2)-Ru(1)	115.08(14)
C(2)-N(1)-C(7)	108.02(17)
C(2)-N(1)-C(3)	109.16(18)
C(7)-N(1)-C(3)	111.73(18)
C(2)-N(1)-Ru(1)	112.94(14)
C(7)-N(1)-Ru(1)	108.13(14)
C(3)-N(1)-Ru(1)	106.91(13)
O(1)-C(15)-Ru(1)	176.6(2)
N(2)-C(4)-C(3)	111.57(19)
N(2)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4A)	109.3
N(2)-C(4)-H(4B)	109.3
C(3)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	108.0
N(1)-C(7)-C(8)	114.61(19)
N(1)-C(7)-H(7A)	108.6
C(8)-C(7)-H(7A)	108.6
N(1)-C(7)-H(7B)	108.6
C(8)-C(7)-H(7B)	108.6
H(7A)-C(7)-H(7B)	107.6
N(2)-C(5)-C(6)	114.48(19)
N(2)-C(5)-H(5A)	108.6
C(6)-C(5)-H(5A)	108.6
N(2)-C(5)-H(5B)	108.6
C(6)-C(5)-H(5B)	108.6
H(5A)-C(5)-H(5B)	107.6
N(1)-C(3)-C(4)	112.77(19)
N(1)-C(3)-H(3A)	109.0

C(4)-C(3)-H(3A)	109.0
N(1)-C(3)-H(3B)	109.0
C(4)-C(3)-H(3B)	109.0
H(3A)-C(3)-H(3B)	107.8
N(2)-C(11)-C(12)	115.94(19)
N(2)-C(11)-H(11A)	108.3
C(12)-C(11)-H(11A)	108.3
N(2)-C(11)-H(11B)	108.3
C(12)-C(11)-H(11B)	108.3
H(11A)-C(11)-H(11B)	107.4
C(2)-C(1)-S(1)	109.60(17)
C(2)-C(1)-H(1A)	109.8
S(1)-C(1)-H(1A)	109.8
C(2)-C(1)-H(1B)	109.8
S(1)-C(1)-H(1B)	109.8
H(1A)-C(1)-H(1B)	108.2
C(14)-C(12)-C(13)	107.70(19)
C(14)-C(12)-C(11)	111.5(2)
C(13)-C(12)-C(11)	107.6(2)
C(14)-C(12)-S(2)	110.10(17)
C(13)-C(12)-S(2)	108.06(17)
C(11)-C(12)-S(2)	111.69(16)
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
N(1)-C(2)-C(1)	113.95(19)
N(1)-C(2)-H(2A)	108.8
C(1)-C(2)-H(2A)	108.8
N(1)-C(2)-H(2B)	108.8
C(1)-C(2)-H(2B)	108.8
H(2A)-C(2)-H(2B)	107.7
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(5)-C(6)-S(1)	113.36(16)
C(5)-C(6)-H(6A)	108.9
S(1)-C(6)-H(6A)	108.9
C(5)-C(6)-H(6B)	108.9

S(1)-C(6)-H(6B)	108.9
H(6A)-C(6)-H(6B)	107.7
C(9)-C(8)-C(10)	107.62(19)
C(9)-C(8)-C(7)	107.4(2)
C(10)-C(8)-C(7)	113.0(2)
C(9)-C(8)-S(3)	108.57(17)
C(10)-C(8)-S(3)	108.28(17)
C(7)-C(8)-S(3)	111.80(16)

Symmetry transformations used to generate equivalent atoms:

Table A30. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **11** The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	8(1)	11(1)	9(1)	-1(1)	-1(1)	0(1)
S(2)	16(1)	14(1)	10(1)	0(1)	-1(1)	-1(1)
S(3)	14(1)	13(1)	11(1)	-2(1)	-1(1)	-1(1)
S(1)	11(1)	16(1)	13(1)	-2(1)	2(1)	0(1)
O(1)	12(1)	21(1)	21(1)	-3(1)	2(1)	2(1)
N(2)	9(1)	13(1)	9(1)	0(1)	0(1)	0(1)
N(1)	9(1)	13(1)	11(1)	2(1)	-1(1)	0(1)
C(15)	15(1)	12(1)	9(1)	0(1)	-4(1)	-4(1)
C(4)	12(1)	16(1)	8(1)	-2(1)	0(1)	-2(1)
C(7)	12(1)	14(1)	13(1)	4(1)	1(1)	0(1)
C(5)	9(1)	15(1)	14(1)	-1(1)	-3(1)	-2(1)
C(3)	12(1)	16(1)	9(1)	1(1)	-3(1)	-2(1)
C(11)	15(1)	12(1)	14(1)	-3(1)	0(1)	0(1)
C(1)	14(1)	14(1)	18(1)	-1(1)	1(1)	2(1)
C(12)	16(1)	12(1)	13(1)	-1(1)	1(1)	-1(1)
C(14)	20(1)	16(1)	17(1)	1(1)	0(1)	-2(1)
C(13)	22(1)	15(1)	19(1)	0(1)	-1(1)	2(1)
C(2)	12(1)	15(1)	15(1)	0(1)	0(1)	2(1)
C(9)	14(1)	20(1)	20(2)	0(1)	0(1)	-3(1)
C(10)	19(1)	16(1)	22(2)	-1(1)	0(1)	-4(1)
C(6)	11(1)	18(1)	17(1)	0(1)	2(1)	-2(1)
C(8)	12(1)	14(1)	16(1)	1(1)	0(1)	-1(1)

Table A31. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **11**.

	x	y	z	U(eq)
H(4A)	8315	2707	8453	15
H(4B)	9914	2805	9044	15
H(7A)	6872	1507	7875	15
H(7B)	7663	845	8081	15
H(5A)	11759	2518	7788	15
H(5B)	11792	3223	7275	15
H(3A)	10535	1773	8646	15
H(3B)	9019	1720	9196	15
H(11A)	9842	3802	7419	16
H(11B)	8250	3544	7225	16
H(1A)	11909	909	6233	18
H(1B)	11934	1466	7231	18
H(14A)	10607	4478	5825	26
H(14B)	10342	4279	4407	26
H(14C)	11286	3841	5353	26
H(13A)	7946	4564	5972	28
H(13B)	6923	3994	5516	28
H(13C)	7732	4390	4539	28
H(2A)	9492	724	6374	17
H(2B)	10202	749	7759	17
H(9A)	4509	943	5575	28
H(9B)	4912	1536	6441	28
H(9C)	4701	858	7039	28
H(10A)	6395	-9	6783	29
H(10B)	7835	99	6133	29
H(10C)	6340	77	5320	29
H(6A)	12922	2447	6018	18
H(6B)	11787	2890	5260	18

Table A32. Torsion angles [°] for **11**.

C(15)-Ru(1)-S(2)-C(12)	71.77(11)
N(2)-Ru(1)-S(2)-C(12)	-21.77(9)
N(1)-Ru(1)-S(2)-C(12)	-57.7(2)
S(3)-Ru(1)-S(2)-C(12)	159.22(8)
S(1)-Ru(1)-S(2)-C(12)	-107.71(8)
C(15)-Ru(1)-S(3)-C(8)	-69.85(11)
N(2)-Ru(1)-S(3)-C(8)	26.5(2)
N(1)-Ru(1)-S(3)-C(8)	31.00(9)
S(2)-Ru(1)-S(3)-C(8)	-157.62(8)
S(1)-Ru(1)-S(3)-C(8)	113.57(8)
N(2)-Ru(1)-S(1)-C(6)	-19.90(10)
N(1)-Ru(1)-S(1)-C(6)	-105.30(10)
S(2)-Ru(1)-S(1)-C(6)	63.72(9)
S(3)-Ru(1)-S(1)-C(6)	173.91(9)
N(2)-Ru(1)-S(1)-C(1)	82.93(10)
N(1)-Ru(1)-S(1)-C(1)	-2.48(10)
S(2)-Ru(1)-S(1)-C(1)	166.55(8)
S(3)-Ru(1)-S(1)-C(1)	-83.26(8)
C(15)-Ru(1)-N(2)-C(11)	-48.33(16)
N(1)-Ru(1)-N(2)-C(11)	-148.52(15)
S(2)-Ru(1)-N(2)-C(11)	39.84(14)
S(3)-Ru(1)-N(2)-C(11)	-144.07(19)
S(1)-Ru(1)-N(2)-C(11)	127.91(14)
C(15)-Ru(1)-N(2)-C(4)	67.14(15)
N(1)-Ru(1)-N(2)-C(4)	-33.05(13)
S(2)-Ru(1)-N(2)-C(4)	155.32(13)
S(3)-Ru(1)-N(2)-C(4)	-28.6(3)
S(1)-Ru(1)-N(2)-C(4)	-116.62(13)
C(15)-Ru(1)-N(2)-C(5)	-175.23(16)
N(1)-Ru(1)-N(2)-C(5)	84.58(15)
S(2)-Ru(1)-N(2)-C(5)	-87.06(15)
S(3)-Ru(1)-N(2)-C(5)	89.0(3)
S(1)-Ru(1)-N(2)-C(5)	1.01(14)
C(15)-Ru(1)-N(1)-C(2)	158.65(16)
N(2)-Ru(1)-N(1)-C(2)	-108.86(15)
S(2)-Ru(1)-N(1)-C(2)	-73.0(3)
S(3)-Ru(1)-N(1)-C(2)	72.21(14)
S(1)-Ru(1)-N(1)-C(2)	-22.61(14)
C(15)-Ru(1)-N(1)-C(7)	39.17(16)
N(2)-Ru(1)-N(1)-C(7)	131.66(15)
S(2)-Ru(1)-N(1)-C(7)	167.50(16)
S(3)-Ru(1)-N(1)-C(7)	-47.26(13)
S(1)-Ru(1)-N(1)-C(7)	-142.08(14)
C(15)-Ru(1)-N(1)-C(3)	-81.27(15)
N(2)-Ru(1)-N(1)-C(3)	11.22(14)
S(2)-Ru(1)-N(1)-C(3)	47.1(3)
S(3)-Ru(1)-N(1)-C(3)	-167.71(14)
S(1)-Ru(1)-N(1)-C(3)	97.47(13)
N(1)-Ru(1)-C(15)-O(1)	178(100)
C(11)-N(2)-C(4)-C(3)	165.77(18)
C(5)-N(2)-C(4)-C(3)	-71.2(2)
Ru(1)-N(2)-C(4)-C(3)	50.63(19)
C(2)-N(1)-C(7)-C(8)	-71.2(2)
C(3)-N(1)-C(7)-C(8)	168.72(18)

Ru(1)-N(1)-C(7)-C(8)	51.3(2)
C(11)-N(2)-C(5)-C(6)	-100.9(2)
C(4)-N(2)-C(5)-C(6)	137.5(2)
Ru(1)-N(2)-C(5)-C(6)	24.5(2)
C(2)-N(1)-C(3)-C(4)	136.59(19)
C(7)-N(1)-C(3)-C(4)	-104.0(2)
Ru(1)-N(1)-C(3)-C(4)	14.1(2)
N(2)-C(4)-C(3)-N(1)	-45.7(3)
C(4)-N(2)-C(11)-C(12)	-160.46(19)
C(5)-N(2)-C(11)-C(12)	78.2(2)
Ru(1)-N(2)-C(11)-C(12)	-50.5(2)
C(6)-S(1)-C(1)-C(2)	123.76(18)
Ru(1)-S(1)-C(1)-C(2)	26.52(17)
N(2)-C(11)-C(12)-C(14)	-94.6(2)
N(2)-C(11)-C(12)-C(13)	147.5(2)
N(2)-C(11)-C(12)-S(2)	29.1(3)
Ru(1)-S(2)-C(12)-C(14)	127.35(16)
Ru(1)-S(2)-C(12)-C(13)	-115.27(16)
Ru(1)-S(2)-C(12)-C(11)	2.94(17)
C(7)-N(1)-C(2)-C(1)	168.2(2)
C(3)-N(1)-C(2)-C(1)	-70.1(2)
Ru(1)-N(1)-C(2)-C(1)	48.7(2)
S(1)-C(1)-C(2)-N(1)	-49.9(2)
N(2)-C(5)-C(6)-S(1)	-45.7(2)
C(1)-S(1)-C(6)-C(5)	-61.93(19)
Ru(1)-S(1)-C(6)-C(5)	39.18(18)
N(1)-C(7)-C(8)-C(9)	-140.2(2)
N(1)-C(7)-C(8)-C(10)	101.3(2)
N(1)-C(7)-C(8)-S(3)	-21.2(2)
Ru(1)-S(3)-C(8)-C(9)	104.15(16)
Ru(1)-S(3)-C(8)-C(10)	-139.28(15)
Ru(1)-S(3)-C(8)-C(7)	-14.16(16)

Symmetry transformations used to generate equivalent atoms:

CURRICULUM VITAE

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Education:

University Degree:

Ph.D. Chemistry 2012 UNIVERSITY OF LOUISVILLE, (UofL) KY, USA.

- Dissertation title: **Sulfur oxygenation of ruthenium-dithiolate nitrile hydratase mimic enhances ligand lability and hydrolysis activity.**
- Mentor: Ph.D. Craig A. Grapperhaus.
- Graduate Dean's Citation. University of Louisville Spring 2012

M.S. Chemistry 2010 UNIVERSITY OF LOUISVILLE, (UofL) KY, USA.

B.S. Chemistry 2000 UNIVERSIDAD PERUANA CAYETANO HEREDIA, (UPCH) LIMA PERU.

- Licenciatura dissertation title: **In vitro antimicrobial activity of 15 Peruvian plants and phytochemical study of Gentianella weberbaueri (Gilg) Fabris.**
- Mentor: M.D. Ph.D. Rosario Rojas

Course:

2005 CRESTCOM INTERNATIONAL, Ltd.

Course and diploma in Bullet Proof® Manager.

Where I:

- Improved leadership strategies in personal and working life.

Professional experience.

In Academia: Courses taught as Teaching Assistant.

Course title	Semester taught	University.
Organic Chemistry Lab.	Spring 1999- Fall 2000	UPCH
Physical Chemistry Lab.	Spring 1999- Fall 2000	UPCH
Organic Chemistry Lab.	Fall 2006 and spring 2006	UofL
	Fall 2007 and summer 2011	UofL

In Industry:

11/2001-07/2006 **CASTILLO GALERIA DE ARTE INTERNACIONAL (ART GALLERY)**

Co-Manager and logistic coordinator. (Family business)

Where:

- Organized, operated and administered the logistic of the company.
- Directed the customer service of the company.

Accomplishments: Set up and run an Art Gallery business.

06/2004-02/2005 **ALS LABORATORY GROUP, LIMA PERU.**

Laboratory of mineral and environmental assays for mining. Head of supply chain.

Where I:

- Coordinated and organized company supply chain.
- Reduced chemical consumable expenses with new vendors and the improvement in the logistic of the company.

Accomplishments: Design, organize and implement a warehouse for mineral sample storage. Warehouse area 6500 square feet.

12/2003-03/2004 **JICA. (JAPAN INTERNATIONAL COOPERATION AGENCY).**

External consultant.

Where I:

- Performed a study about “Drinking water quality in Peru” and “Drinking water characteristics in Peru” in coordination with “**SUNASS**”. The National Sanitation Service Superintendence of Peru.
- Developed, organized and implemented a quality system in the laboratory of “**SUNASS**”.

Accomplishments: One book publication as collaborators, Sunass is owner of the manuscript rights.

12/2002-09/2003 **CORPORACION JOSE R. LINDLEY S.A. (CORPORATION INCA KOLA).**

Coke, Fanta and Sprite are bottled for this company.

Co-op in quality control assurance.

Where:

- Performed and coordinated physical and chemical assays of quality control, in the pet bottle production line.

Accomplishments: Reduction of time in physical determinations report. 3h/day of saved time in Quality Assurance process.

08/2001 – 10/2001 **MOLITALIA S.A.**

Food industry. Noodles and flour are produced for this company.

Co-op as Quality control supervisor.

Where:

- Inspected and performed quality controls in different stages of the production in the company in coordination with the production division.

04/2001 – 07/2001 **REFINERIA CAJAMARQUILLA S.A. (VOTORANTIN METALS).**

Mining Industry. Refining zinc company.

Co-op. In assurance quality control.

Where:

- Performed analytic chemistry analysis in mineral and environmental samples.
- Analyzed and coordinated routine atomic absorption (AA), ICP and electrochemistry analysis.

Accomplishments: Acquire technical expertise in spectroscopic instrumentation and performed a professional position as analyst for two months due to regular personal went on strike.

01/1998-12/1998 **QUALITY CONTROL LABORATORY. (UPCH).**

Co-op in quality control of pharmaceutical products.

Where:

- Performed Chemical and Physical-Chemical Testing. (e.g. HPLC, GC, UV/VIS, IR).
- Performed the identification of active ingredients and impurities.
- Performed Physical and physical-chemical determinations (e.g. pH, viscosity, melting point, osmolality and osmolarity).
- Residual solvents (volatile organic compounds [VOC], organic volatile impurities [OVI]).
- Pharmaceutical technical procedures (e.g. disintegration, dissolution, hardness, friability).

01/1995 – 12/1997 **MASITAS ING.**

Design and construction of metallic structures.

I was a field supervisor, sale representative and supply chain administrator.

- Organized, operated and administered the logistic of the company.
- Trained in the construction of metallic structure and use of construction equipment. Welding experience of 3 years.
- Directed the customer service of the company.

Accomplishments: Set up and run a metallic structure company, get strong experience dealing with vendors and clients.

Skills and training:

Workshops:

- **Chemistry of Metals in Biological Systems**, 15-22 May 2011, Université Catholique de Louvain, Louvain-la-Neuve, Belgium. Organized by Robert R Crichton.
- Principles of EPR Training Workshop, August 19-21, 2009, **National Biomedical EPR Center, Medical College of Wisconsin, USA**.

Skills

- Performed physic-chemistry determinations during my Ph.D. studies in Nitrile hydratase mimics. I am capable to analyze data, formulate hypothesis and elaborate scientific literature.
- I worked all my doctoral degree in air free synthesis and spectroscopic characterization, using physical and spectroscopic technique to analyze air sensitive compound. Daily use Schlenk line- flask and dry box. Between the techniques that I used on my research I can mention, X-ray, UV-visible, IR, ESI-MS, Electrochemistry, NMR-(use of J-young tubes), GC-MS, EPR and analysis of DFT calculations.
- I can work, organize, coordinate and cooperate in interdisciplinary research in academia and industry.
- I define myself as a synthetic, analytical scientist; I am capable to synthesize complex of 12-15 steps and characterize them. In addition of perform Kinetic evaluation by UV-VIS, NMR and GC-MS as it was the case of the nitrile hydratase analogue that catalyzes the hydrolysis of nitrile to amide.
- Trained in transition metal organic synthesis with emphasis in metal, amine-thiolates. Metal include ruthenium, nickel and iron.
- I have experience analytical chemistry in technical and administrative position in the food and mining industry, and in an international agency. These experiences allow me to work with independence if it is required.
- I strive for continued excellence and social work. I provided exceptional contributions to student organizations as member and Vice-president in the University of Louisville. I am Member of Golden Key and Omicron Delta Kappa Honor Societies.
- Excellent communication and networking abilities.
- I balance an effective work time with sport activities, social relations and family.
- I lead and develop research projects. I implemented improvements on the research labs (from time-cost reduction to technical protocols). I had experience in solve instrumental problems from software to hardware malfunction laboratory instruments.
- I had industrial experience with internal and external customers as head of supply chain.
- I speak English and Spanish fluently.

Papers:

Influence of Sequential Thiolate Oxygenation on a Nitrile Hydratase Mimic Probed by Multi-edge X-ray Absorption Spectroscopy.

Shearer, J.; Callan, Paige E.; Masitas C. A.; Grapperhaus, C. A. *Inorg. Chem.* **2012** (submitted)

Controlled Sulfur Oxygenation of the Ruthenium Dithiolate (bmmp-TASN)RuPPh₃ under Limiting O₂ Conditions Yields Thiolato/Sulfinato, Sulfenato/Sulfinato, and Bis-Sulfinato Derivatives

Masitas, C. A.; Kumar, M.; Mashuta, M. S.; Kozlowski, P. M.; Grapperhaus, C. A. *Inorg. Chem.* **2010**, *49*, 10875–10881.

Asymmetric Oxygenation of a Ruthenium Dithiolate Mimics the Mixed Sulfenato/Sulfinato Donor Sets of Nitrile Hydratase and Thiocyanate Hydrolase

Masitas, C. A.; Mashuta, M. S.; Grapperhaus, C. A. *Inorg. Chem.* **2010**, *49*, 5344-5346.

Conference and poster Presentation:

- International Symposium on Molecular Coordination Chemistry at the Max Planck Institute for Bioinorganic chemistry. Nov. 2010. Mulheim and der Ruhr, Germany (Poster), the meeting was developed to honor the retirement of Prof. Karl Wieghardt.
- Gordon Research Seminars. Feb 2010 - January 2012. Ventura-California, USA (Poster-Presentation).
- Annual National Conference of the American Chemistry Society. Fall 2009. Washington DC, USA (Poster).

Awards and Honors:

- **Golden Key** (International Honor Society) member.
- **Omicron Delta Kappa** (National Leadership Society) member.
- Graduate Dean's Citation. University of Louisville Spring 2012

Languages: Spanish and English. Basic French.

Sports: Tennis, soccer, field hockey and polo.

Organization (position):

- The University of Louisville Polo Club (member); Sport organization.
- **American Chemistry Society** (member); Professional organization.
- C³ Cardinals celebrating cultures (Vice-president) first Hispanic recognized organization in UofL.