Nitrene Transfer Reactions by Late Transition Metal Complexes

by

Charles W. Hamilton

B.S. Chemistry
Texas A&M University, 2001

Submitted to the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY IN
INORGANIC CHEMISTRY

At the

Massachusetts Institute of Technology

February, 2007

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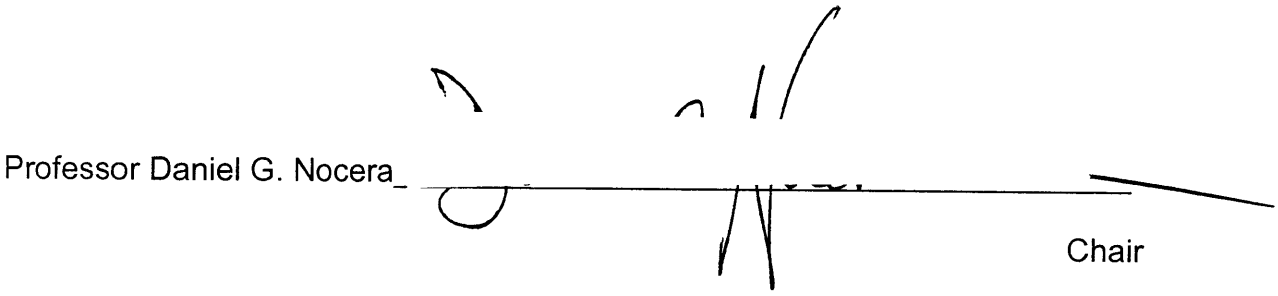

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Abstract

This thesis presents nitrene transfer reactions that are catalyzed or mediated by late transition metal complexes. Sterically large, fluorinated supporting ligands are used to minimize potential side reactions. A new 1,10-phenanthroline ligand has been synthesized with 2,4,6-$(CF_3)_3C_6H_2$– groups in the 2- and 9-positions (**1**). A cationic copper(I) complex of **1** catalyzes nitrene transfer from *N*-(*p*-toluenesulfonylimino)phenyliodinane (PhINTs) to the C–H bonds of 1,3-dimethoxybenzene in 63% yield. Altering the stoichiometry results in the formation of a different major product, *N,N*-bis(2',4'-dimethoxyphenyl)-*p*-toluenesulfonamide, in 33% yield.

Treatment of a cationic copper(I) complex of **1** with *p*-nitrobenzenesulfonyl azide (NsN_3) results in the formation of a rare mononuclear sulfonamido complex of copper(II), **2**. This complex is presumably formed via decomposition of a reactive sulfonimido complex of copper(III). Although not a proficient nitrene transfer reagent to benzene, complex **2** is a precatalyst for nitrene transfer from NsN_3 to benzene.

Deprotonation of a palladium(II) sulfonamido complex of **1** results in the formation of the first mononuclear sulfonimido complex of palladium, **3**. The sulfonimido

ligand is bound in a κ^2-N,O chelate. This complex is a proficient nitrene transfer reagent to carbon monoxide, phosphines, and ethyl vinyl ether.

A rhodium(III) hydride chloride complex containing two N-heterocyclic carbene ligands, one of which is cyclometallated, is a convenient synthetic equivalent of a rhodium(I) chloride complex. Treatment of the rhodium(III) hydride with acetonitrile results in reductive elimination to form a rhodium(I) chloride complex. The chloride is readily abstracted by sodium azide to form a cationic rhodium(I) complex coordinated by two molecules of acetonitrile and containing an unbound azide. Upon exposure to UV light, this molecule undergoes cyclometallation to form a cationic rhodium(III) hydride complex. The rhodium(III) hydride chloride complex can be treated with oxygen to form a rhodium(III) peroxide complex. The neutral peroxide complex has poor reactivity with trimethylphosphite and *t*-stilbene. However, a cationic rhodium peroxide complex oxidizes trimethylphosphite and *t*-stilbene at elevated temperatures.

Thesis Supervisor: Joseph P. Sadighi

Title: Associate Professor of Chemistry

Acknowledgements

The first acknowledgement is to my advisor, Prof. Joseph Sadighi. I feel very fortunate to be one of the first students to join his research group. We had the unique opportunity to be trained directly by someone of his knowledge and insight. I am amazed about how much I learned in the short time I worked for him. Joseph let me work on projects that I found interesting and was particularly adept of giving me the freedom to explore new ideas and making suggestions when I ran into obstacles. I also had a great time trying to stump him on cheesy 80s movie trivia, but was never successful.

I would also like to thank Prof. Dan Nocera. Dan was my thesis chair and I also was a teaching assistant for a graduate level group theory class taught by him. Dan was always kind and gracious when I "tagged along" with his group, and we have had some great chats about science and life. Dan is also a talented and inspirational scientist. He shows us all what great heights science can achieve.

Prof. Nocera co-taught the group theory class with Prof. Alan Davison, and I had an amazing time teaching with him. His warm personality and great insight into life and science is a big influence on how I evaluate my own research.

I am very grateful to numerous staff members, without whose help none of my graduate work would be possible. As a synthetic chemist, I relied heavily on the training and facilities of the DCIF: Dr. David Bray, Dr. Jeffery Simpson, Dr. Mark Wall, Dr. Bob Kennedy, Li Li, and Anne Gorham. I am grateful to Dr. David Laitar in my group (more on him later) who is a talented crystallographer, and mounted and solved most of my structures. Many of my earlier structures were also solved by Dr. Bill Davis and my later structures were solved by Dr. Peter Müller.

My two undergrad advisors, Prof. Joseph Natowitz and Dr. Christopher Marshall, were instrumental in piquing my interest in science and helping me make career choices along the way.

A big thanks to my group members, both past and present. I'll start with Jennifer Akana, who was a student of mine during the infamous group theory class. She grew to become a great colleague, and I had a great time planning our domination of the nitrene world with her. Jennifer is also a very talented chemist, and I'm sure she will have even more successes to add to her already impressive research. Dr. David Laitar joined the lab at the same time I did, and we became roommates as well. David and I remained friends the entire time, which is a large accomplishment. David was a great resource to bounce ideas off of, and his suggestions often led me in new directions in my research career. David is also an excellent chemist, and he will continue to do great things in our field. Greg Sirokman has a very creative mind and personality. Every complicated experimental rig that I setup will be in honor of him. Greg is one of those rare people that would excel in pretty much anything he wants to do. Ryan Rieth was one of my first friends here, and I had a great time taking in Red Sox, Celtics and Bruins games with him. Ryan is also a talented and dedicated chemist, and continues to do outstanding research. Changhoon Lee is a new comer to our lab, but has already left his mark. I wish him the best on his future endeavors, and very excited to see where his amazing research will lead to next.

We were fortunate to have a number of very talented undergrads during my time here. A special thanks to Neal Mankad, Emily Tsui, and Koyel Bhattacharyya.

I want to give a huge thanks to the Nocera group both past and present. They were always very nice to me and I felt like an adopted group member. Some of my fondest (and most embarrassing) memories of graduate school happened while hanging out with them. A special thank you goes to Jenny Yang. Her friendship and baking skills

helped me get through the often very stressful graduate school environment. I wish her and Dr. David Lahr (an amazing guy and great friend) the best.

I have been blessed to have a number of great friends throughout MIT. I want to send a big thank you to all of them. There are too many to name them all, but thank you to Dr. Will Neeley, Adam Hock, Dr. Nathan Smythe, Prof. Matt Shores, Dr. David Manke. Also, I would like to give a big thank you to all basketball people.

I want to send a big thank you to Allison Kelsey, who was always cheerful and fun to be around. Throughout grad school, Allison kept our group running smoothly. I want to especially thank her for her help in preparing this thesis. I don't know how I would have finished it without her.

Finally, I want to thank my family. My parents were great resource for support and encouragement. Their belief in me always bolstered my spirits. I always enjoyed talking with my siblings Allen and Helen. No matter what was going on around me, talking with them brought me back home. I also would like to thank my grandfather (known around our lab as grandpa). His selflessness and concern for others is a great model for anyone to live their life.

Respective Contributions

Much of this work presented in this thesis was the result of collaborative efforts:

Prof. Joseph Sadighi first prepared 2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline which is a critical starting material for much of the work in this thesis.

In the chapter titled "Sterically demanding, oxidation resistant phenanthroline as supporting ligands for copper(I) nitrene transfer catalysis," the amidation of benzene by sulfonyl azide catalyzed by a copper(I) complex was performed by Jennifer Akana. Greg Sirokman was responsible for developing an improved preparation of 2,9-Bis(pentafluorophenyl)-1,10-phenanthroline in the same chapter.

Preface

Parts of this thesis have been adapted from articles co-written by the author. The following article was reproduced in part with permission from the Royal Society of Chemistry

Hamilton, C. W.; Laitar, D. S.; Sadighi, J. P. "Oxidation-resistant, sterically demanding phenanthrolines as supporting ligands for copper(I) nitrene transfer catalysts." *Chem. Commun.* **2004**, 1628–1629.

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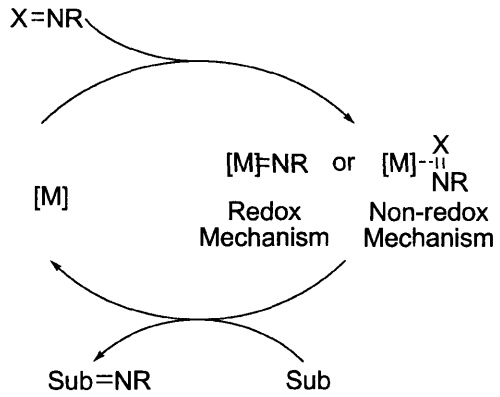
Introduction

1. Nitrene transfer reactions in organic synthesis

Nitrene transfer reactions are fundamental tools in organic chemistry. In organic methodology, nitrene transfer reactions encompass aziridination and amination. These reactions have been used to synthesize new compounds and to streamline existing synthetic routes,[1] and the use of transition metal catalysts is the key to achieving selective processes.

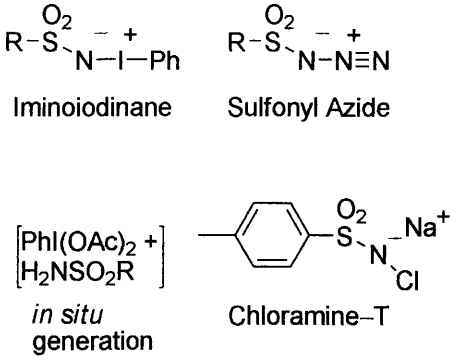
Scheme 1. General metal-catalyzed nitrene transfer mechanism



Fundamentally, a metal-catalyzed nitrene transfer reaction involves two steps (Scheme 1). In the first step, the metal-based catalyst reacts with a nitrene source to form an active intermediate. In the second step, the active intermediate reacts with the substrate and regenerates the metal-based catalyst. The first step can proceed by two different routes, the non-redox pathway and the redox pathway. In the non-redox pathway, the nitrene transfer reagent and catalyst form a complex without oxidative transfer of a nitrene group to the catalyst. Then the complex transfers a nitrene group to the substrate. In the redox pathway, the nitrene transfer reagent transfers the nitrene group, with formal oxidation of the metal center, to form a metal imido complex. The oxidized metal complex then transfers the nitrene group to the substrate.

When the mechanism follows the redox pathway, the stability of the metal-bound nitrene complex greatly affects the reactivity. Often, a too-stable complex is too

Figure 1. Nitrene transfer reagents



unreactive to perform efficient transfer. A complex that is too unstable undergoes undesirable side reactions.

In the first section of this introductory chapter, selected examples of metal-catalyzed nitrene transfer are presented. Emphasis is placed on the nature of the active intermediate. The scope of this section encompasses aziridination and electrophilic amination reactions. More general reviews on atom/group transfer reactions are available.[2]

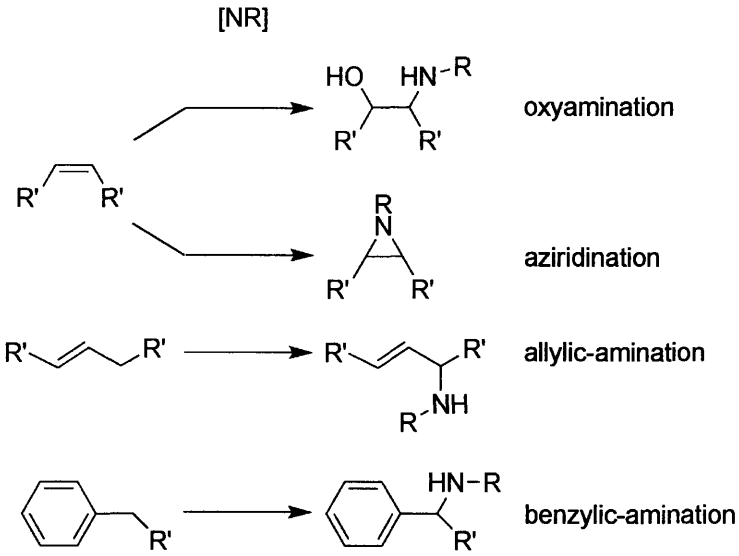
A discussion about mononuclear late-metal imido complexes is presented in the second section of this chapter. A general discussion of bonding is followed by examples from the literature. For brevity, this section will only discuss mononuclear complexes with d-electron counts between six and eight. Excellent reviews have been written on early- and mid-transition metal imido complexes,[3] as well as on multinuclear late-metal imido complexes.[4]

2. Late-metal catalyzed nitrene transfer

2.1 Early example: Osmium catalyzed oxyamination

One of the earliest examples of metal-catalyzed nitrene transfer is the Os-catalyzed oxyamination (Scheme 2) of olefins by Chloramine-T (Figure 1) introduced by Sharpless and coworkers.[5a] This reaction is proposed to proceed by an $Os(O)_3(NTs)$

Scheme 2. Types of nitrene transfer

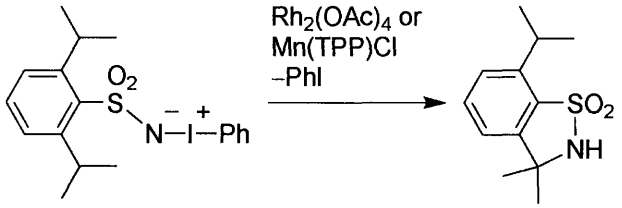


(Ts = *p*-toluenesulfonyl) intermediate in analogy to the stoichiometric oxyamination of olefins by $Os(O)_3(NR)$ [R = *t*-Bu, 1-adamantyl (Ad)].[5b]

2.2 Manganese and Iron catalyzed nitrene transfer reactions

In 1982, Breslow and coworkers reported that 5,10,15,20-tetraphenylporphyrinato (TPP) complexes of Mn and Fe catalyzed the electrophilic sulfonamidation of cyclohexane by *N*-(p-toluenesulfonyl)iminophenyliodinane (PhINTs).[6] This work was based on the related Fe(TPP)(Cl)-catalyzed hydroxylation of cyclohexane by iodosobenzene (PhIO), reported by Groves.[7] Unfortunately, the yields of intermolecular amidation products are low in both the [Fe(TPP)(Cl)]- and [Mn(TPP)(Cl)]-catalyzed reactions. However, the [Fe(TPP)(Cl)]-catalyzed intramolecular benzylic amidation of N-(2,6-diisopropylbenzenesulfonyl)iminophenyliodinane proceeds in high yields (Scheme 3).[6b] Dawson and Breslow discovered that microsomal cytochrome P-450-LM2 purified from rabbit liver catalyzed inter- and intramolecular amidation reactions in similar yields.[8] In analogy to the mechanism proposed for cytrochrome P-450

Scheme 3. Intramolecular amidation of *N*-(2,6-diisopropylbenzenesulfonyl)iminophenyliodinane



hydroxylation reactions, in which high-valent iron oxo intermediates are believed to participate, the amidation reactions are proposed to proceed via high-valent iron or manganese imido intermediates.

Mansuy and coworkers developed [Fe(TPP)(Cl)]- and [Mn(TPP)(Cl)]-catalyzed nitrene transfer to olefins.[9a–c,10] Surprisingly, the [Fe(TPP)(Cl)]- or [Mn(TPP)(Cl)]-catalyzed aziridination of *cis*-stilbene leads to the formation of *trans*-*N*-tosyl-2,3-diphenylaziridine. This change in stereochemistry is not found for the related [Fe(TPP)(Cl)]-catalyzed epoxidation of *cis*-stilbene.[7b] This indicates that epoxidation and aziridination need not proceed by analogous mechanisms.

The [Fe(TPP)(ClO_4)]-catalyzed nitrene transfer to aliphatic alkenes displays poor selectivity, forming nearly equal amounts of allylic amidation and aziridination products. However, selectivity for allylic amidation can be vastly improved when catalyzed by Mn(TPP)(ClO_4), resulting in a 20:1 ratio of allylic amidation to aziridination.[9c]

In many cases, the yields of aziridination and amidation products can be greatly improved by altering the aryl substituents on the meso positions of the porphyrinato ligand.[9b,d] For instance, aziridination of 1,1-diphenylethylene proceeds in only 40% yield when catalyzed by Fe(TPP)(ClO_4), but in 90% yield when catalyzed by the analogous tetrakis(2,6-dichlorophenyl)porphyrinato complex.[9b] The higher yield is possibly due to catalyst robustness, and to a more reactive active intermediate.

Manganese-catalyzed enantioselective aziridination and amidation reactions

have also been developed.[11a,12] Asymmetric [Mn(por)*(OH)(MeOH)]- [por* = 5,10,15,20-tetrakis(1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl)porphyrinato] catalyzed aminations of allylic and benzylic substrates, and aziridinations of substituted styrenes, result in modest yields and modest to poor % ee.[11a,c] The UV–Vis spectrum and EPR measurements of the stoichiometric reaction between [Mn(por)*(OH)(MeOH)] and PhINTs are characteristic of a reduced Mn(IV) instead of a Mn(V) or Mn(VI) complex. Also, the electrospray mass spectrum has a peak of a *m/z* consistent with $[Mn(por^*)PhINTs]^+$. This indicates that this reaction probably does not proceed via high-valent imido intermediates. Improved enantioselectivities result when allylic amination is catalyzed by a chiral Mn(III) complex supported by a brominated salen ligand.[12d]

2.3 Ruthenium catalyzed nitrene transfer reactions

Che and coworkers discovered that $[Ru(Me_3tacn)(CF_3CO_2)_3]$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) and *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2Cl_2]$ (6,6'-Cl_2bpy = 6,6'-dichloro-2,2'-bipyridine) catalyze a variety of amidations by PhINTs.[11b,e] The yields (based on PhINTs) are good (81%-93%) for adamantane, cyclohexene, and a number of benzylic substrates. These reactions are proposed to involve metal imido intermediates. $[Ru(Me_3tacn)(NTs)_2]$, complexes generated in situ by $AgClO_4$ oxidation of $[Ru(Me_3tacn)(NHTs)_2(OH)]$, are competent amidation reagents.[11b]

Che and coworkers also found that Ru complexes with substituted porphyrin ligands (por) catalyze aziridination and benzylic/allylic amidation. They discovered that a competent nitrene transfer reagent, $[Ru(por)(NSO_2C_6H_4R)_2]$, could be isolated from the stoichiometric reaction of [Ru(por)CO] and $PhINSO_2C_6H_4R$. The rates of stoichiometric amidation or aziridination by $[Ru(por)(NSO_2C_6H_4R)_2]$ can be substantially affected by varying the R-group or varying the substituted-porphyrin ligand. For instance, changing R = –OMe to $–NO_2$ increases the rate of styrene aziridination 56-fold; changing the *meso* substituents of the porphyrin ligand from mesityl to pentafluorophenyl results in a 19-fold

increase in the rate of styrene aziridination. In general, electron-withdrawing substituents increase the rate of aziridination and amidation.[11l]

2.4 Rhodium catalyzed nitrene transfer reactions

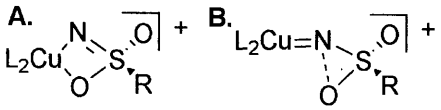
Dimeric Rh(II) catalysts have been used in a variety of nitrene insertion reactions. In an early example, Breslow found that $Rh_2(OAc)_4$ catalyzed the intramolecular benzylic amidation of *N*-(2,6-diisopropylbenzenesulfonyl)-iminophenyliodinane in excellent yields.[6b] Müller and coworkers developed Rh-catalyzed aziridination, intermolecular allyic/benzylic/ethereal amination, and intramolecular amination.[13] Changing the group-transfer reagent from PhINTs to PhINNs (Ns = *p*-nitrobenzenesulfonyl) resulted in a large increase in aziridine yields (see section 2.4 for a discussion of PhINNs).[13b] Because stereospecificity is maintained in the aziridination reactions, a metal-bound nitrene has been proposed as an intermediate.

DuBois and coworkers discovered the [$Rh_2(OAc)_4$]-catalyzed intramolecular amination of carbamates to oxazolidinones.[14a] The commercially available, inexpensive oxidant iodosobenzene(diacetate) [$PhI(OAc)_2$] is used in conjunction with MgO and H_2NR for *in situ* generation of PhI=NR species. This convenient method has been subsequently extended to intramolecular aziridination,[14b,11h,15a] intramolecular amidation,[14a,b,d–f,15b,16] intermolecular allylic amidation,[11h] enantioselective intramolecular aziridination,[11i] and finally intermolecular amidation of *p*-ethylanisole and cyclooctane.[14f]

2.5 Copper-catalyzed nitrene transfer reactions

Copper complexes are among the most widely used and active precatalysts for nitrene transfer. In a landmark discovery, Kwart and Kahn found that heating solutions of cyclohexene and $PhSO_2N_3$ in the presence of copper metal resulted in cyclohexene activation.[17] The variety of products formed suggests a mixture of reaction pathways. However, the formation of aziridination and allylic amidation products implies that metallonitrene intermediates are involved.

Figure 2. Proposed active intermediates for copper-catalyzed aziridination



In 1991, copper-catalyzed aziridination was revisited by Evans and coworkers.[18a] They found that simple Cu(I) or Cu(II) salts efficiently catalyzed the aziridination of a variety of olefins by PhINTs. Soon, asymmetric aziridination was developed concurrently by both the Evans and Jacobsen groups.[18b,c,19] Forty years after the initial report by Kwart and Kahn, copper-catalyzed aziridination is still a very active topic.[20–29]

The nature of the active intermediate in copper-catalyzed aziridination is still a controversial subject. Evans has proposed that Cu(II) intermediates are the catalytically relevant species. He notes that Cu(I) and Cu(II) both catalyze aziridination of olefins by PhINTs, and it is more likely that Cu(I) is oxidized to Cu(II) instead of Cu(II) being reduced to Cu(I) in the oxidizing conditions. Furthermore, when [Cu(bisoxazoline*)(OTf)] [bisoxazoline* = (4S,4'S)-2,2'-(propane-2,2-diyl)bis(4-phenyloxazoline)] is treated with PhINTs, the UV–Vis spectrum is identical to that of [Cu(bisoxazoline*)$(OTf)_2$]. Oxidation of Cu(I) is a pathway to enter a catalytic cycle involving Cu(II) intermediates.[18c]

In the Jacobsen system, experimental and theoretical evidence support a Cu(I)/Cu(III) cycle. Varying the aryl group on ArINTs, or replacing the iminoiodinane with photolytically activated TsN_3 as the nitrene precursor, had no effect on enantioselectivity.[19b] These results strongly imply a common intermediate, probably an $[L_2CuNTs]^+$ complex. A theoretical investigation by Norrby and Andersson also supports this conclusion.[24d] The minimized energy calculations on $[L_2CuNTs]^+$ propose that the NTs ligand binds as a κ^2-N,O chelate (Figure 2A). The triplet and singlet energies were insufficiently separated to determine whether either one is the active intermediate. Norrby and Andersson also outlined a mechanism in which a dicationic $L_2Cu(II)$ complex

can enter a Cu(I)/Cu(III) cycle by oxidation with PhINTs.

Scott and Deeth proposed a similar Cu(III) imido intermediate in a related copper-catalyzed asymmetric aziridination reaction.[25] The DFT-optimized structure has an interaction between an oxygen atom and the nitrogen atom (Figure 2B).[25b]

Andersson evaluated the effects of different arenesulfonyl substituents on the reactivity of iminoiodinanes, $PhINSO_2Ar$, in copper-catalyzed nitrene transfer reactions.[24a,c] Paradoxically, the best yields of aziridination products were found for both the electron-rich case (Ar = *p*-$MeOC_6H_4$) and the electron-poor case (Ar = *p*-$O_2NC_6H_4$). The greater stability of the more electron-rich intermediate is believed to slow side reactions relative to productive nitrene transfer, whereas the high reactivity conferred by the nitroaryl group is believed to accelerate productive transfer relative to decomposition.

Copper-catalyzed C–H bond activation has been less widely studied. Katsuki and coworkers developed Cu(II)-catalyzed benzylic and allylic amination reactions using *t*-butyl peroxycarbamates [*t*-BuOOCONHR] as the group-transfer reagent.[12c] Vedernikov and Caulton developed a tandem dehydrogenation/aziridination reaction using a copper catalyst. In this reaction, cyclic alkanes are dehydrogenated and then aziridinated, the sequence consuming two equivalents of PhINTs.[30] Although the yields of aziridine are low, the net functionalization of vicinal alkane C–H bonds is an intriguing result. Taylor and coworkers reported that *N*-(2-pyridinylmethylene)-1-pentanamine complexes of Cu(I) catalyzed allylic amination in modest yield.[31a] Finally, Pérez and coworkers reported the amidation of cyclohexane, toluene, mesitylene and benzene, in moderate yields.[21b,d]

2.6 Silver-catalyzed nitrene transfer reactions

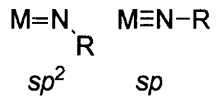
Despite the higher stability of Ag(I) toward oxidation than Cu(I), dinuclear complexes of terpyridine-supported Ag(I) have been found to catalyze aziridination[32a] and intramolecular amidation[32b] reactions. High-valent Ag species were proposed to be

intermediates in these reactions due to a change in the color of the reaction mixture. The electrospray mass spectrum of the reaction product obtained from $[Ag_2(t\text{Bu}_3t\text{py})_3(NO_3)](NO_3)$ ($t\text{Bu}_3t\text{py}$ = 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine) and PhINTs displayed a small peak consistent with a $\{[Ag_2t\text{Bu}_3t\text{py})_3(NO_3)](NO_3)$ + NTs} fragment. However, further analysis is necessary to identify what the identity of the reactive intermediate is in this catalytic reaction.

3.1 Late transition metal imido complexes: Introduction

Metal imido complexes are often implicated as active intermediates in nitrene transfer catalysis. However, isolation of chemically competent intermediates of this type is rare. Only in the case of $[Ru(por)(NSO_2Ar)_2]$[11f] catalyzed nitrene transfer reactions are the active intermediates isolated and well-characterized.

Figure 3. Linear vs. bent linkages in metal imido complexes



The metal-nitrogen bond order in a metal imido complex can greatly affect its reactivity toward nitrene transfer. In a localized valence bond description, the imido ligand can function as a 4- or 6-electron donor (for the ionic ligand formalism), yielding bond orders of 2 or 3. In this simplified description, the M–N–R linkage can be linear or bent, depending on the hybridization of the N atom (Figure 3).[3b] A classic example of a linear vs. bent linkage is found in $Mo(NPh)_2(S_2CNEt_2)_2$, first described by Haymore and Wentworth.[33] This molecule has two distinct imido ligands: one with a near-linear linkage [Mo–N–C = 169.4(4)°, Mo–N = 1.754(4) Å] and one bent [Mo–N–C = 139.4(4)°, Mo–N = 1.789(4) Å]. The N atom in the near-linear linkage can be described as *sp* hybridized, and the N atom in the bent linkage can be described as sp^2 hybridized.

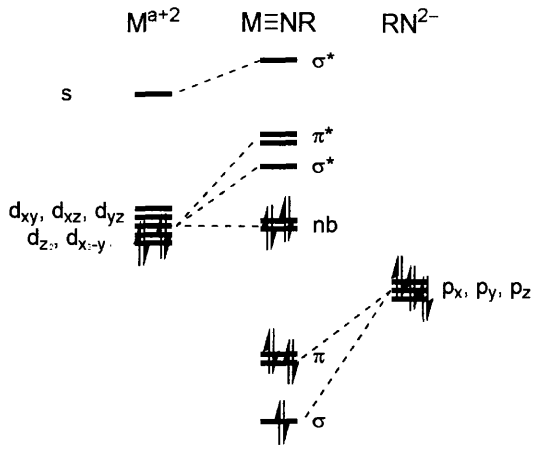


Figure 4. A qualitative MO diagram of the interaction between a metal fragment (M^{a+2}) and an imido fragment (RN^{2-})

Although valence bond theory can be a useful tool for a descriptive picture of metal imido bonding, a delocalized approach is necessary for a deeper understanding. Using a fragment (MO) approach, a metal imido bond (L_xM^a=NR) can be described in terms of the interaction between an L_xM^{a+2} fragment and a RN^{2-} fragment. The bonding in this approach consists of σ– and π-donation of electrons from the RN^{2-} fragment to the metal (Figure 4). For productive π-bonding to occur, the metal must have empty d-orbitals of π-symmetry (d_π-orbitals). For early and mid transition metals, most of the d-orbitals are empty. Consequently, early and mid transition metals often form stable bonds to imido ligands, and there are many known examples.[3] For late transition metals most of the d-orbitals are filled. Consequently, late-metals rarely form stable bonds to imido ligands, and there are only a few examples of isolated mononuclear imido complexes with d-electron counts higher than d^6. Instead, these complexes typically form dimers/multimers. However, a weaker metal imido bond can also result in a more reactive complex. Indeed, many of the most active nitrene-transfer catalysts are complexes of late transition metals.

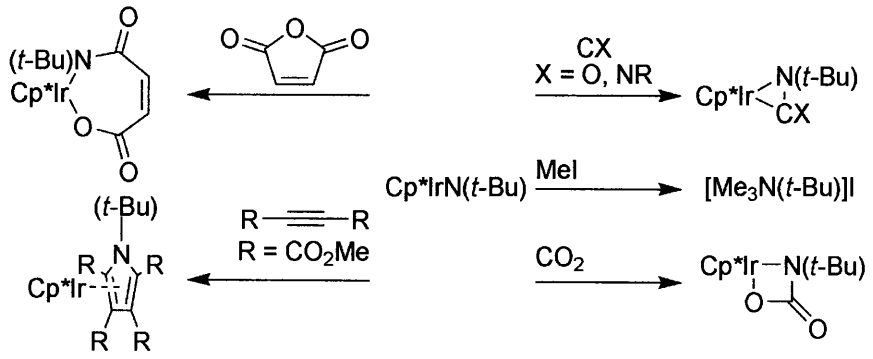
Supporting ligands can play two roles to stabilize imido complexes of late transition metals. Electron donation from the supporting ligands can raise the energy of d_π-orbitals in an L_xM^{a+2} fragment. When these orbitals are empty, they can accept π-

electron density from the RN^{2-} fragment, greatly enhancing the stability of the $M–N_{imido}$ bond. Large supporting ligands can suppress the formation of imido bridges between metal centers. Often, large imido groups are also necessary to stabilize monomeric species.

Finally, the bonding between a metal and an imido ligand is more complicated than the qualitative pictures presented in this section. Metal ligand multiple bonds can have significant ionic character. A more sophisticated analysis is necessary to ascertain a complete picture of bonding and reactivity. However, the qualitative pictures are a useful tool for a descriptive understanding of bonding and reactivity.

3.2 Mononuclear iridium(III) imido complexes

Scheme 4. Reactions of a terminal imido complex of Co(III)



The first well-characterized terminal imido complex of a late 0transition metal was synthesized in the Bergman lab.[34] Various imido complexes, Cp*IrNR, were synthesized by treatment of $[Cp^*IrCl_2]_2$ with four equivalents of LiNH(R) [R = (*t*-Bu); $SiMe_2$(*t*-Bu); 2,6-$(Me)_2C_6H_3$; or 2,6-$(i\text{-}Pr)_2C_6H_3$], by deprotonation of $Cp^*Ir(RNH_2)Cl_2$ using $KN(SiMe_3)_2$ [R = (*t*-Bu) or 2,6-$(i\text{-}Pr)_2C_6H_3$], or by treatment of Cp*IrN(*t*-Bu) with H_2NR [R = 2,6-$(Me)_2C_6H_3$, or 2,6-$(i\text{-}Pr)_2C_6H_3$]. Attempts to isolate Cp*IrNR complexes with smaller R groups led to the formation of dimeric compounds.[34c,35,36]

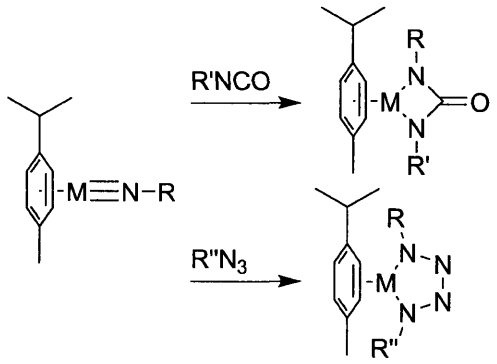
The near-linear linkages (Ir–N–C(Si) > 170°) indicate that these complexes are

best formulated as having two π-bonds between Ir and N. In a qualitative sense, the fragment Cp^*Ir^{2+} contains an empty e_1 set of orbitals that have π^*-symmetry relative to the imido ligand. When bonded to a RN^{2-} fragment, both π^*-orbitals would have low occupancy, making two π-bonds between Ir and N.

The imidoiridium(III) complex, Cp*IrN(*t*-Bu) reacts with a variety of substrates (Scheme 4). Treatment of Cp*IrN(*t*-Bu) with excess MeI forms $[Me_3N(t\text{-Bu})]I$ and $[Cp^*IrI_2]_2$. Carbon monoxide and *tert*-butyl isonitrile add across the metal-nitrogen multiple-bond to form three-membered rings. Carbon dioxide undergoes a formal[37] [2+2] cycloaddition to form a four-membered ring containing Ir, N, C and O. Treatment of Cp*IrN(*t*-Bu) with two equivalents of MeO_2CCCCO_2Me results in the formation of an η^5-pyrrole complex of Cp*Ir, via cycloaddition of the alkynes with the imido nitrogen. Also, Cp*IrN(*t*-Bu) undergoes a formal nucleophilic attack on maleic anhydride to form a 7-membered metallocycle. Finally, Cp*IrNR reacts with reduced metal centers to form heteronuclear bimetallic complexes.[34c]

3.3 Mononuclear osmium(II) imido complexes

Scheme 5. Reactions of terminal imido complexes of group VIII metals. M = Ru(II) or Os(II).



In 1993, Bergman and coworkers reported the preparation of $[(\eta^6\text{-arene})OsNR]_x$ complexes [arene = *p*-cymene (cym) or C_6Me_6, R = (*t*-Bu); arene = cym, R = 2,6-$Me_2C_6H_3$, 2,6-$(i\text{-Pr})_2C_6H_3$], synthesized by treatment of $[(\eta^6\text{-arene})OsNCl_2]_2$ with four

equivalents of LiN(H)R or treatment of [(η^6-cym)OsN(*t*-Bu)] with H_2NR (R = 2,6-$Me_2C_6H_3$, 2,6-*i*-$Pr_2C_6H_3$).[38] [(η^6-C_6Me_6)OsN(*t*-Bu)] is a monomer and has a near-linear linkage [Os–N–C = 174.1(7)°] and a short Os–N bond [1.737(7) Å] indicating that this bond can be best described as a triple bond.

Upon heating with (*t*-Bu)NCO, [(η^6-cym)OsN(*t*-Bu)] undergoes a formal [2+2] cycloaddition to form a 4-membered metallocycle containing Os, N_{imido}, N, and C. [(η^6-cym)OsN(*t*-Bu)] also reacts with organic azides (N_3R') to form a tetrazene metallocycle (Scheme 5). Finally, the Os=N bond can be cleaved by a variety of organic acids (HXR, X = N, S, O) to form Os–X bonds.[38b]

3.4 Mononuclear Ru(II) Imido Complex

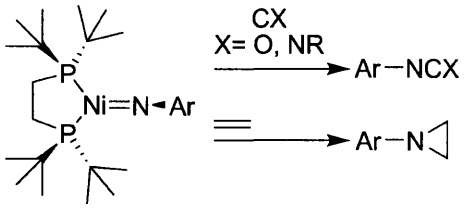
In 1995, Burrell and coworkers synthesized a series of [(η^6-arene)RuNR]$_x$ complexes.[39] Similar to the analogous [(η^6-arene)OsNR] complexes, stabilization of mononuclear [(η^6-arene)RuNR]$_x$ complexes requires a large degree of steric encumbrance.[39,40] For instance, [(η^6-cym)RuNAr'] [Ar' = 2,6-(*i*-Pr)$_2C_6H_3$] dimerizes; [(η^6-cym)RuNAr*] [Ar* = 2,4,6-(*t*-Bu)$_3C_6H_2$] is a stable monomer. The near-linear linkage (Ru–N–C = 178.5(12)°) and short Ru–N distance (1.751(14) Å) in [(η^6-cym)RuNAr*] are consistent with formulating the bond between Ru and N as a triple bond.

Wilkinson and coworkers determined that [(η^6-cym)RuNAr*] undergoes a formal [2+2] cycloaddition with mesityl isocyanate at room temperature to form a four-membered metallocycle containing Ru, N_{imido}, C and N. Also, treatment of [(η^6-cym)RuNAr*] with mesityl azide forms a tetrazene metallocycle (Scheme 5).[35]

3.5 Mononuclear Ni Imido Complexes

Currently, the only example of a d^8-terminal imido complex is [(dtpbe)NiNAr] (dtpbe = (*t*-Bu)PCH_2CH_2P(*t*-Bu), Ar = 2,6-(*i*-Pr)$_2C_6H_3$), synthesized in the Hillhouse group.[41] This complex was synthesized by treatment of [(dtpbe)NiN(H)Ar][PF_6] with

Scheme 6. Group transfer reactions from a terminal imido complex of Ni(II)



$NaN(SiMe_3)_2$. The Ni–N–C bond is severely bent [134.6(2)°] indicating that the Ni–N linkage has a bond order of two. The Ni–N bond distance is also shortened [1.702(2) Å] compared to the parent amido complex, [(dtpbe)NiN(H)Ar][PF_6] [Ni–N = 1.768(14)°]. In a qualitative sense, L_2Ni^{2+} would have an empty b_1-orbital and a filled b_2-orbital (in C_{2v} symmetry). When bonded to a RN^{2-} fragment, one π^*-orbital is filled and one π^*-orbital is left empty. This results in a net double-bond (a σ- and a π-bond) between Ni and N.

Carbon monoxide and benzyl isonitrile add across the Ni–N bond of [(dtpbe)NiNAr] to form 3-membered metallocycles. The isocyanate (OCNAr) and carbodiimide ($PhCH_2NCNAr$) products can be obtained by treatment of the metallocyclic products with excess CO.[41b] The imido complex [(dtpbe)NiNAr] also transfers an aryl-nitrene moiety to ethylene (Scheme 6).[41c]

In 2005, Warren and coworkers reported the synthesis of a mononuclear Ni(III) imido complex.[42b] Treatment of [(Me_3NN)Ni(2,6-lutidine)] (Me_3NN = *N,N*-dimesityl-2,4-dimethyl-1,5-diaza-1,3-pentadiene) with N_3Ad forms the terminal imido complex, [(Me_3NN)NiNAd]. A sterically demanding supporting ligand is necessary to stabilize a mononuclear complex. For instance, with a smaller supporting ligand, [(Me_2NN)Ni(2,6-lutidine)] (Me_2NN = *N,N*-bis(2,6-xylyl)-2,4-dimethyl-1,5-diaza-1,3-pentadiene) forms a bridged imido complex upon treatment with N_3Ad.

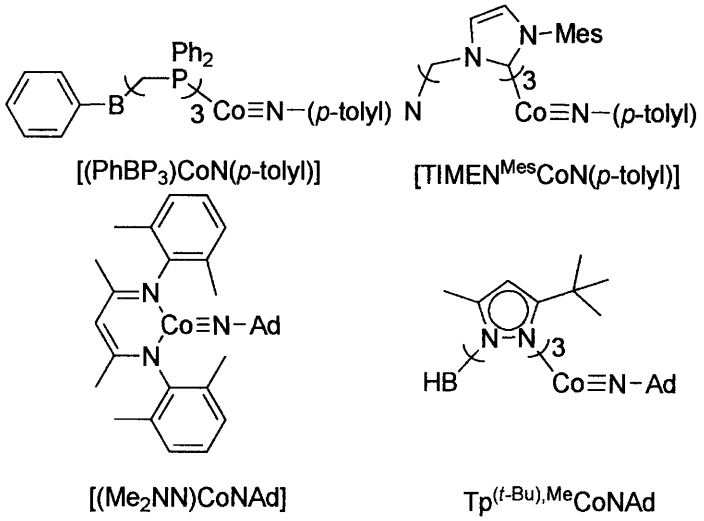
The imido linkage in [(Me_3NN)NiNAd] is slightly bent (Ni–C–N = 164.5(2)°), with a short Ni–N bond (1.662(2) Å). In a qualitative description, [(Me_3NN)Ni]$^{2+}$ has a partially

filled b_2 orbital and an empty b_1 orbital (in c_{2v} symmetry). Bonding with a RN^{2-} fragment would result in a partially-filled π^*-orbital and an empty π^*-orbital resulting in a net bond order of 2.5.

Like [(dtpbe)NiNAr], [(Me_3NN)NiNAd] reacts with CO and CN(*t*-Bu) to form AdNCO and AdNCN(*t*-Bu) respectively. Surprisingly, [(Me_3NN)NiNAd] also reacts with PMe_3 to form $AdNPMe_3$. This is a rare demonstration of both electrophilic and nucleophilic group-transfer from a single complex. The reaction of [(Me_3NN)NiNAd] with Cp_2Co results in formation of a C–N bond between the imido nitrogen and a Cp ring carbon, forming the dinuclear complex [(Me_3NN)NiN(Ad)C_5H_5CoCp]. Upon treatment with H-atom donors, such as 1,3-cyclohexadiene, [(Me_3NN)NiNAd] forms an (amido)Ni(II) complex, [(Me_3NN)NiN(H)Ad].

3.6 Mononuclear Co(III) Imido Complexes

Figure 5. Terminal imido complexes of Co(III)



[($PhBP_3$)CoN(*p*-tolyl)] [TIMEN^{Mes}CoN(*p*-tolyl)]

[(Me_2NN)CoNAd] Tp$^{(t\text{-Bu}),Me}$CoNAd

Following the discovery of a nickel(II) terminal imido complex by Hillhouse and coworkers, several examples of terminal imido complexes of Co(III) were reported (Figure 5). Although most of these complexes have similar oxidation states and geometries, they display a wide range of reactivity. The following sections present a discussion of the synthetic methods, a descriptive picture of bonding, and a discussion

of reactivity.

3.6a Synthesis of terminal imido complexes of cobalt(III):

In 2002, Peters and coworkers reported the first example of a terminal imido complex of cobalt.[43a] The reaction of [($PhBP_3$)Co(PMe_3)] [see Figure 5 for ($PhBP_3$)] with two equivalents of *p*-tolyl azide affords the cobalt(III) imido complex [($PhBP_3$)CoN(*p*-tolyl)]. The imido linkage in this complex is nearly linear [Co–N–C = 169.51(2)°], with a short Co–N distance [1.658(2) Å].

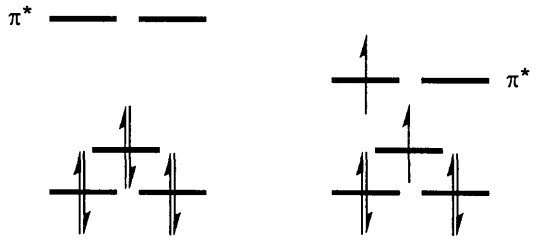
In 2004, Warren and coworkers reported the isolation of another terminal imido complex of cobalt.[42a] Treatment of a Co(I) precursor, [(Me_2NN)Co(η^6-PhMe)], with N_3Ad yields the diamagnetic [(Me_2NN)CoNAd] complex, with a nearly linear imido linkage [Co–N–C = 161.5(3)°] and a short Co–N bond [1.624(4) Å]. Large imido groups are necessary to stabilize a monomeric complex: Treatment of [(Me_2NN)Co(η^6-PhMe)] with (3,5-$Me_2C_6H_3$)-N_3 leads to the formation of a dimeric, imido-bridged complex.

Meyer and coworkers reported the synthesis of a cationic Co(III) imido complex with tripodal N-heterocyclic carbene supporting ligands (see Figure 5 for $TIMEN^{mes}$).[44] These complexes were formed by treatment of a Co(I) precursor with N_3Ar (Ar = *p*-tolyl or *p*-anisyl). The Co(III) imido complex [$TIMEN^{Mes}$CoN(*p*-tolyl)]$^+$ has a near linear linkage [Co–N–C = 168.6(2)°] and a short Co–N bond [1.675(2) Å].

Finally, Theopold and coworkers reported the synthesis of a neutral Co(III) imido complex with substituted tris(pyrazolyl)borate supporting ligands.[45b] Treatment of $Tp^{(t\text{-}Bu),Me}$Co(N_2) [$Tp^{(t\text{-}Bu),Me}$ = hydrotris(3-(*t*-Bu),5-Me'-pyrazolyl)borate] with N_3Ad results in the formation of $Tp^{(t\text{-}Bu),Me}$CoNAd. This complex contains a near-linear imido linkage (Co–N–C = 178.3(2)°) and a short Co–N bond (Co–N = 1.655(2) Å).

3.6b Bonding

Figure 6. Qualitative MO diagram of terminal imido complexes of Co(III) containing tripodal supporting ligands



S = 0 for
[(TIMEN^{Mes})CoN(*p*-tolyl)]$^+$
(PhBP$_3$)CoN(*p*-tolyl)

S = 1 for
Tp$^{(t\text{-Bu}),Me}$CoNAd

A DFT study of [TIMEN^{Mes}CoN(*p*-tolyl)]$^+$ by Meyer and coworkers revealed that multiple bonding between Co and N_{imido} is dictated by π-bonding.[44] The calculated LUMOs are an e set of π*-orbitals, and the HOMO is a σ*-orbital. Thus this complex has two π-bonds. This theoretical framework can be used as a base for a qualitative description of the other Co imido complexes with tripodal supporting ligands (Figure 6). Both [TIMEN^{Mes}CoN(*p*-tolyl)]$^+$ and [(PhBP$_3$)CoN(*p*-tolyl)] have supporting ligands which raise the energy of an e set of orbitals, decreasing the π*-occupancy. The low π*-occupancy results in diamagnetic complexes. The supporting ligand in Tp$^{(t\text{-Bu}),Me}$CoNAd is a weaker donor. The e set of orbitals are at a low enough energy to be partially occupied in the ground state. As a result, Tp$^{(t\text{-Bu}),Me}$CoNAd is a paramagnetic complex.

A DFT study of [(Me$_2$NN)CoNAd] by Warren and coworkers indicates that the LUMO and LUMO+1 are both π*-orbitals.[42a] The Me$_2$NN ligand helps to raise the energy of the LUMO+1 (and consequently to lower the energy of the π-bond), further stabilizing the Co–N_{imido} bond. As in the complexes [TIMEN^{Mes}CoN(*p*-tolyl)]$^+$ and [(PhBP$_3$)CoN(*p*-tolyl)], the HOMO is mostly metal-based, and the complex is diamagnetic.

3.6c Imido Transfer Reactivity

Carbon monoxide reacts sluggishly with [($PhBP_3$)CoN(*p*-tolyl)] to form *p*-tolyl isocyanate.[43a] At room temperature [$TIMEN^{Mes}$CoN(*p*-tolyl)]$^+$ is unstable, inserting its nitrene group into one of the cobalt–carbene bonds.[44] Finally, $Tp^{(t\text{-}Bu),Me}$CoN(Ad), upon heating, transfers its nitrene group into a *tert*-butyl C–H bond in the supporting ligand.[39b] Interestingly, $Tp^{(t\text{-}Bu),Me}CoNSiMe_3$ was not isolable, and instead a *tert*-butyl C–H bond of the supporting ligand is activated to form a cyclometallated complex with a Co–C bond.[45a] Clearly, altering supporting ligand and imido group has drastic effects on the stability and reactivity of cobalt(III) imido complexes.

3.7 Mononuclear Fe(II) Imido complex

In 2005, Peters reported the reduction of [($PhBP_3$)FeN(Ad)] by Na/Hg to form an anionic d^6-Fe(II) imido complex, [($PhBP_3$)FeN(Ad)]$^-$, isolated as its tetra-*n*-butylammonium salt.[43e] This complex has a near linear Fe-imido linkage (Fe–N–C = 178.57°) and a short Fe–N bond [1.651(3) Å]. A DFT study indicated that the LUMO was a degenerate set of orbitals in π^*-symmetry relative to the imido ligand. This results in the formation of two π-bonds and a diamagnetic complex.

4. Research Goals

Late transition metal catalysts for nitrene transfer have been used in a variety of aziridination and amination reactions. Often, supporting ligands can confer greater reactivity and selectivity by minimizing side reactions of active intermediates. To this aim we have synthesized sterically demanding, oxidatively robust ligands to support metal-catalyzed nitrene transfer reactions. We are especially interested in the little-explored functionalization of arene C–H bonds through these processes. Moreover, we sought to isolate reactive mononuclear imido complexes. Sulfonimido complexes of late transition metals are of particular interest because they are commonly proposed as

active intermediates in metal-catalyzed nitrene transfer reactions.

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Chapter 1: Sterically demanding, oxidation resistant phenanthroline as supporting ligands for copper(I) nitrene transfer catalysis

Introduction

The efficient and selective functionalization of carbon–hydrogen bonds represents an ongoing challenge in inorganic and organic chemistry. New methodology for efficient C–H bond activation has a wide range of applications from large-scale industrial synthesis to small-scale fine-chemical synthesis.[1] We are interested in the less-explored area of arene C–H activation by metal-nitrene species.

Metal nitrenes have been implicated in a variety of metal-catalyzed aziridination and amidation reactions.[2–6] Although active metal nitrenes are rarely isolated,[7] indirect experimental and theoretical investigation supports their involvement in many nitrene-transfer reactions.[8]

Among the most active catalysts for nitrene transfer are copper-based catalysts. Copper-catalyzed nitrene transfer to olefins is well known.[9–11] Copper-catalyzed nitrene activation of C–H bonds is less well-known. Among the few examples, copper-catalyzed amidation of allylic and benzylic C–H bonds was reported by Katsuki[12] and by Taylor.[13] Caulton and Vedernikov reported the dehydrogenation/aziridination of cyclic alkanes.[14]

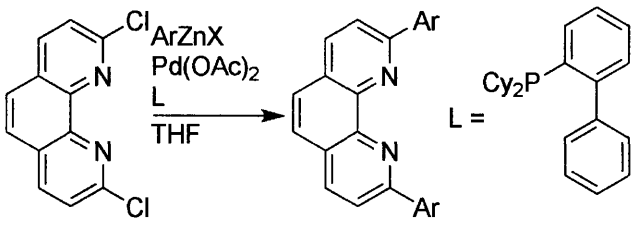
Often, the reactivity and selectivity of metal-catalyzed nitrene-transfer reactions are greatly affected by the suppression of side reactions by the supporting ligand. Ligands such as 2,9-diphenyl-1,10-phenanthroline,[15] and its 2,9-dimesityl analogue,[16] project considerable steric bulk about the metal, but expose C–H bonds to the metal center. In this chapter, we report the synthesis of two new 1,10-phenanthroline ligands with heavily fluorinated aryl substituents[17] in the 2- and 9-positions to avoid oxidative ligand modification.[18] Copper(I) complexes of both phenanthrolines have been prepared and structurally characterized; the more sterically demanding ligand gives rise to a reactive precatalyst for the transfer of a nitrene group from iminoiodinanes to the C–H bonds of electron-rich arenes. This copper(I) precatalyst also activates *p*-nitrobenzenesulfonyl azide to form a sulfonamido complex of copper(II).

Preceding the publication of a communication of this work, Peréz and coworkers reported that perbrominated tris(pyrazole)borate complexes of Cu(I) catalyzed amidation of cyclohexane, toluene, mesitylene and benzene by *N*-(*p*-toluenesulfonylimino)phenyliodinane (PhINTs) in modest yields.[19a] A recent report found that the yields of benzene amidation can be greatly increased by heating.[19b] Also, concurrent with the publication of our communication, Che and coworkers reported the ruthenium-catalyzed amidation of aromatic heterocycles by PhINTs.[20]

Results and Discussion

The new phenanthrolines were prepared by cross-coupling reactions using $Pd(OAc)_2$ precatalyst and the 2-(dicyclohexylphosphino)biphenyl ligand developed by

Scheme 1. Synthesis of fluorinated 2,9-diaryl-1,10-phenanthrolines.



1: Ar = C_6F_5

2: Ar = 2,4,6-$(CF_3)_3C_6H_2$

Buchwald and coworkers[21] (Scheme 1). The reaction of 2,9-dichloro-1,10-phenanthroline[22] with C_6F_5ZnBr[23] or 2,4,6-$(CF_3)_3C_6H_2ZnCl$ affords 2,9-bis(pentafluorophenyl)-1,10-phenanthroline (**1**) or 2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline (**2**). The Negishi coupling has been used previously to prepare a variety of 2,9-diaryl-1,10-phenanthrolines.[24]

The electronic effect of the addition of fluorinated aryl groups on the 1,10-phenanthroline ligands was investigated by comparing the IR stretches of $[L_2Rh(CO)_2]^+$ complexes. Changing L_2 from 2,9-dimesityl-1,10-phenanthroline to **2** results in a 13 cm^{-1} shift in the A_1 IR stretch of the CO ligands (Table 1). Since different placements of methyl and/or phenyl groups results in larger effects on the carbonyl stretching frequencies (Table 1),[25] the electronic effect of these aryl rings appears relatively small.

Table 1. IR stretches of CO in $[L_2Rh(CO)_2]^+$ complexes.

L_2	A_1 (cm^{-1})	B_1 (cm^{-1})
2	2095	2035
2,9-dimesityl-1,10-phenanthroline	2082	2015
2,9-dimethyl-1,10-phenanthroline[a]	2100	2040
5,6-dimethyl-1,10-phenanthroline[a]	2110	2070
4,7-diphenyl-1,10-phenanthroline[a]	2105	2050

[a]Ref 25

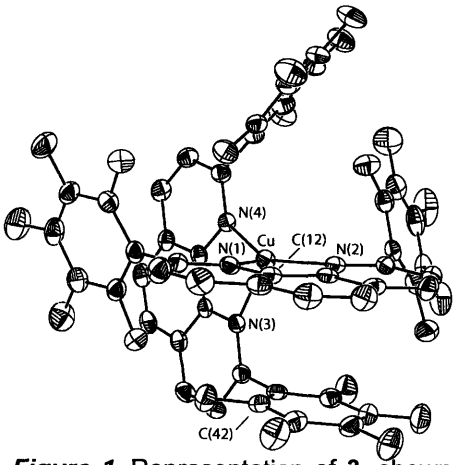


Figure 1. Representation of **3**, shown as 50% ellipsoids. The SbF_6^- ion, one molecule of CH_2Cl_2 and hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and bond angles (°): Cu–N(1) 2.109(3), Cu–N(2) 2.025(3), Cu–N(3) 2.079(3), Cu–N(4) 2.048(3), C(12)–C(42) 3.343(5); N(1)–Cu–N(2) 83.39(11), N(3)–Cu–N(4) 82.77(11), N(1)–Cu–N(3) 102.6(11), N(2)–Cu–N(3) 119.89(11).

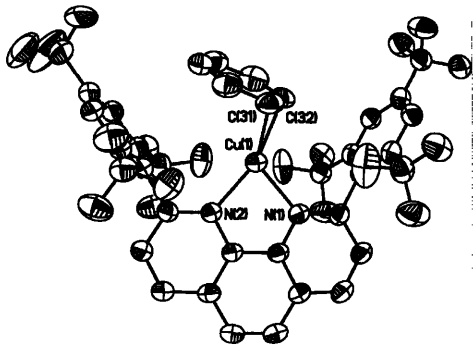
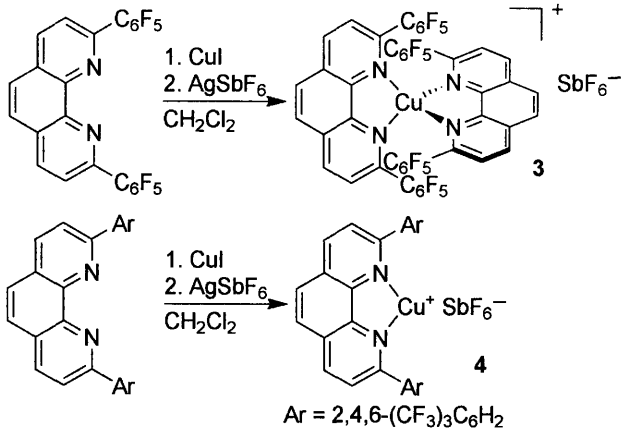


Figure 2. Representation of **4'**, shown as 50% ellipsoids. For clarity, the SbF_6^- ion, solvent, and hydrogen atoms have been omitted, and only one molecule in the asymmetric unit is shown. Selected interatomic distances (Å) and bond angles (°): Cu(1)–N(1) 2.108(4), Cu(1)–N(2) 2.026(4), Cu(1)–C(31) 2.232(5), Cu(1)–C(32) 2.113(5), C(31)–C(32) 1.397(9); N(1)–Cu(1)–N(2) 82.71(15), N(1)–Cu(1)–C(31) 127.1(2), N(1)–Cu(1)–C(32) 117.2(2).

Scheme 2. Synthesis of copper(I) complexes **3** and **4**.



Reaction of **1** with $[Cu(NCMe)_4][BF_4]$ or CuI in CH_2Cl_2 at ambient temperature (Scheme 2) results in the formation of a homoleptic complex $[(\mathbf{1})_2Cu]^+$, crystallized as its SbF_6^- salt **3**. The X-ray crystal structure of **3** (Figure 1) shows bond lengths and bite angles similar to those of the analogous 2,9-diphenyl-1,10-phenanthroline complexes;[15] however, one phenanthroline is canted, permitting a π-stacking interaction with a pentafluorophenyl group; the distance between rings is 3.343(5) Å. The lack of open coordination sites of **3** prevents reaction with group-transfer reagents.

Ligand **2** presents considerably greater steric demand than **1**, and reacts with $[Cu(NCMe)_4][BF_4]$ or 0.5 equivalent of $(C_6H_5CH_3)\cdot 2(CuOTf)$ in CH_2Cl_2 to afford [**2**·Cu(NCMe)][BF_4] or **2**·Cu(OTf). Both complexes react slowly with many common group-transfer reagents. For example, complete consumption of **2**·Cu(OTf) by reaction with PhINTs requires 20 h.

To increase the reactivity, we sought to synthesize a copper(I) complex of **2** with a more reactive coordination site. We synthesized **2**·CuI by treatment of **2** with excess CuI in CH_2Cl_2. Iodide is readily abstracted by $AgSbF_6$ in CH_2Cl_2 to form the light yellow compound, **2**·$CuSbF_6$ (**4**). Initially a CH_2Cl_2 adduct of **4** is formed. The coordinated solvent molecule may be removed by heating *in vacuo* to form solvent-free **4**,

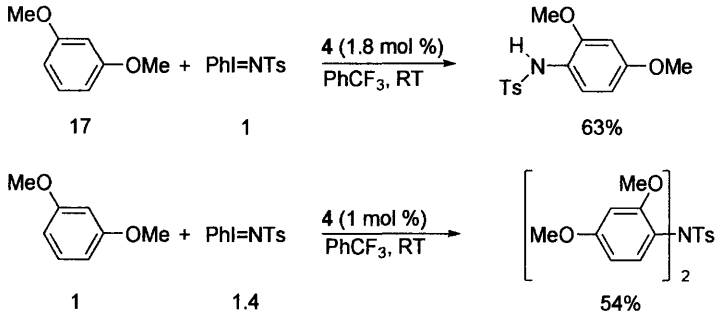
characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and by elemental analysis. The poor solubility of this complex in weakly coordinating solvents (such as hexanes and pentane) has precluded crystallization of solvent-free **4**. However, exposure of a concentrated solution of **4** in CH_2Cl_2 to a small amount of benzene vapor resulted in crystallization of the η^2-benzene adduct **4'** (Figure 2). Like other copper(I)–benzene adducts,[26] **4'** shows no substantial lengthening of the coordinated C–C bond.

Solutions of complex **4**, on addition of PhINTs, formed a green intermediate with liberation of free iodobenzene. Complete consumption of **4** occurred within 10 minutes in α,α,α-trifluorotoluene ($PhCF_3$). The solution magnetic moment[27] {μ_{eff}=1.42 Bohr Magnetons, measurement in $PhCF_3$ after treatment with $NaBAr^f_4$ salt [Ar^f = 3,5-bis(trifluoromethyl)benzene]} and UV–Vis spectroscopy [λ_{max} = 637.92 nm, ε = 220 L mol^{-1} cm^{-1}, reaction performed in $PhCF_3$, measurement in 1,1,1,3,3,3-hexafluoropropan-2-ol, (HFIP)] were consistent with the formation of Cu(II) products. The paramagnetic ^{1}H NMR spectrum contained multiple broad peaks. Each paramagnetic product displayed only a single peak. We believe that this peak is the resonance for the [2,4,6-$(CF_3)_3C_6\underline{H}_2$–] proton. The other ligand protons did not give rise to observable resonances. Similarly, only a single broad ^{19}F peak was evident for each species in the ^{19}F NMR spectrum. This resonance was believed to arise from the 4'-CF_3 groups on the ligand. Attempts to observe a reactive intermediate, perhaps a Cu(III) sulfonimido complex, by ^{1}H and ^{19}F NMR at low temperature were unsuccessful. It is likely the decomposition of this reactive intermediate is faster than its formation. In lieu of direct isolation of a reactive complex, we have investigated its activity in the transfer of tosylnitrene group to arene C–H bonds.

The reaction of PhINTs with anisole (17 equiv) in $PhCF_3$ solution, catalyzed by **4** (0.5 mol%), resulted in the rapid dissolution of the iminoiodinane, with the formation of *o*- and *p*-sulfonamidation products, $TsNH_2$, and poorly soluble oligomers that were removed

during NMR and GC-MS sample preparation. The substrate 1,3-dimethoxybenzene was chosen next, to temporarily sidestep the issue of *o*/*p* selectivity, and to examine whether the desired reaction would occur more readily with this doubly activated arene, minimizing the subsequent side-reactions (Scheme 3). Indeed, the reaction of PhINTs with this substrate (20 equiv in $PhCF_3$ at ambient temperature), catalyzed by **4** (2 mol%) led to the formation of *p*-tosyl-1,3-dimethoxyaniline in an isolated yield of 63% based on iminoiodinane.

Scheme 3. Divergent outcomes for nitrene transfer to C–H bonds.

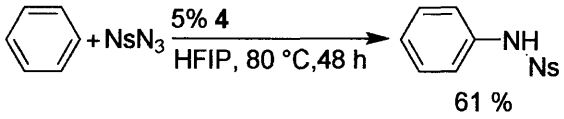


A change in stoichiometry resulted in a notably different outcome. With arene as the limiting reagent, the major product was the *N,N*-diarylsulfonamide. Only a trace of monoarylsulfonamide was observed; the other products appear to be sulfonated oligoarylamines. This seemingly paradoxical result suggests that the initially formed *N*-arylsulfonamide can be activated under the reaction conditions to generate a nitrogen-based electrophile.

We next looked into increasing the scope of nitrene transfer by using sulfonyl azides as nitrene transfer reagents. Unlike iminoiodinanes, sulfonyl azides are soluble, easy to obtain in anhydrous form and stable in most solvents. The byproduct of nitrene generation, dinitrogen, is environmentally benign and trivially removed. We found that under specific conditions, electron-poor sulfonyl azides can be efficiently activated. The synthetic flexibility of these reagents allowed us to expand the scope of this tranfser to a

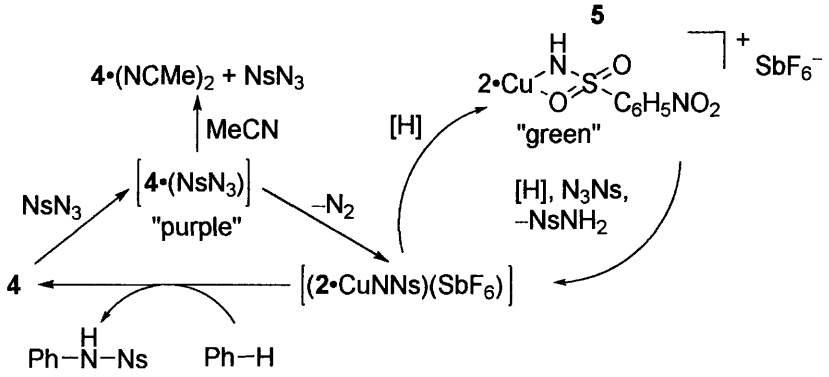
variety of alkyl and arene substrates. For instance, **4** catalyzed benzene sulfonamidation by [*p*-nitrobenzenesulfonyl azide] (NsN_3) in 61% yield (Scheme 4).[28] The electron-poor solvent [1,1,1,3,3,3-hexafluoro-2-propan-2-ol] (HFIP) is optimal for this transfer.

Scheme 4. **4**-catalyzed sulfonamidation of benzene by NsN_3



To elucidate the function of **4** in this catalysis, the stoichiometric reaction of NsN_3 with **4** was investigated. We have isolated a monomeric copper(II) sulfonamido complex from this reaction. The reactivity of this complex and its relevance to the catalytic cycle has been explored.

Scheme 5. Proposed scheme for C–H bond activation and azide activation.



Treatment of **4** with a slight excess of NsN_3 in HFIP initially generated a purple intermediate (Scheme 5). When acetonitrile was added to this solution, NsN_3 and **4**·$(NCMe)_2$ is formed. The liberation of intact sulfonyl azide suggests that the purple intermediate was probably an NsN_3 adduct of **4**. After five minutes, the purple color dissipated and a dark green color formed. Analysis by ^1H NMR indicated complete consumption of **4**, and the solution magnetic moment[27] of 1.62 Bohr magnetons (based on the amount of **4** initially added) was consistent with the Cu(II) oxidation state. Initial

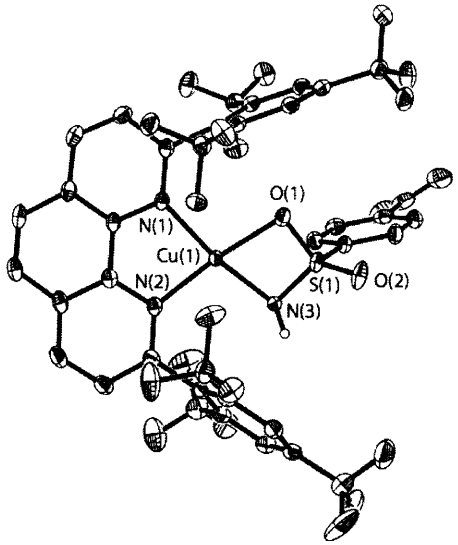
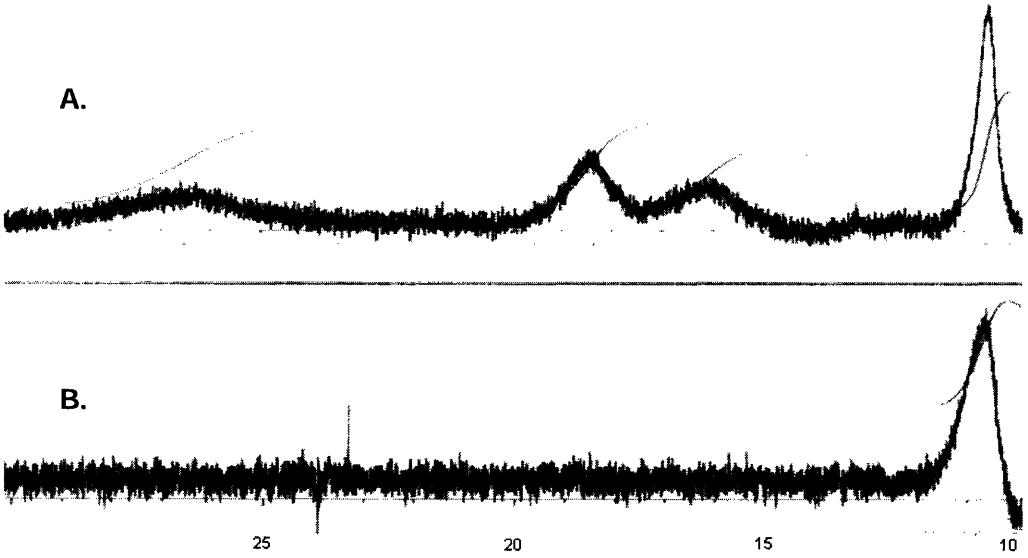


Figure 3. X-ray crystal structure of **5**. For clarity, SbF_6^- anion and HFIP solvate are omitted. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 2.005(2), Cu(1)–N(2) 1.992(2), Cu(1)–N(3) 1.973(2), Cu(1)–O(1) 2.021(2), S(1)–O(1) 1.499(2), S(1)–O(2) 1.433(2), S(1)–N(3) 1.552(3); N(1)–Cu(1)–N(2) 84.20(10), O(1)–Cu(1)–N(3) 70.87(10), N(1)–Cu(1)–N(3) 168.15(10), N(2)–Cu(1)–N(3) 105.12(10), N(1)–Cu(1)–O(1) 101.30(10), N(2)–Cu(1)–O(1) 168.67(10), N(3)–S(1)–O(1) 98.74(13), N(3)–S(1)–O(2) 117.98(16), O(1)–S(1)–O(2) 116.92(15).

NMR analysis indicated that a mixture of products formed (Figure 4A). After 20 h, only a single peak remained in both the ^1H and ^{19}F NMR spectra (Figure 4B).

Single crystals suitable for X-ray diffraction were formed by slow diffusion of pentane into a solution of this product and excess NsN_3 in a 1:1 HFIP/$PhCF_3$ mixture. X-ray diffraction studies identifies this product as {**2**·Cu[N(H)Ns]}[SbF_6], **5**. The sulfonamido ligand binds in a κ^2-N,O-bound chelate, making a four-coordinate complex. The high moisture-sensitivity of this complex precluded its isolation from excess NsN_3 without partial decomposition.[29] However, heating a NsN_3-free solution of **5** (at 80 % purity) with benzene resulted in no discernible amidation of benzene. It is therefore unlikely that **5** is the active intermediate in this catalysis. Although not chemically competent for stoichiometric nitrene transfer, **5** acts as an efficient precatalyst for the sulfonamidation of benzene by N_3Ns in 80% yield. This suggests that **5** can reenter the catalytic cycle, possibly by oxidation with N_3Ns, to form [**2**·CuNNs][SbF_6] and $NsNH_2$ (with the second hydrogen possibly obtained by abstraction from reaction medium, Scheme 5).

Figure 4. ^{1}H NMR spectra of the addition of two equivalents of NsN_3 to **2** in HFIP after 10 min (**A.**), and after 20 h (**B.**). Excess NsN_3 and solvent resonances omitted for clarity.



Conclusion:

We have prepared new 1,10-phenanthroline ligands substituted with heavily fluorinated aryl rings to confer steric bulk while resisting oxidation. With the C_6F_5-substituent, the ligand is small enough to form a homoleptic copper(I) complex, whereas the larger 2,4,6-$(CF_3)_3C_6H_2$-substituted ligand supports the formation of a reactive copper(I) cation. This complex catalyzes nitrene transfer to the C–H bonds of an electron-rich arene, leading to either of two major products depending on the reaction stoichiometry. The stoichiometric reaction of the reactive copper(I) cation and *p*-nitrobenzenesulfonyl azide leads to formation of a sulfonamido complex of copper(II). This complex is not an efficient stoichiometric nitrene-transfer reagent; however, it is an active precatalyst for benzene amidation by *p*-nitrobenzenesulfonyl azide.

Experimental:

General Considerations. Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an

Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA, or Desert Analytics, Tucson, AZ. Anhydrous dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), hexanes, and diethyl ether (Et_2O) were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for diethyl ether and tetrahydrofuran; the tetrahydrofuran was also passed through a third column packed with activated 4 Å molecular sieves) or through neutral alumina and copper(II) oxide (for hexanes). Molecular sieves (3 Å) were activated by heating at 190 °C for several days. *N,N*-Dimethylformamide (DMF) was purchased anhydrous from Aldrich and used as received. α,α,α-Trifluorotoluene ($PhCF_3$) was purchased anhydrous from Aldrich and was stored over 3 Å activated molecular sieves under argon. Benzene (Aldrich) was purchased anhydrous and further dried over sodium benzophenone ketal. Benzene was vacuum-transferred prior to use. All non-dried solvents used were reagent grade or better.

The starting material 1,3,5-tris(trifluoromethyl)benzene (Aldrich) was degassed by three freeze-pump-thaw cycles immediately before use. Zinc dust (Aldrich) was activated by washing with 1M HCl, followed by water, ethanol and diethyl ether, then drying *in vacuo*. Copper(I) iodide (Strem), zinc(II) chloride (Alfa Aesar), palladium(II) acetate (Strem), 2-(dicyclohexylphosphino)biphenyl (Strem), 2-(di-*tert*-butylphosphino)biphenyl (Strem), chlorobis(ethylene)rhodium(I) dimer (Strem), silver(I) hexafluoroantimonate (Strem), silver(I) trifluoromethanesulfonate (Alfa Aesar) and bromopentafluorobenzene (Oakwood Products) were used as received. *n*-Butyllithium solution was purchased from Alfa Aesar and used as received. 1,3-Dimethoxybenzene was dried over calcium hydride and vacuum-distilled prior to use. [*N*-(*p*-

toluenesulfonyl)imino]phenyliodinane (PhINTs),[30] 4-nitrobenzenesulfonyl azide (NsN_3),[31] 2,9-dichloro-1,10-phenanthroline,[32] and tetrakis(acetonitrile)copper (I) hexafluoroantimonate[33] were prepared according to literature methods.

IR spectra were recorded on a Nicolet Impact 410 spectrometer as KBr pellets. NMR solvents were dried as follows: methylene chloride-d_2 (Cambridge Isotope Laboratories) over calcium hydride, acetone-d_6 (Cambridge Isotope Laboratories) over calcium sulfate, 1,1,1,3,3,3-hexafluoro-2-propan-2-ol-d_2 (HFIP-d_2) over 3 Å molecular sieves. All NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ^{1}H NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. ^{19}F NMR were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm). ^{13}C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak.

2,9-Bis(pentafluorophenyl)-1,10-phenanthroline (1)

In the glovebox, a flame-dried resealable Schlenk tube, equipped with a Teflon-coated magnetic stir bar, was charged with activated Zn (2.553 g, 39.04 mmol) and sealed with a Teflon screwcap. The tube was brought out from the glovebox, the Teflon screw cap was replaced with a rubber septum, and THF (60 mL) was added via syringe, followed by bromopentafluorobenzene (4.6 mL, 36.9 mmol, added cautiously). The septum was replaced with a screwcap, and the tube was sealed; the reaction mixture was then subjected to sonication for 12 h.[345] The Schlenk tube was reopened in the glovebox, and 2,9-dichloro-1,10-phenanthroline (3.00 g, 12.0 mmol), palladium(II) acetate (0.139 g, 0.618 mmol, 2.6 mol% per Cl) and 2-(di-*tert*-butylphosphino)biphenyl (0.434 g, 1.45 mmol, 2.3 eq per Pd) were added. The tube was resealed and brought out of the glovebox; the reaction mixture was heated at 85 °C for 12 h, then at 90 °C for

3 days. After cooling to room temperature, the reaction mixture was taken up in methylene chloride (300 mL). The organic layer was washed with ten portions of a solution prepared from ethylenedinitrilotetraacetic acid disodium salt (Na_2EDTA) (6 g) in acetic acid (10 mL) and water (300 mL), and then with water (2 x 350 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Crystallization from toluene afforded the pure product **1** (4.00 g, 65%). ^1H NMR (300.1 MHz, $CDCl_3$): δ 8.43 (d, J = 8.3 Hz, 2 H), 7.96 (s, 2 H), 7.84 (d, J = 7.5 Hz, 2 H). ^{19}F NMR (282.3 MHz, $CDCl_3$): δ –143.22 (m, 4 F), –153.56 (t, J = 20.3 Hz, 2 F), –162.03 (dt, J = 8.5 Hz, J = 21.3 Hz, 4 F). ^{13}C NMR (125 MHz, acetone-d_6): δ 147.6, 146.8, 145.5 (dm, J = 249.3 Hz), 142.1 (dm, J = 235.3 Hz), 138.5 (dm, J = 247.0 Hz), 138.1, 129.6, 128.4, 126.1, 116.7 (t, J = 15.8 Hz). IR (KBr, cm^{-1}): 1654, 1551, 1524, 1502, 1360, 1068, 991. Anal. calcd for $C_{24}H_6N_2F_{10}$: C, 56.27; H, 1.18; N, 5.47. Found: C, 55.97; H, 1.14; N, 5.22.

Preparation of 2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline (2)

1,3,5-Tris(trifluoromethyl)benzene (2.40 mL, 12.8 mmole) was added to a Schlenk tube equipped with a Teflon-coated magnetic stir bar and capped with a Teflon screw cap. The Teflon screw cap was replaced with a rubber septum and diethyl ether (20 mL) was added via syringe. A solution of *n*-butyl lithium (7.67 mL, 2.72 M, 20.9 mmole) was then slowly added at -78 °C via syringe. The tube was sealed and the solution was allowed to stir for 1.5 h at 0 °C and 1 h at 25 °C. The tube was brought into a dry box where a diethyl ether solution of zinc(II) chloride (15 mL of a 0.85 M solution, 12.8 mmol) was slowly added. The white suspension was then stirred overnight. The solution was concentrated *in vacuo*. 2,9-dichloro-1,10-phenanthroline (0.800 g, 3.21 mmole), palladium(II) acetate (0.144 g, 0.641 mmole), and 2-(dicyclohexylphosphino)biphenyl (0.248 g, 0.708 mmole) were added to the Schlenk

tube. The Teflon screw cap was replaced with a rubber septum and THF (30 mL) was added via syringe. The Schlenk tube was sealed and then heated to 100 °C for 2 days. The reaction mixture was allowed to cool and was then placed into a round bottom flask. The solution was concentrated *in vacuo*. Dichloromethane (6 mL) was added and then hexanes (200 mL) were added. The off-white solid was collected via filtration and was further washed with hexanes (3 x 10 mL). The solid was dissolved in dichloromethane (80 mL), and filtered. A saturated solution of Na_2EDTA solution in water (100 mL) was added and the mixture was stirred for 2 hours, then filtered. The dichloromethane phase was separated, washed with water (30 mL), then with brine (15 mL). The dichloromethane solution was dried over $MgSO_4$, filtered through a silica gel plug and evaporated *in vacuo*. Crystallization from hot *N,N*-dimethylformamide yielded the product as a colorless solid (1.21 g, 51%). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.70 (d, J = 8.3 Hz, 2 H), 8.44 (s, 4 H), 8.22 (s, 2 H), 7.97 (d, J = 8.3 Hz, 2 H). ^{19}F NMR (300 MHz, acetone-d_6): δ –57.43 (s, 12 F), –63.04 (s, 6 F). ^{13}C NMR (125 MHz, acetone-d_6): δ 154.1, 146.4, 144.3, 137.3, 133.2 (q, J = 31.7 Hz), 132.5 (q, J = 34.5 Hz), 130.1, 129.0, 128.6, 126.0, 124.3 (q, J = 272.1 Hz), 124.2 (q, J = 274.9 Hz). IR (KBr, cm^{-1}): 1303, 1289, 1207, 1189, 1144, 919, 845. Anal. calcd for $C_{30}H_{10}N_2F_{18}$: C, 48.67; H, 1.36; N, 3.78. Found: C, 48.59; H, 1.59; N, 3.61.

Preparation of {2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}rhodium(I) dicarbonyl trifluoromethanesulfonate [2•Rh(CO)$_2$][OTf]

In the glovebox, in the absence of light, bis(ethylene)rhodium (μ-chloride) dimer (0.044 g, 0.061 mmol), silver(I) trifluoromethane sulfonate (0.060 g, 0.23 mmol) and THF (2 mL) were added to an oven-dried vial equipped with a Teflon-coated magnetic stir bar. THF (2 mL) was added at –10 °C.[35] The suspension was stirred for 0.5 h at –10 °C. **2** (0.100 g, 0.135 mmol) was added, and the suspension was allowed to slowly

warm to RT. The suspension was stirred for 2 h, and then filtered through dry Celite. THF was removed *in vacuo*, and the brown solid was dissolved in α,α,α-trifluorotoluene (5.5 mL). The solution was stirred under an atmosphere of carbon monoxide for 15 h. The solution was filtered through Celite and the precipitate was extracted with acetone (10 mL). The solvent was removed *in vacuo*, to yield [**2**·$Rh(CO)_2$][OTf] (0.0520 g, 0.0500 mmol, 43%) ^{1}H NMR (300 MHz, acetone-d_6): δ 8.70 (d, J = 8.3 Hz, 2 H), 8.44 (s, 4 H), 8.22 (s, 2 H), 7.97 (d, J = 8.3 Hz, 2 H). ^{19}F NMR (300 MHz, acetone-d_6): δ –56.22 (s, 12 F), –66.37 (s, 6 F), –78.14 (s, 3 F). ^{13}C NMR (125 MHz, acetone-d_6): δ 180.0 (d, J = 71.7 Hz) 157.0, 147.97, 143.3, 140.5, 135.6 (q, J = 35.2 Hz), 133.3 (q, J = 32.8 Hz), 130.3, 130.0, 129.6, 127.6 (q, J = 268.0 Hz), 124.2, 122.1 (q, J = 235.2 Hz), 122.0 (q, J = 231.4 Hz). IR (KBr, cm^{-1}): 2082, 2015.

Bis[2,9-bis(pentafluorophenyl)-1,10-phenanthroline]copper(I) hexafluoroantimonate (3)

In the glovebox, in an oven-dried vial equipped with a Teflon-coated magnetic stir bar, tetrakis(acetonitrile)copper(I) hexafluoroantimonate (0.220 g, 0.475 mmol) and **1** (0.500 g, 0.976 mmol) were dissolved in anhydrous CH_2Cl_2 (4 mL). The resulting orange suspension was allowed to stir overnight. The vial was brought out of the glovebox and opened to air, and hexanes (10 mL) were added. The orange solid that precipitated was isolated by filtration and washed with hexanes (3 x 1 mL), then dissolved in acetone (8 mL) and filtered to remove a small amount of insoluble solid. The resulting solution was concentrated *in vacuo*, affording **3** as an orange, microcrystalline solid (0.623 g, 99 %). ^{1}H NMR (300.1 MHz, acetone-d_6): δ 9.16 (d, J = 8.53 Hz, 2 H), 8.57 (s, 2 H), 8.26 (d, J = 8.53, 2 H). ^{19}F NMR (282.3 MHz, acetone-d_6): δ –140.14 (m, 4 F), –152.83 (t, J = 21.36 Hz, 2 F), –162.39 (m, 4 F). ^{13}C NMR (125.8 MHz, acetone-d_6): δ 146.8, 144.8 (dm, J =

265.4 Hz), 144.6, 142.3 (dm, J = 255.1 Hz), 140.4, 137.9 (dm, J = 249.9 Hz), 130.9, 129.7, 129.4, 114.7. IR (KBr, cm^{-1}): 1654, 1528, 1503, 1357, 1076, 994.

Preparation of {2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}copper(I) iodide (2•CuI)

Copper (I) iodide (0.206 g, 1.08 mmol) and **2** (0.515 g, 0.696 mmol) were added to a dried, resealable Schlenk tube equipped with a Teflon-coated magnetic stir bar. The vessel was evacuated and backfilled with argon, and then the Teflon screwcap was replaced with a rubber septum. Anhydrous CH_2Cl_2 (7 mL) was added via syringe. The septum was replaced with a screwcap, the Schlenk tube was sealed, and the reaction mixture was stirred for 12 h. The resulting suspension opened to air and filtered, and the filtered solid was washed with CH_2Cl_2 (3 mL). The solution was concentrated under reduced pressure, affording the title compound as a red powder (0.520 g, 80%). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 8.73 (d, J = 8.5 Hz, 2 H), 8.28 (s, 4 H), 8.21 (s, 2 H), 8.05 (d, J = 8.5 Hz, 2 H). ^{19}F NMR (282.3 MHz, CD_2Cl_2): δ –58.28 (s, 12 F), –64.07 (s, 6F). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ 153.1, 143.1, 140.2, 138.3, 133.0 (q, J = 34.7 Hz), 132.6 (q, J = 31.9 Hz), 129.5, 128.2, 127.9, 127.5, 123.1 (q, J = 272.9 Hz), 123.0 (q, J = 275.2 Hz). IR (KBr, cm^{-1}): 1303, 1289, 1210, 1142, 912, 845. Anal. calcd for $C_{30}H_{10}N_2F_{18}CuI$: C, 38.71; H, 1.08; N, 3.01. Found: C, 38.63; H, 1.20; N, 2.83.

Preparation of {2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}copper(I) hexafluoroantimonate (4)

In the glovebox, in an oven-dried vial equipped with a Teflon-coated magnetic stir bar, **2**•CuI (0.195 g, 0.210 mmol) was dissolved in CH_2Cl_2 (5 mL). Silver hexafluoroantimonate (0.074 g, 0.22 mmol) was added; the resulting mixture was stirred for 5 min, filtered through a plug of dried Celite, and concentrated *in vacuo*. Prolonged drying (2.5 days at rt, or 1.5 days at 60 °C, and $1x10^{-3}$ torr) was necessary to remove all

CH_2Cl_2. Care must be taken to avoid exposure of the solid to donor solvents such as water, tetrahydrofuran, diethyl ether, and acetone, as these bind irreversibly to form an inactive catalyst. The product **4**, a pale yellow powder (0.190 g, 87%), was stored in a drybox, in a vial with a Polyseal cap. ^{1}H (300 MHz, acetone-d_6): δ 9.20 (d, J = 8.25 Hz, 2 H), 8.63 (s, 4 H), 8.57 (s, 2 H), 8.50 (d, J = 8.53 Hz, 2 H). ^{19}F (282.3 MHz, acetone-d_6): δ –57.14 (s, 12 F), –62.90 (s, 6 F). ^{13}C (125.8 MHz, acetone-d_6): δ 153.9, 143.8, 141.4, 140.9, 133.9 (q, J = 34.7 Hz), 133.3 (q, J = 31.9 Hz), 131.2, 129.8, 129.4, 129.1, 124.0 (q, J = 272.7 Hz), 124.0 (q, J = 275.2 Hz). IR (KBr, cm^{-1}): 1636, 1302, 1278, 1212, 1143, 916, 846, 686, 667. Anal. calcd For $C_{30}H_{10}N_2F_{24}CuSb$: C, 34.66; H, 0.97; N, 2.69. Found: C, 34.46; H, 1.00; N, 2.65.

Catalytic sulfonamidation of 1,3-dimethoxybenzene: Preparation of *p*-toluenesulfonyl-1,3-dimethoxyaniline

Activated 3 Å molecular sieves (~0.4 g) were added to a resealable Schlenk tube equipped with a Teflon-coated magnetic stir bar and capped with a Teflon screwcap. The tube was flame-dried and cooled under vacuum, then opened, charged with PhINTs (0.200 g, 0.536 mmol), evacuated, and brought into the glovebox, where catalyst **4** (0.010 g, 9.6 μmol) was added. The capped tube was brought out of the glovebox, the Teflon screwcap was replaced with a rubber septum, and $PhCF_3$ (4 mL) was added via syringe, followed by 1,3-dimethoxybenzene (1.18 ml, 9.00 mmol). The septum was replaced with a screwcap, and the tube was sealed. The reaction mixture was stirred 10 h at room temperature, then concentrated *in vacuo*. Purification of the residual solid by column chromatography on silica gel, using CH_2Cl_2 as eluant, afforded the title compound (0.107 g, 65%). ^{1}H (300.1 MHz, $CDCl_3$): δ 7.56 (d, J = 8.3 Hz, 2 H), 7.43 (d, J = 8.8 Hz, 1 H), 7.17 (d, J = 8.1 Hz, 2 H), 6.61 (s, 1 H), 6.43 (dd, J = 8.7 Hz, 2.6 Hz, 1 H), 6.27 (d, J = 2.6 Hz, 1 H), 3.76 (s, 3H), 3.49 (s, 3 H), 2.36 (s, 3 H). ^{13}C (125.8 MHz,

$CDCl_3$): δ 158.5, 152.0, 143.5, 136.3, 129.2, 127.4, 124.7, 118.8, 104.4, 98.8, 55.6, 55.6, 21.6. IR (KBr, cm^{-1}): 3246, 2963, 2940, 1615, 1506, 1337, 1309, 1212, 1167, 1124, 1034, 842, 812, 707, 696, 535. Anal. calcd for $C_{15}H_{17}NO_4S$: C, 58.61; H, 5.57. Found: C, 58.51; H, 5.53.

Catalytic sulfonamidation of 1,3-dimethoxybenzene: Preparation of *N,N*-bis(2',4'-dimethoxyphenyl)-*p*-toluenesulfonamide

Activated 3 Å molecular sieves (0.4 g) were added to a resealable Schlenk tube equipped with a Teflon-coated magnetic stir bar and capped with a Teflon screwcap. The tube was flame-dried and cooled under vacuum, then opened, charged with PhINTs (0.332 g, 0.890 mmol), evacuated, and brought into the glovebox, where catalyst **4** (0.010 g, 9.6 μmol) was added. The capped tube was brought out of the glovebox, the Teflon screwcap was replaced with a rubber septum, and $PhCF_3$ (10 mL) was added via syringe, followed by 1,3-dimethoxybenzene (0.070 mL, 0.54 mmol). The septum was replaced with a screwcap, the tube was sealed, and the suspension was allowed to stir for 5 h. The resulting dark solution was transferred to a round-bottom flask and concentrated *in vacuo.* Column chromatography on silica gel, using CH_2Cl_2:EtOAc (95:5) as eluant, afforded the title compound as a colorless solid (0.0397 g, 33%). ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.61 (d, J = 8.23 Hz, 2 H), 7.53 (d, J = 8.60 Hz, 2 H), 7.23 (d, J = 7.94 Hz, 2 H), 6.42 (dd, J = 8.64 Hz, J = 2.69 Hz, 2 H), 6.38 (d, J = 2.57 Hz, 2 H), 3.78 (s, 6 H), 3.62 (s, 6 H), 2.43 (s, 3 H). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 160.7, 158.1, 142.5, 139.3, 133.3, 128.8, 128.1, 122.6, 104.2, 99.3, 55.6, 55.4, 21.7. IR (KBr, cm^{-1}): 1601, 1508, 1458, 1343, 1320, 1243, 1211, 1161, 1028, 843, 733, 678, 566. Anal. calcd for $C_{23}H_{25}NO_6S$: C, 62.29; H, 5.68; N, 3.16. Found: C, 62.15; H, 5.62; N, 3.08.

{2,9-Bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}(4''-nitrobenzenesulfonyl-amido)copper(II) hexafluoroantimonate (5)

In the glove box, an oven-dried resealable Teflon-capped NMR tube was charged with **1** (0.050 g, 0.048 mmol) and 4-nitrobenzenesulfonyl azide, NsN_3 (0.022 g, 0.097 mmol). HFIP (0.7 mL) was added via pipette, and a violet solution was initially formed. (In a separate experiment, addition of acetonitrile to this solution generated **1**·$(NCMe)_2$ and free NsN_3, suggesting that the violet-colored intermediate was an adduct formed prior to azide activation by **1**). The solution quickly changed in color to dark green, and after 10 minutes, the ^1H NMR (Figure 4A) and ^{19}F NMR spectra indicated the presence of several paramagnetic species. ^1H NMR (HFIP, 300.107 MHz): δ 27.2 (br); 18.8 (br); 16.0 (br); 10.8 (br). ^{19}F NMR (HFIP, 282.347 MHz): δ –59.6; –59.9; –66.4; –66.8.

After 20 h, the only significant peak in the ^1H NMR spectrum, outside of the diamagnetic region, was the broad resonance at δ 10.8 (Figure 4B). We tentatively assign this resonance to the ring protons of the 2,4,6-$(F_3C)_3C_6H_2$– groups; being distant from the metal center, and attached to a ring rotated out of conjugation with the phenanthroline π-system, these protons seem the most likely to give visible resonances despite paramagnetic broadening. In the new ^{19}F NMR spectrum, only a single resonance at δ –66.8 is distinct from the (very large) solvent CF_3 resonance. The magnetic susceptibility of the product complex in HFIP solution was measured by the Evans NMR Method[27] at μ_{eff}=1.62 Bohr magnetons, consistent with a single unpaired electron per copper center.

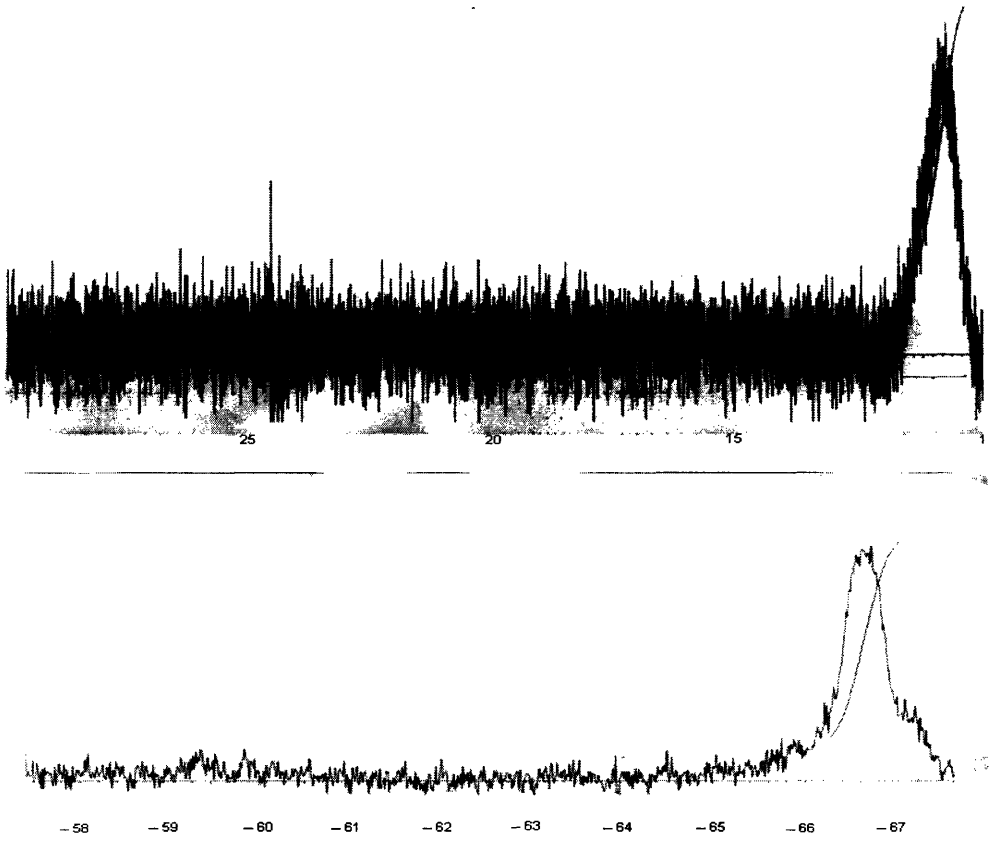
The diamagnetic region of the ^1H NMR spectrum shows resonances for solvent and the excess NsN_3, and will be discussed below. No resonances for the diamagnetic **1** remain. The key conclusion to be drawn here is that on reaction with excess NsN_3 in HFIP at ambient temperature, **1** is completely consumed; several paramagnetic intermediates, and a single stable paramagnetic product, are observed.

A small portion of this HFIP solution was diluted with an equal volume of α,α,α-trifluorotoluene, in which the product complex is less soluble. Slow diffusion of pentane into the resulting solution afforded crystals suitable for X-ray diffraction analysis, which identified this species as {2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}(4"-nitrobenzenesulfonylamido) copper(II) hexafluoroantimonate, **2**. The oxidation state assignment is based on the presence of a single anion per copper center, the location of the N-bound hydrogen in the Fourier difference map, and the solution magnetic susceptibility (*vide supra*).

Nitrene transfer from NsN_3 to benzene using 5 as precatalyst

In the glove box, an oven-dried resealable, Teflon-capped NMR tube was charged with **1** (0.020 g, 0.192 mmol) and 4-nitrobenzenesulfonyl azide (0.092 g, 0.404 mmol). HFIP (0.7 mL) was added via pipette. After 5 h, ^{1}H NMR and ^{19}F NMR indicated that all of **4** had converted to **5** (Figure 5).

Figure 5. ^{1}H (top spectrum) and ^{19}F NMR (lower spectrum) spectra of **5** in the presence of 20 equivalents of NsN_3 in HFIP-d_2 after 5 h. Excess NsN_3 (^{1}H) and solvent resonances omitted for clarity.



This solution was transferred to a Teflon-capped Schlenk tube equipped with a Teflon-coated magnetic stir bar in the glove box. HFIP (0.6 mL) and benzene (0.728 mL, 8.14 mmol) were added via pipette. The tube was sealed and heated at 80 °C for 2 d. The solution was cooled, added to a saturated aqueous ammonium acetate solution (5 mL), and extracted into CH_2Cl_2 (3 x 5 mL). Hexamethylbenzene was added as an internal standard, and the solution was shaken vigorously. An aliquot (3 mL) was concentrated *in vacuo*, and analysis by ^{1}H NMR, with integration of product relative to

internal standard, indicated the formation of 0.323 mmol *N*-phenyl-4-nitrobenzenesulfonamide (80% NMR yield).

Attempted stoichiometric reaction of 5 with benzene

The procedure used to isolate X-ray quality crystals of **5** appears to work only on very small scales; isolation of pure complex on preparative scale proved difficult. The heavily fluorinated, ionic complex tends to form oils or amorphous films readily, or to precipitate with occluded NsN_3 (present in excess). Because **5** acts as a precatalyst for the reaction of NsN_3 with benzene, it was essential to remove all NsN_3 to learn whether **5** itself would mediate stoichiometric amidation. The extreme moisture-sensitivity of **5** has led, during the multiple solvent treatments and manipulations needed to remove all detectable NsN_3, to significant hydrolysis; new resonances are observed in the paramagnetic region (Figure 6), as well as significant $NsNH_2$ in the diamagnetic (δ 7–9) region (Figure 7). The two regions are shown separately because their vertical scales are very different, paramagnetic broadening leading to far lower and broader signals for the copper complex.

NsN_3-free samples of **5** were prepared as follows. Complex **5** was generated by the procedure described above (0.048 mmol **4**, 0.097 mmol NsN_3, 0.7 mL HFIP, rt, 20 h). The solution was concentrated to 0.2 mL. Benzene (6 mL) and hexanes (2 mL) were added, and a green solid precipitated. The green solid was collected by filtration, washed with benzene (3 x 2 mL), and dissolved in HFIP (0.5 mL). The solution was concentrated to yield a green solid (0.030 g, 0.019 mmol, 40%).

Figure 6. ^{1}H NMR spectrum, in HFIP solution, of crude **5** as isolated after washing to remove NsN_3. $NsNH_2$ (see Figure S7, bottom) and solvent resonances omitted for clarity.

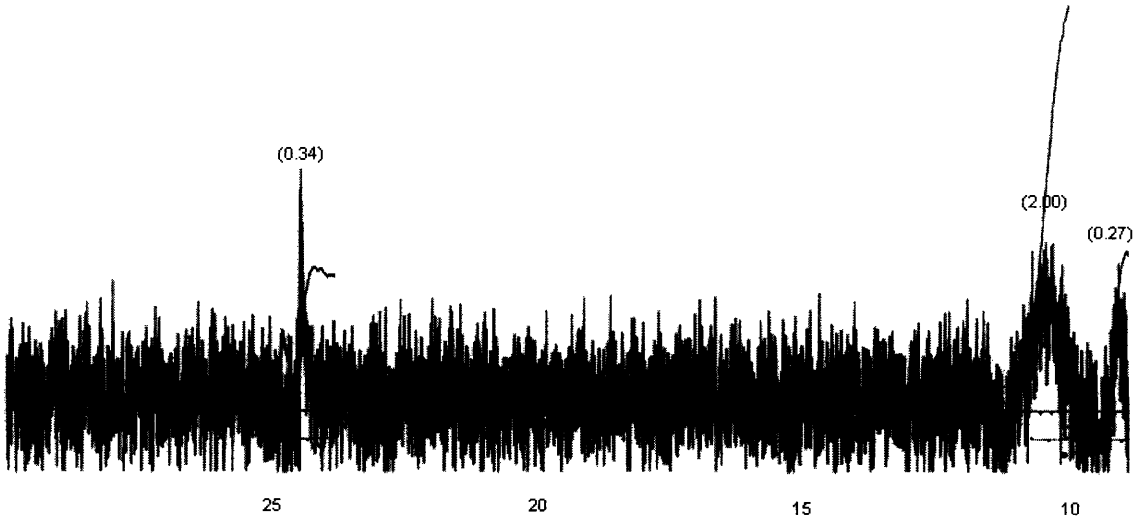
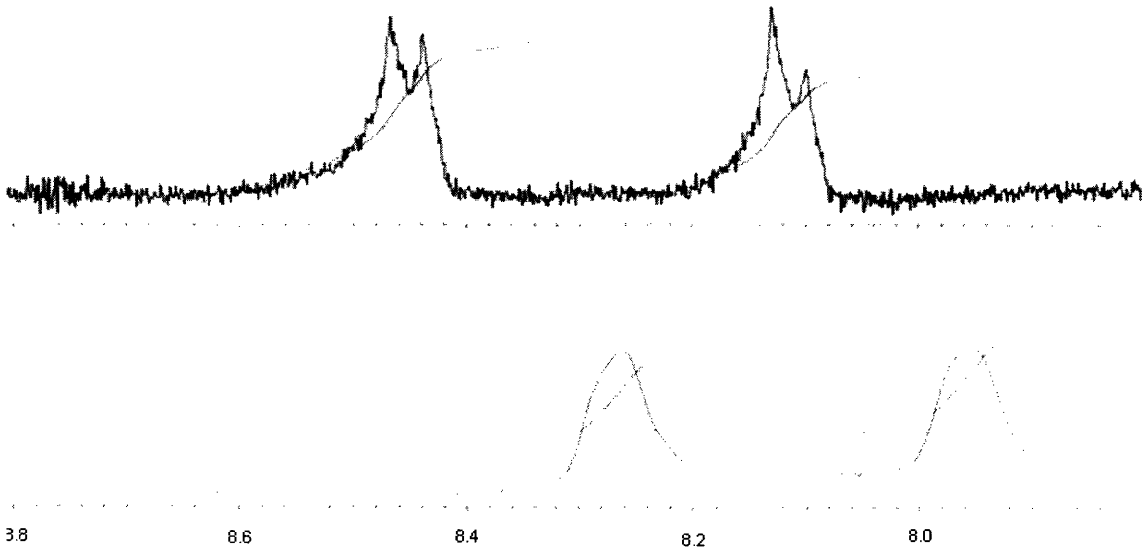


Figure 7. ^{1}H NMR spectra showing a portion of the diamagnetic region for a sample of **5** in HFIP, before (top) and after (bottom) washing to remove NsN_3. Paramagnetic and solvent regions omitted for clarity. Top spectrum shows NsN_3, and bottom spectrum shows $NsNH_2$.



Despite this degradation, the resonance for **5** remains the dominant peak in the paramagnetic region of the ^{1}H NMR spectrum, while the diamagnetic region shows little if any remaining NsN_3.

In the glove box, a flame-dried resealable Teflon-capped Schlenk tube equipped with a magnetic stir bar was charged with this crude **5** (0.030 g, 0.019 mmol). A mixture of HFIP (1.3 mL) and benzene (0.728 mL, 8.14 mmol) was added and the tube was sealed and heated at 80 °C for 2 days. The flask was cooled and a crude ^{1}H NMR spectrum (in HFIP) indicated no formation of *N*-phenyl-4-nitrobenzenesulfonamide. The solution was taken up in saturated aqueous ammonium acetate solution (5 mL), and extracted with CH_2Cl_2 (3 x 2 mL). The only products detected by ^{1}H NMR (CD_2Cl_2) and by GC/MS were 2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline and 4-nitrobenzenesulfonamide.

X-Ray Crystallography

General considerations. Crystals of **3**, **4'**, and **5** were transferred onto a microscope slide from a scintillation vial and coated with STP. A crystal was selected, mounted on a glass fiber, and optically centered. The data were collected on a Siemens platform goniometer with a CCD detector. The structures were solved by direct methods in conjunction with standard difference Fourier techniques (SHELXTL v5.1, Sheldrick, G. M. and Siemens Industrial Automation, 1997). Non-hydrogen atoms were treated anisotropically, and hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 Å).

Bis[2,9-bis(pentafluorophenyl)-1,10-phenanthroline]copper (I) hexafluoroantimonate (3):

Single crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of **3** (0.010 g) in CH_2Cl_2 (0.7 mL) and C_6F_5CN (0.2 mL). One molecule of CH_2Cl_2 co-crystallized per molecule of **3**.

{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}copper(I)(η^2-benzene) hexafluoroantimonate (4'):

A solution of **4** (0.070 g) in CH_2Cl_2 (1 mL) was exposed to a small concentration of benzene vapor. On standing for several hours at ambient temperature, the resulting solution deposited single crystals of **4'** (**4**•C_6H_6) suitable for X-ray diffraction. Two molecules of **4'** and two dichloromethane molecules were found in the asymmetric unit. Four fluorine atoms of one SbF_6 (Sb1) were modeled over two positions, each with half occupancy. All six fluorine atoms of the other SbF_6 (Sb2) were modeled over two positions, each with half occupancy. Significant residual electron density was found at four positions (in e/A^3): 1.36 near Sb2, 1.22 near C68, 1.17 near Cl4, 1.00 near C69.

{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}rhodium(I) dicarbonyl Trifluoromethanesulfonate [2•Rh(CO)$_2$][OTf]:

A solution of [**2**•Rh(CO)$_2$][OTf] (0.010 g) in chloroform (1 mL) was allowed to slowly evaporate deposited single crystals of [**2**•Rh(CO)$_2$][OTf] suitable for X-ray diffraction. [**2**•Rh(CO)$_2$][OTf] and two chloroform molecules were found in the asymmetric unit.

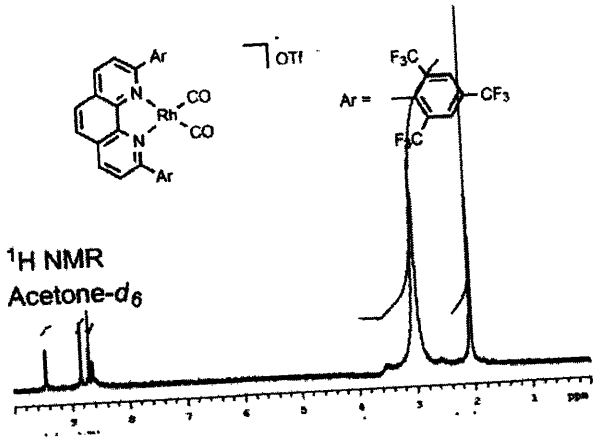
{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}copper(I) hexafluoroantimonate (5)

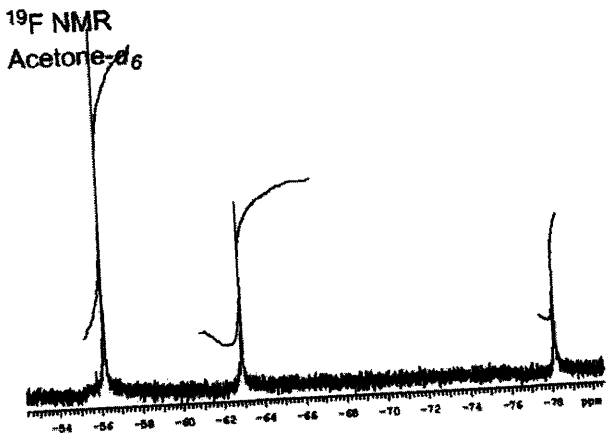
A solution of **5** in a 1:1 mixture of HFIP and benzene was treated with hexanes. On standing overnight, the resulting solution deposited crystals of **5** suitable for X-ray diffraction. A co-crystallized HFIP molecule was found to be significantly disordered, and was modeled over two positions with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The occupancies for the disordered parts were refined freely. A semi-empirical absorption correction was applied based on equivalent reflections.

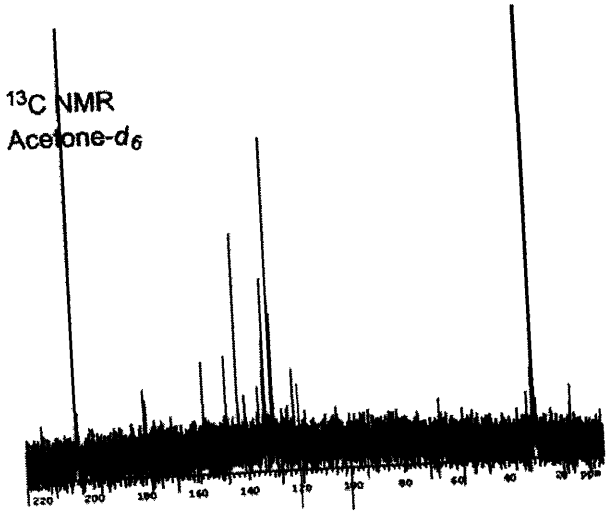
Table 2. Crystallographic data for **3**, **4**, [**2**·Rh(CO)$_2$][OTf], and **5**.

	3	**4**	[**2**·Rh(CO)$_2$][OTf]	**5**
Empirical formula	$C_{49}H_{14}Cl_2CuF_{26}N_4Sb$	$C_{37}H_{18}Cl_2CuF_{24}N_2Sb$	$C_{35}H_{12}F_{21}N_2O_5RhS$	$C_{39}H_{17}Cu_{F30}N_4O_5SSb$
FW	1408.83	1202.72	1287.14	1408.92
T, K	193(2)	194(2)	194(2)	173(2)
Crystal syst,	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P-1(bar)	P-1	P2(1)/C	P-1
a, Å	12.5042(13)	12.8498(11)	14.7595(14)	9.4544(6)
b, Å	14.2178(15)	17.2274(14)	20.149(2)	11.7376(5)
c, Å	14.2393(15)	19.3942(16)	15.5069(15)	20.9391(12)
α, deg	74.479(2)	88.865(2)	90	78.585(2)
β, deg	85.194(2)	85.991(2)	100.668(2)	83.165(2)
λ,deg	74.395(2)	72.624(2)	90	88.681(2)
V, Å^3	2349.1(4)	4087.3(6)	4531.9(8)	2261.5(2)
ρ, g/cm^{-1}	1.992	1.955	1.886	2.069
Z	2	4	4	2
μ, mm^{-1}	1.289	1.455	0.908	1.289
F(000)	1368	2336	2512	2512
Cryst size, mm^3	0.36 x 0.30 x 0.22	0.33 x 0.33 x 0.18	0.38 x 0.36 x 0.27	0.15 x 0.12 x 0.12
θ-range, deg	1.97 to 23.30	1.62 to 28.32	1.40 to 24.71	1.85 to 28.28
Total no. of reflns	9642	25968	7733	47175
GOF on F^2	1.041	1.124	1.108	1.048
Final *R* indices [I>2σ(I)]	0.0355	0.0687	0.0830	0.0421
	0.0895	0.1748	0.2056	0.1073
R indices (all data)	0.0409	0.0893	0.0943	0.0526
	0.0926	0.2015	0.2136	0.1138

NMR Spectra:


Ar
N
Rh
CO
CO
N
Ar
OTf
Ar =
F3C
CF3
F3C
1H NMR
Acetone-d6
ppm


19F NMR
Acetone-d6
ppm


13C NMR
Acetone-d6
ppm

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Chapter 2: Synthesis and reactivity of monomeric sulfonylamido and sulfonylimido complexes of palladium

Introduction

The previous chapter describes the use of 2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline (**1**) as a supporting ligand for the copper-catalyzed sulfonamidation of arenes. The high reactivity of the presumed catalytic intermediate, a d^8-sulfonimido Cu(III) complex, precluded its direct observation. Other d^8-sulfonimido complexes, such as those of Pd(II), were expected to be more stable. Unlike Cu(III), Pd(II) is a common oxidation state, is not easily reduced in one electron steps, and would form a neutral sulfonimido complex when supported by a neutral phenanthroline ligand. In this chapter, the first isolation of a mononuclear[1,2] (sulfonimido)palladium complex is described. Its group transfer chemistry, and the reactivity of its cationic (sulfonamido)palladium precursor, are presented.

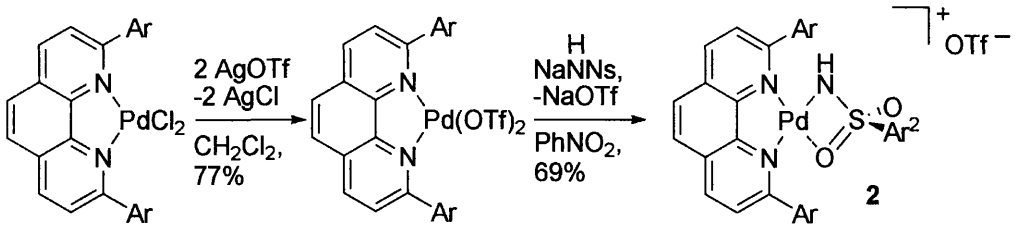
Although sulfonimido complexes have been invoked as active intermediates in Cu,[3-5] Ag,[6] Au,[7] Rh,[8] Ru,[9] V,[10] Pd,[11] Fe,[12-14] and Mn[12-14] catalyzed sunfonylnitrene transfer reactions,[15] well characterized examples of these complexes are rare. To date, only Mo,[16] W,[17] Os,[18] and Ru[19] sulfonimido complexes have been isolated and well-characterized in monomeric form.[20] The isolation of monomeric late metal imido complexes has been the subject of great recent interest. By using supporting ligands to impart steric control and electronic stability, Ir,[21] Ni,[22,23] and Co[24-27] complexes bound to terminal imido ligands have been discovered. However, none of these complexes contains a sulfonimido ligand, although many metal-catalyzed nitrene transfer reactions involve the sulfonylnitrene moiety.[3-14,28,29]

Results and Discussion

1•$PdCl_2$ is formed by treating $(PhCN)_2PdCl_2$ with **1** in THF. The attempted reaction between **1**•$PdCl_2$ with NaN(H)Ns (Ns=*p*-$SO_2C_6H_4NO_2$) eventually led to intractable mixtures of products. Reasoning that the palladium–chloride bond is too kinetically inert for direct substitution with NaN(H)Ns, we treated **1**•$PdCl_2$ with 2

equivalents of AgOTf in CH_2Cl_2 which yields the more the more substitutionally labile **1**•$Pd(OTf)_2$. Treatment of **1**•$Pd(OTf)_2$ with NaN(H)Ns in $PhNO_2$ results in the formation of a cationic palladium sulfonamido complex, **2** (Scheme 1).

Scheme 1. Synthesis of **2**. Ar is –2,4,6-tris(trifluoromethyl)phenyl; Ar^2 is –4-nitrophenyl.



The X-ray structure reveals the presence of a chelating sulfonamido ligand, bound through the nitrogen and oxygen atoms to form a cationic complex (Figure 1), with the triflate anion fully dissociated from the Pd center. The 1,10-phenanthroline plane is bent by 15.97° out of the plane containing N and O in the sulfonamido ligand and Pd (Figure 1b). This bending likely relieves some steric crowding about the metal-center. A characteristic peak at δ 2.21 ppm in the ^1H NMR spectrum, integrating to a single hydrogen per complex, has been assigned as the N–H resonance. This peak disappears upon treatment with methanol-d_4. A sharp peak at –79.12 ppm in the ^{19}F NMR spectrum is consistent with the presence of unbound $[OTf]^-$ anion.

Monomeric palladium sulfonamido complexes have been previously reported in the literature. One notable example was reported by Osborn and coworkers.[30] Using terdentate supporting ligands, cationic palladium sulfonamido complexes were synthesized as possible precursors to neutral palladium sulfonimido complexes. However, attempts to deprotonate the sulfonamido ligand led to the formation of intractable mixtures of products.

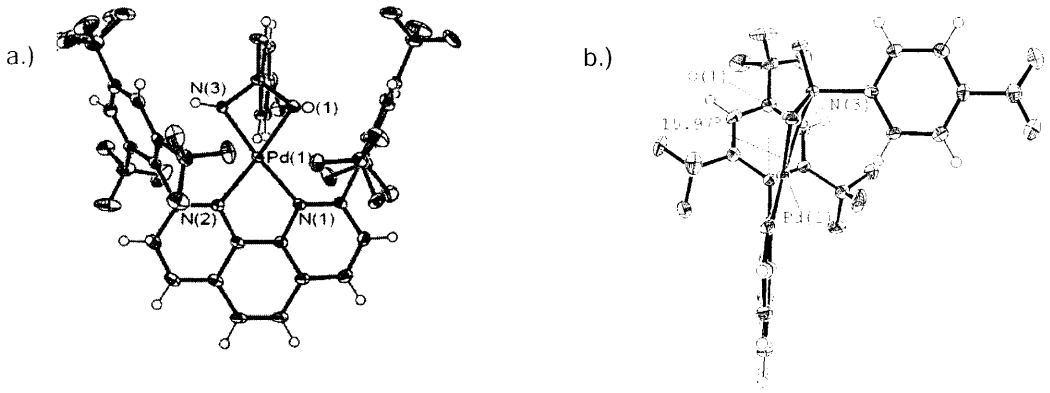
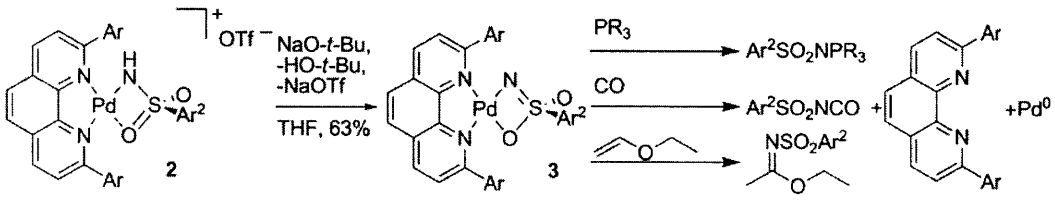


Figure 1. X-ray crystal structure, shown at 50% thermal ellipsoid representation, of **2**. OTf^- anions, solvent, and second molecule in unit cell omitted for clarity. **a)** Top view of molecule showing square planar structure. **b)** Side view of molecule showing slight bend of 2,9–diaryl–1,10–phenathroline ligand away from Pd(1), N(3), and O(1) plane. Front 2,4,6–tris(trifluoromethyl)phenyl ring removed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–(N1) 2.036(3), Pd(1)–(N2) 2.033(3), Pd(1)–N(3) 2.037(3), Pd(1)–O(1) 2.063(3), N(1)–Pd(1)–N(2) 81.74(12), N(3)–Pd(1)–O(1) 69.36(12).

In contrast to previous work with smaller supporting ligands, **2** reacts cleanly with NaO-*t*-Bu in THF to form the first example of a monomeric palladium sulfonimido complex, **3** (Scheme 2). Deprotonation is evident in the ^1H and ^{19}F NMR spectra, both of which indicate the complete consumption of **2** and the formation of a new product. The characteristic N–H peak in the ^1H NMR spectrum disappears, and the ^{19}F NMR spectrum of the purified complex shows no resonance for the OTf^- anion.

Scheme 2. Synthesis of **3**, and subsequent group-transfer to nucleophiles (PR_3), electrophiles (CO), and ethyl vinyl ether. R = –Me, –OMe, or –Ph.



Crystals suitable for X-ray diffraction were grown via diffusion of hexane into a saturated dichloromethane solution. The X-ray crystal structure of **3** revealed bidentate binding of the sulfonimido ligand to the metal center (Figure 2), similar to the binding of

the sulfonamido ligand in **2**.[31] Despite the use of analytically pure compound for crystallization, an impurity co-crystallized as indicated by residual electron density representing approximately 10% of the total electron density. Although the residual electron density is too small to refine accurately, the pattern is consistent with the presence of a monodentate sulfonamido ligand. It is possible that this slight impurity is a product of dichloromethane decomposition by **3**, forming **1**•PdCl(NHNs), and that this byproduct crystallizes preferentially. This decomposition occurs slowly, with only ~5% of a new product detected by ^{1}H NMR spectroscopy after 6 days in CD_2Cl_2 solution. Attempts to form X-ray quality crystals in other solvent systems were unsuccessful.

Although less basic than an aryl- or alkylamido ligand, the sulfonamido ligand of **2** acts as a reactive Brønsted base in protonolysis reactions. Both 2,4-pentanedione (pK_a = 13.3),[32b] and malononitrile (pK_a = 11.1)[32a] are deprotonated to form new palladium complexes plus $NsNH_2$ (Scheme 3). A possible mechanism of protonolysis is

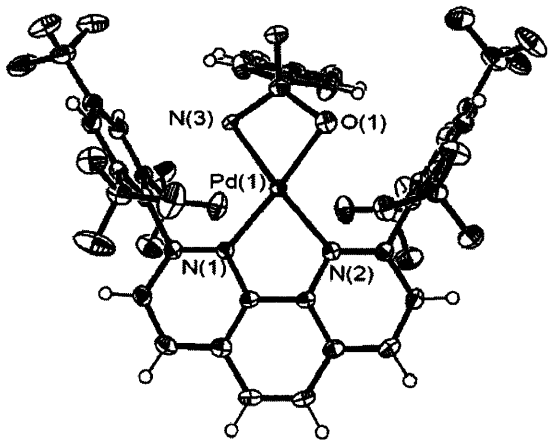
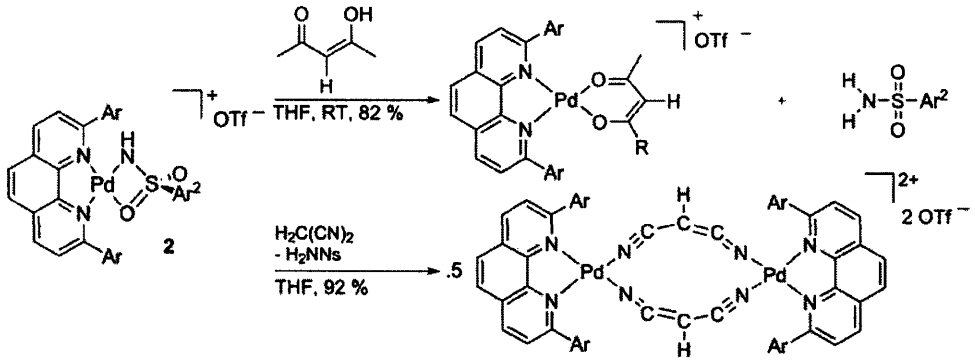


Figure 2. X-ray crystal structure, shown at 50% thermal ellipsoid representation, of **3**. Disorder and solvent removed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.070(3), Pd(1)–N(2) 2.071(3), Pd(1)–N(3) 2.040(2), Pd(1)–O(1) 2.036(3), N(1)–Pd(1)–N(2) 80.52(10), N(3)–Pd(1)–O(1) 72.64(10), N(1)–Pd(1)–O(1) 175.68(10).

Scheme 3: Reaction of **2** with 2,4-petanedione and malononitrile.



coordination of the substrate to the Lewis-acidic metal, with subsequent deprotonation by the sulfonamido ligand. Complex **2** also reacts with nitroalkanes (pK_a range=16.7–17.2),[32a] however the reaction is slow, and an intractable mixture of products is formed upon heating.

Complex **2** reacts with 2,4-pentanedione to form [**1**•Pd(2,4-pentanedionate)][OTf]. X-ray quality crystals of the 2,4-pentanedionate complex were grown by slow diffusion of hexanes into a saturated solution in dichloromethane. The solid-state structure reveals a 166.88° arch in the 1,10-phenanthroline ligand instead of the normal planar structure (Figure 3b). This distortion results in a C3–C8 distance in **1** of 6.829 Å, compared to the distance of 6.857 Å found for **1** in complexes **2** and **3**. The 1,10–phenanthroline plane is also bent out of the plane defined by Pd and the O atoms of pentanedionate by 36.12° (Figure 3c), likely reducing steric crowding.

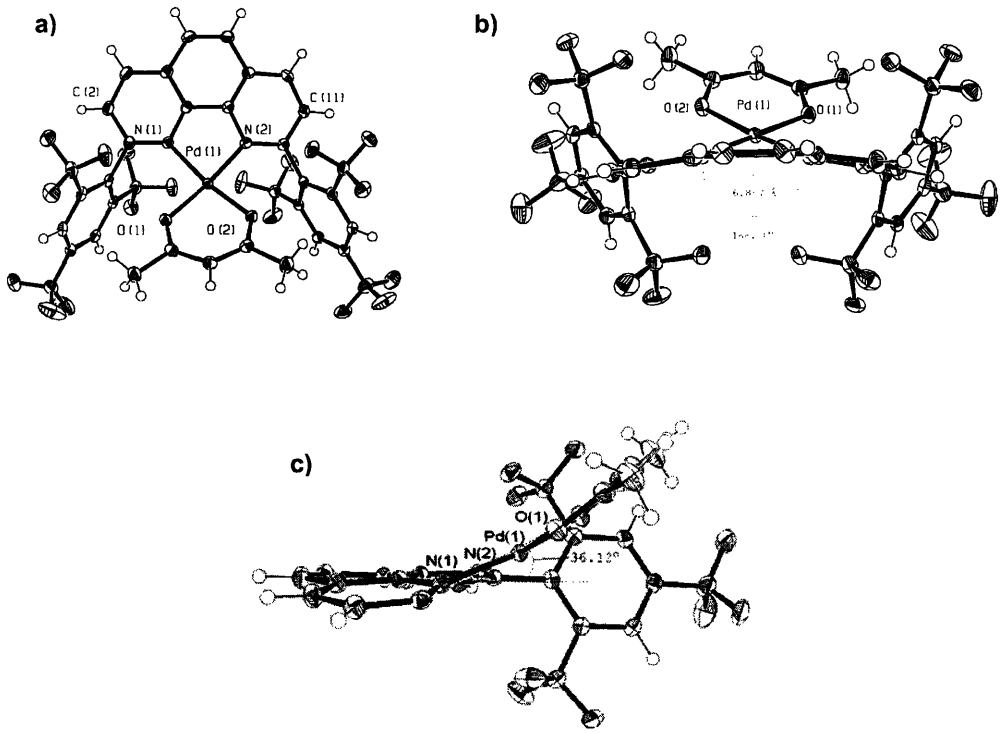


Figure 3. X-ray crystal structure, shown at 50% thermal ellipsoid representation, of **1**•Pd(pentanedionate)$^{+}$ OTf^{-} complex. OTf^{-} anion and solvent molecule omitted for clarity. **a)** Top view of molecule showing four-coordinate, square-planar structure. **b)** The phenanthroline portion of 1 arches due to steric constraints. **c)** The phenanthroline ligand plane bends out of the Pd(1), O(1) and O(2) plane to accommodate the steric constraints about metal. Front 2,4,6–tris(trifluoromethyl)aryl ring removed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.064(2), Pd(1)–N(2) 2.043(2), Pd(1)–O(1) 1.9807(18), Pd(1)–O(2) 1.9847(18), N(1)–Pd(1)–N(2) 81.74(8), O(1)–Pd(1)–O(2) 93.26(7), N(1)–Pd(1)–O(2) 169.03(8).

Complex **2** reacts with malononitrile in THF to form {[**1**•Pd(μ-NCCHCN)]$_2$}{2·OTf}. Single crystals of the $BAr^f_4{}^-$ [Ar^f = 3,5-bis(trifluoromethyl)phenyl] salt of this complex were grown by slow diffusion of pentane into a saturated THF/diethyl ether solution. The two Pd centers are linked by two dicyanomethide bridges to form a twelve-membered ring. Despite the five-atom bridge, steric interactions cause the two 1,10–phenanthroline planes to shift away from one another. The two nearly parallel plains are separated by 3.165 Å at the mid-point between the Pd atoms.

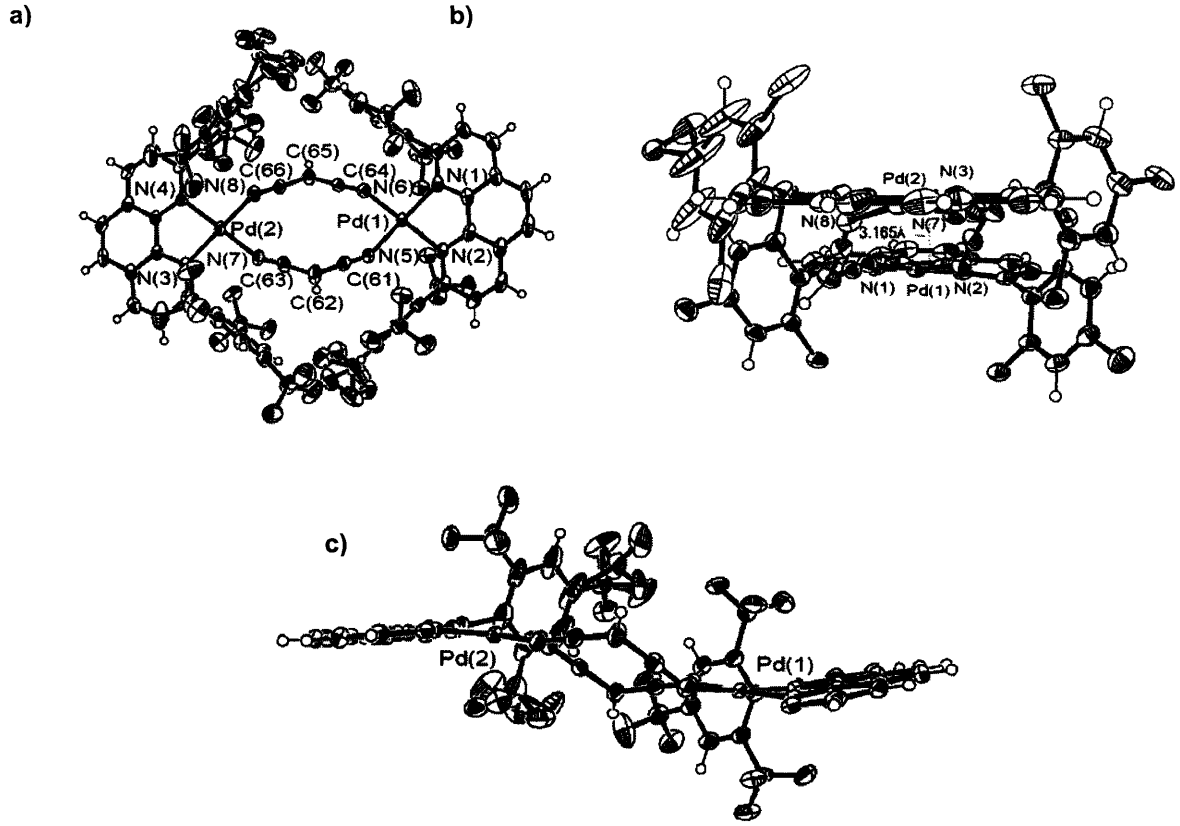


Figure 4. X-ray crystal structure, shown at 50% thermal ellipsoid representation, of $[(\mathbf{1}\bullet\text{Pd-NCCHCN-})_2]^{2+}$ 2 $BAr^f{}_4^-$ [Ar^f is 3,5-(trifluoromethyl)phenyl], solvent molecules and $BAr^f{}_4^-$ anions omitted for clarity. **a)** Top view of molecule. **b)** Back view of molecule demonstrating the shift of the two phenanthroline planes, F atoms removed for clarity. **c)** Side view of molecule, two forward facing 2,4,6-tris(trifluoromethyl)phenyl rings removed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.049(4), Pd(1)–N(2) 2.043(4), Pd(1)–N(5) 1.982(4), Pd(1)–N(6) 1.983(4), Pd(2)–N(3) 2.045(4), Pd(2)–N(4) 2.041(4), Pd(2)–N(7) 1.980(4), Pd(2)–N(8) 1.986(4), N(5)–C(61) 1.159(6), C(61)–C(62) 1.376(7), C(62)–C(63) 1.386(7), C(63)–N(7) 1.154(6), N(1)–Pd(1)–N(2) 82.07(17), N(3)–Pd(2)–N(4) 82.64(16), N(5)–Pd(1)–N(6) 84.58(17), N(7)–Pd(2)–N(8) 84.19(17), C(61)–C(62)–C(63) 120.1(5), C(64)–C(65)–C(66) 121.1(5).

Complex **3** transfers the sulfonylnitrene group to suitable substrates (Scheme 2), although arenes have not been observed to react. For example, phosphines (PR_3: R = –Me, –OMe, –Ph) are rapidly converted to iminophosphoranes ($NsN{=}PR_3$). The presumed byproduct, $\mathbf{1}\bullet Pd^0$, decomposes to form free **1**, with precipitation of metallic Pd. Similar instability has been observed for other (phenanthroline)palladium(0) complexes.[33] When R is –Me or –OMe, the reaction is nearly instantaneous. When R is –Ph, the reaction is complete after 2 h. The slow reaction with PPh_3 is likely due to

steric congestion about the metal center. Complex **3** also reacts rapidly with carbon monoxide to give NsNCO, **1**, and Pd^0 (Scheme 2). Complex **2** displays similar reactivity toward carbon monoxide, forming NsNCO, **1**•HOTf, and Pd.[34]

Finally, the reactivity of **3** with olefin substrates was investigated. The electron-poor maleic anhydride reacts to form a complex mixture of products, some of which were indicative of nucleophilic additions. Relatively electron-neutral olefins such as styrene and ethylene underwent no discernible reaction. The electron-rich ethyl vinyl ether reacts with **3** upon mild heating to form an imidate product (Scheme 2) in 43% yield.[34,35]

Conclusion

A cationic sulfonamido palladium complex and the first monomeric sulfonimido palladium complex were synthesized. The cationic sulfonamido complex is the precursor to several new palladium complexes formed through protonolysis by acidic substrates. The monomeric sulfonimido palladium complex transfers a sulfonylnitrene group to both nucleophiles and electrophiles. Nitrene transfer to ethyl vinyl ether results in the formation of a C=N double bond.

Experimental

General Considerations. Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA, or Desert Analytics, Tucson, AZ. Anhydrous dichloromethane, tetrahydrofuran, hexanes, and diethyl ether were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for diethyl ether and tetrahydrofuran) or through neutral alumina and copper(II) oxide (for hexanes).

3 Å molecular sieves were activated by heating in a 190 °C oven for several days. Nitrobenzene (Aldrich) was dried over P_2O_5, distilled prior to use, and stored over 3 Å molecular sieves. IR spectra were recorded on a Nicolet Impact 410 spectrometer as KBr pellets. NMR solvents were dried as follows: methylene chloride-d_2 (Cambridge Isotope Laboratories) over calcium hydride, acetone-d_6 (Cambridge Isotope Laboratories) over calcium sulfate, nitrobenzene-d_5 over P_2O_5. All NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ^{1}H NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. ^{19}F NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm). ^{13}C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak. The starting material malononitrile (Aldrich) was dried over P_2O_5 (at 50 °C) and vacuum-distilled prior to use. The starting material sodium 4-nitrobenzenesulfonamide was synthesized by treatment of nitrobenzenesulfonamide with sodium methoxide in methanol. The starting materials bis(benzonitrile)palladium(II) chloride (Strem), silver hexafluoroantimonate (Strem), sodium *tert*-butoxide (Aldrich) and 2,4-pentanedione (Aldrich) were used as received.

{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}palladium(II) chloride, 1•$PdCl_2$

Bis(benzonitrile)palladium(II) chloride (0.464 g, 1.21 mmol), **1** (0.896 g, 1.21 mmol) and THF (10 mL) were added to a oven-dried vial equipped with a Teflon-coated magnetic stir bar in the box. The orange solution was allowed to stir for 13 h. After 2 h, an orange precipitate formed. The solution was concentrated *in vacuo*. The residual orange solid was transferred to a fritted funnel, washed with a mixture of diethyl ether and hexanes (190 mL, 1:17 mixture), then with pure hexanes (2 x 15 mL), and dried *in vacuo* to afford the title complex (0.979 g, 88% yield). ^{1}H NMR (300 MHz, methylene

chloride-d_2): δ 9.19 (d, J = 8.4 Hz, 2 H), 8.54 (s, 2 H), 8.40 (s, 4 H), 8.16 (d, J = 8.4 Hz, 2 H). ^{19}F NMR (300 MHz, CD_2Cl_2): δ –57.18 (s, 12 F), –63.66 (s, 6F). Anal. calcd for $C_{30}H_{10}N_2F_{18}Cl_2Pd$: C, 39.26; H, 1.10; N, 3.05. Found: C, 39.29; H, 0.99; N, 2.97.

{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}palladium (II) 2–nitrobenzenesulfonylamido trifluoromethanesulfonate, 2

1•$PdCl_2$ (0.200 g, 0.218 mmol) and silver trifluoromethanesulfonate (0.122 g, 0.475 mmol) were added in the dark to an oven-dried vial in the dry box. Dichloromethane (4 mL) was added to the vial. The resulting suspension was allowed to stir for 22 h, and then filtered in the dark. The collected solid was washed with dichloromethane (3 x 1 mL), then dissolved in nitrobenzene (4 mL) and filtered through a dry Celite plug. The plug was the extracted with nitrobenzene (2 x 1 mL) and the nitrobenzene solutions were combined. The yield of **1**•$Pd(OTf)_2$ (0.168 mmol, 77%) was determined by ^{19}F NMR using a hexafluorobenzene internal standard. Sodium 4-nitrobenzenesulfonamide (0.043g, 0.19 mmol) was added and the solution was allowed to stir. After 14 h, the reaction was judged complete by ^{19}F NMR spectroscopy. Dichloromethane (6 mL) was added to further precipitate sodium trifluoromethanesulfonate, and the solution was filtered. The filtrate was washed with dichloromethane (3 x 1 mL). Diethyl ether (40 mL) was added. The resulting solution was layered with hexanes (70 mL). After 6 h, an orange microcrystalline solid was formed. The solid was collected by filtration, washed with diethyl ether (3 x 2 mL) and hexanes (10 x 2 mL), then dried in vacuo . The product was obtained as an orange solid (0.139 g, 69% for this step, 53% from **1**·$PdCl_2$). ^{1}H NMR (300.1 MHz, nitrobenzene-d_5): 9.04 (d, J = 8.5 Hz, 1 H), 9.02 (d, J = 8.3 Hz, 1 H), 8.34 (s, 2 H), 8.31 (s, 2 H), 8.10 (d, J = 8.1 Hz, 2 H), 8.08 (d, J = 8.1 Hz, 2 H), 8.03 (s, 2 H), 7.88 (d, J = 8.0 Hz, 2 H), 2.21 (s, 1 H). ^{19}F NMR (300 MHz, THF-d_8): δ –57.56 (s, 6 F), –57.88 (s, 6 F), –63.73 (s, 3 F), –

64.00 (s, 3 F), –79.12 (s, 3 F). IR (KBr, cm^{-1}): 1540, 1302, 1291, 1214, 1143, 1032, 920, 846, 738, 686, 639. Anal. calcd For $C_{37}H_{15}N_4O_7F_{21}S_2Pd$: C, 37.12; H, 1.26; N, 4.68. Found: C, 36.97; H, 1.12; N, 4.35.

{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}palladium (II) 2–nitrobenzenesulfonylimido, 3

2 (0.200 g, 0.167 mmol) and sodium *tert*-butoxide (0.019 g, 0.20 mmol) were added to an oven-dried vial in a dry box. THF (6 mL) and the reaction mixture was shaken for 5 minutes. Diethyl ether (10 mL) was added and the solution was layered with hexanes (24 mL). The precipitate was collected by filtration, washed with hexanes (2 x 2 mL) and dissolved in dichloromethane (10 mL). The solution was filtered though a dry Celite plug, and layered with hexanes (30 mL). Yellow needles formed, and were collected via filtration. The needles were washed with hexanes (3 x 2 mL) and dried *in vacuo* (0.156 g, 90%). ^1H (300 MHz, methylene chloride-d_2): δ 8.71 (d, J = 8.3 Hz, 2 H), 8.29 (s, H), 8.24 (s, H), 8.20 (s, H), 8.10 (d, J = 8.8 Hz, 2 H), 7.95 (s, H), 7.93 (s, H), 7.88 (d, 9.9 Hz, H), 7.85 (d, 8.8 Hz, H), 7.62 (d, 8.5 Hz, H) ^{19}F NMR (300 MHz, methylene chloride-d_2): δ –59.99 (s, 3 F), –60.06 (s, 3 F), –60.23 (s, 6 F), –65.72 (s, 3 F), –65.86 (s, 3 F). ^{13}C (125 MHz, $CDCl_3$): δ 152.4, 151.0, 149.3, 139.8, 133.8, 132.9, 132.7, 129–126 (overlapping quartets), 124.3, 121.6 (q, J = 280 Hz), 123.7 (q, J = 278 Hz), 122.7, 122.2, 118.0. IR (KBr, cm^{-1}): 1529, 1351, 1289, 1211, 1140, 1089, 914, 802, 686. Anal. calcd for $C_{36}H_{14}F_{18}N_4O_4SPd$: C, 41.30; H, 1.35; N, 5.35. Found: C, 40.83; H, 1.54; N, 4.85.

{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}palladium (II) 2,4–pentanedionate trifluoromethanesulfonate

2 (0.050 g, 0.042 mmol) and 2,4-pentanedione (0.250 mL, 2.43 mmol) were added to a oven-dried vial in a dry box. THF (5 mL) was added and the reaction mixture was stirred for 12 h. The solvent was removed *in vacuo*, and the yellow solid was

washed with hexanes. The solid was further dried *in vacuo* (0.030 g, 76%). ^{1}H NMR (300 MHz, methylene chloride-d_2): δ 8.98 (d, J = 8.3 Hz, 2 H), 8.43 (s, 2 H), 8.37 (s, 4 H), 7.78 (d, J = 8.53 Hz, 2 H), 1.12 (s, 6 H). ^{19}F NMR (300 MHz, methylene chloride-d_2): δ –57.16 (s, 12 F), –63.74 (s, 6 F), –79.13 (s, 3 F). ^{13}C NMR (125 MHz, acetone-d_6): δ 185.8, 164.4, 156.0, 148.0, 141.6, 137.4, 133.7, 133.57 (q, J = 37.2 Hz), 132.4 (q, J = 33.4 Hz), 132.2, 130.9, 130.2, 128.1, 122.9 (q, J = 275.9 Hz), 119.1 (q, J = 164 Hz), 23.8. Attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.

Bis{2,9-bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline palladium (II)-μ-dicyanomethene} [BAr$^{f}_{4}$]$_2$

2 (0.200 g, 0.167 mmol) and malononitrile (0.025 mg, 0.379 mmol) were added to an oven-dried vial in a dry box. THF (8 mL) was added and the solution was allowed to sit for 10 h. An orange-red precipitate formed and was collected by filtration. The orange solid was washed with THF (3 x 2 mL) and dried *in vacuo* to yield [**1**•Pd(μ-NCCHCN)]$_2$[OTf]$_2$ (0.122 g, 0.115 mmol, 69 %). [**1**•Pd(μ-NCCHCN)]$_2$[OTf]$_2$ (0.100 g, 0.0943 mmol) and NaBAr$^{f}_{4}$ were added to an oven-dried vial in the box. Dichloromethane (10 mL) was added and the suspension was stirred for 10 h. Nitrobenzene (2 mL) was added and the suspension was filtered through a dry Celite plug. The solvent was removed *in vacuo* at 40 °C. The solid was washed with hexanes and further dried *in vacuo* (0.120 g, 72 %) ^{1}H NMR (300 MHz, methylene chloride-d_2): δ 8.89 (d, J = 12.1 Hz, 2 H), 8.34 (s, 4 H), 8.26 (s, 2 H), 7.85 (d, J = 9.0 Hz, 2 H), 7.69 (m, 8 H), 7.52 (m, 4 H), 1.95 (s, 1 H). ^{13}C NMR (128 MHz, $CDCl_3$): δ 157.4 (q, J = 51 Hz), 156.8, 151.9, 143.7, 138.0, 130.2, 129.1 (q, J = 91 Hz), 127.8, 127.5 (q, J = 25 Hz), 124.6 (q, J = 32 Hz), 124.1 (q, J = 256 Hz), 124.1 (q, J = 246 Hz), 123.1, 121.2, 119.0, 116.8, 112.7, 10.2. IR (KBr, cm^{-1}): 2227, 2114, 1356, 1285, 1217, 1124, 919, 839, 683.

Attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.

Group Transfer to Carbon Monoxide

An oven dried J. Young NMR tube was charged with **2** (0.025 g, 0.021 mmol). Methylene chloride-d_2 (1 mL) was added and the tube was cooled to –78 °C, evacuated, and then warmed to RT. An atmosphere of carbon monoxide was admitted and a black precipitate formed. Yield of OCNNs was determined by ^{1}H NMR (48%). A full equivalent of **1**·HOTf is present which was identified by ^{1}H NMR (shifts in ^{1}H and ^{19}F NMR spectra are identical to shifts in NMR spectra of a solution of **1** and HOTf in methylene chloride-d_2).

A similar procedure was followed for group transfer to carbon monoxide by **3**, except a full equivalent of **1** is formed instead of **1**·HOTf.

Oxidation of PR_3 (R = -Me, -OMe, -Ph)

General procedure: An oven dried J. Young NMR tube was charged with **3** and PR_3 (1 equivalent). THF (1 mL) was added causing the rapid formation of a black precipitate. Yield (>73%) of $NsNPR_3$ was based on ^{31}P NMR using $OPPh_3$ as an internal standard. Identification of $NsNPR_3$ was based on independent synthesis by treatment of NsN_3 with PR_3 in THF.

Group transfer to ethyl vinyl ether

A flame-dried Schlenk tube was charged with **3** (0.100 g, 0.0955 mmol), ethyl vinyl ether (0.091 mL, 0.950 mmol) and THF (6 mL). The tube was sealed and heated at 40 °C for 13 h. Yield was determined by ^{1}H NMR compared to a hexamethylbenzene internal standard (43 %).

Independent synthesis of ethyl *N*-(4-nitrophenyl)sulfonylacetimidate

The title compound was synthesized by a modification to a previously published procedure.[36] ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.37 (d, J = 9.1 Hz, 2 H), 8.14 (d, J = 8.8

Hz, 2), 4.12 (q, J = 7.2 Hz, 2), 2.56 (s, 3), 1.31 (t, J = 7.2 Hz, 3 H). ^{13}C (125 MHz, DMSO-d_6): δ 176.8, 151.5, 148.4, 129.6, 126.3, 67.0, 22.4, 15.1. Anal. calcd for $C_{10}H_{12}N_2O_5S$: C, 44.11; H, 4.44; N, 10.29. Found: C, 44.37; H, 4.27; N, 10.16.

X-Ray Crystallography

General considerations. Crystals of **2, 3,** [**1**·Pd(2,4-pentanedionate)][OTf], and [**1**•Pd(μ-NCCHCN)]$_2$[BAr$^f_4$]$_2$ were transferred onto a microscope slide from a scintillation vial and coated with STP. A crystal was selected, mounted on a glass fiber, and optically centered. The data were collected on a Siemens platform goniometer with a CCD detector. The structures were solved by direct methods in conjunction with standard difference Fourier techniques (SHELXTL v5.1, Sheldrick, G. M. and Siemens Industrial Automation, 1997). Non-hydrogen atoms were treated anisotropically, and hydrogen atoms were placed in calculated positions ($d_{C\text{-}H}$ = 0.96 Å).

{2,9-Bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}palladium (II) 2-nitrobenzenesulfonylamido trifluoromethanesulfonate, 2:

Single crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of **2** (0.010 g) in CH_2Cl_2 (0.7 mL). One molecule of CH_2Cl_2 co-crystallized per two molecules of **2**.

{2,9-Bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}palladium (II) 2-nitrobenzenesulfonylimido, 3:

Single crystals suitable for X-ray diffraction were grown by slow diffusion of hexanes into a solution of **3** into a mixture of dichloromethane (0.5 mL) and THF (0.1 mL). One molecule of **3** and one THF molecule were found in the asymmetric unit. Three fluorine atoms of **3** were modeled over two positions. The THF molecule was modeled over two positions. Significant residual electron density was found at one positions (in e/A^3): 1.08 near S2.

{2,9-Bis[2',4',6'-tris(trifluoromethyl)phenyl]-1,10-phenanthroline}palladium (II) 2,4-pentanedionate Trifluoromethanesulfonate, [1·Pd(2,4-pentanedionate)][OTf]:

Crystals suitable for X-ray diffraction were formed by diffusion of hexane into a solution of [**1**·Pd(2,4-pentanedionate)][OTf] (0.010 g) in dichloromethane (0.3 mL). One molecule of dichloromethane and [**1**·Pd(2,4-pentanedionate)][OTf] were found in the asymmetric unit. Three fluorine atoms of [**1**·Pd(2,4-pentanedionate)] were modeled over two sites.

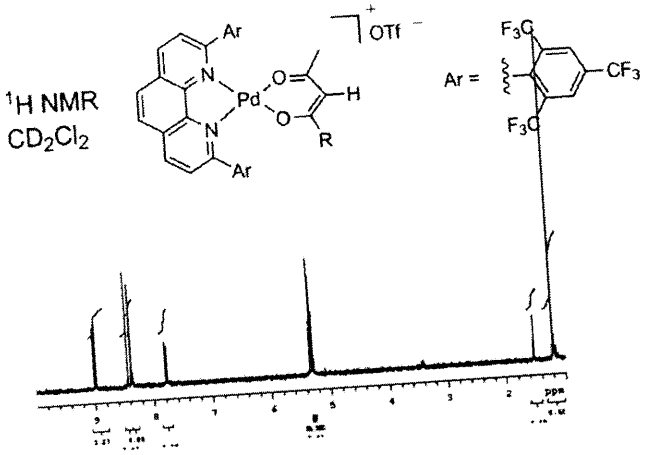
Bis{2,9–bis[2',4',6'–tris(trifluoromethyl)phenyl]–1,10–phenanthroline palladium (II)-μ-dicyanomethene}, [2·BAr$^f_4$], [1•Pd(μ-NCCHCN)]$_2$[BAr$^f_4$]$_2$:

Crystals suitable for X-ray diffraction were formed by slow diffusion of pentane into a solution of [**1**•Pd(μ-NCCHCN)]$_2$[BAr$^f_4$]$_2$ (0.030 g) in THF (0.3 mL) and diethyl ether (0.3 mL). [**1**•Pd(μ-NCCHCN)]$_2$[BAr$^f_4$]$_2$ and six molecules of THF cocrystallized. The THF molecules were significantly disordered and had to be modeled over two sites each. Fifteen fluorine atoms {nine on [**1**•Pd(μ-NCCHCN)]$_2^{2+}$ and six on (BAr$^f_4$)$^-$} were modeled over two sites each.

Table 1. Crystallographic data for **2, 3,** [**1**·Pd(2,4-pentanedionate)][OTf], [(**1**•Pd-NCCHCN-)$_2$][2·BAr$^f_4$].

	2	**3**	[**1**·Pd(2,4-pentanedionate)][OTf]	[(**1**•Pd-NCCHCN-)$_2$][2·BAr$^f_4$]
Empirical formula	$C_{38}H_{17}Cl_2F_{21}N_4O_7PdS_2$	$C_{40}H_{22}F_{18}N_4O_5PdS$	$C_{37}H_{19}Cl_2F_{21}N_2O_5PdS$	$C_{65}H_{23}BF_{42}N_4OPd$
FW	1281.98	1119.08	1179.90	1791.08
T, K	100(2)	100(2)	100(2)	100(2)
Crystal syst,	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	P2(1)/c	P-1	P2(1)/n
a, Å	9.2691(3)	14.5054(12)	12.063(3)	23.9887(10)
b, Å	21.0428(7)	12.9044(9)	13.551(4	23.1763(10)
c, Å	23.2599(9)	21.9900(16)	15.295(5)	30.6052(14)
α, deg	87.6770(10	90	114.285(8)	90
β, deg	84.7490(10)	96.232(3)	96.005(9)	105.9440(10)
λ,deg	77.5160(10)	90	109.796(8	90
V, Å^3	4409.9(3)	4091.8(5)	2055.9(11)	16361.0(12)
ρ, g/cm^{-1}	1.931	1.817	1.906	0.727
Z	4	4	2	4
μ, mm^{-1}	0.781	1.817	0.775	0.181
F(000)	2520	2216	1160	3512
Cryst size, mm^3	0.05 x 0.05 x 0.02	0.05 x 0.05 x 0.05	0.10 x 0.10 x 0.10	0.15 x 0.15 x 0.15
θ-range, deg	0.88–29.57	1.86–29.13	1.73–25.68	0.96–24.71
Total no. of reflns	93781	74507	34774	260799
GOF on F^2	1.122	1.067	1.049	1.021
Final *R* indices [I>2σ(I)]	0.0555	0.0468	0.0329	0.0604
	0.1181	0.1114	0.0788	0.1549
R indices (all data)	0.0812	0.0679	0.0404	0.0940
	0.1271	0.1205	0.0830	0.1849

NMR Data: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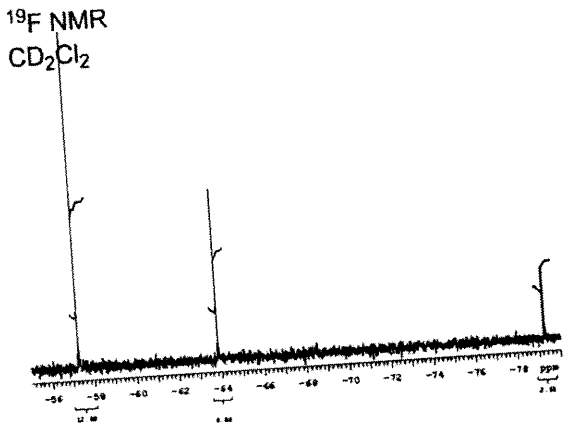
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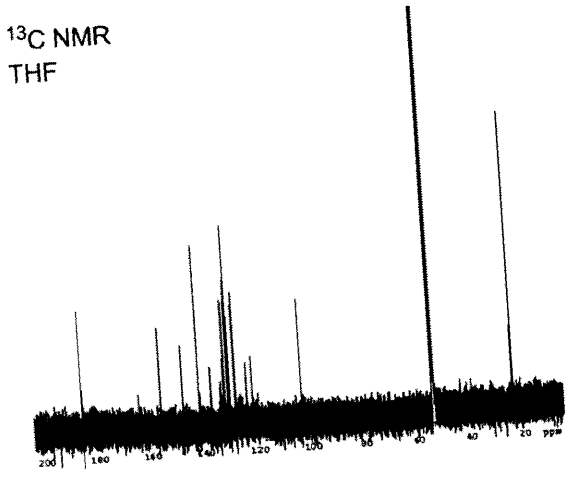
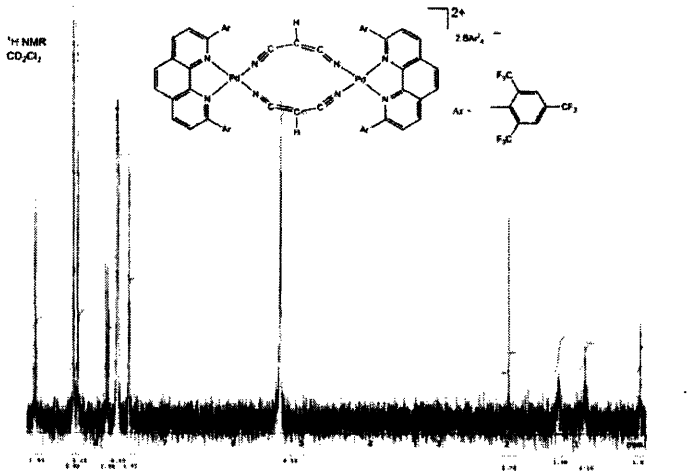
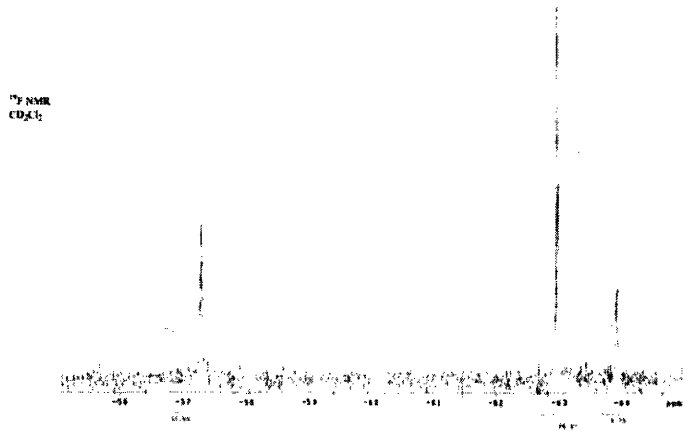
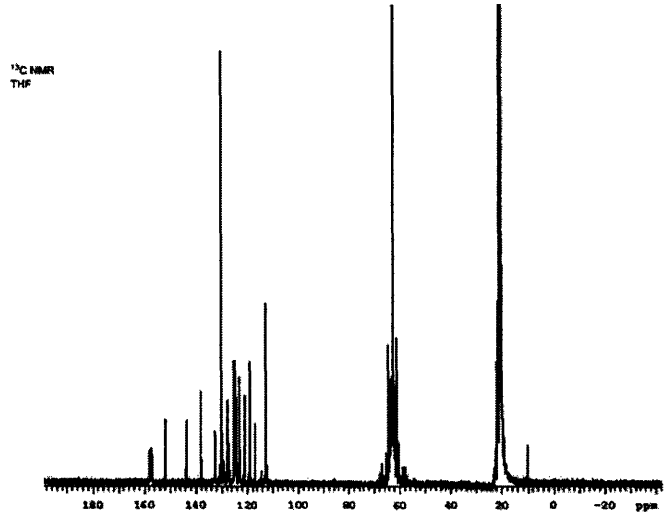

^{13}C NMR
THF






180
160
140
120
100
80
60
40
20
0
-20
ppm

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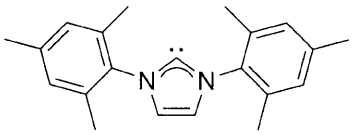
Chapter 3: Study of the reversible orthometallation of Rh(I) complexes containing N-heterocyclic carbene ligands: Synthesis of a Rh(III) peroxide complex

Introduction

In the previous chapter, we described the synthesis of the first mononuclear sulfonimido complex of palladium, [**1**·PdNNs] {**1** = 2,9-bis[2',4',6'-tris(trifluoromethylphenyl)]-1,10-phenanthroline, Ns = *p*-nitrobenzenesulfonyl}. A X-ray diffraction study revealed that in the solid state, the sulfonimido ligand binds as a κ^2-N,O chelate instead of forming a terminal imido complex. Despite the added stability of the sulfonimido chelate, [**1**·PdNNs] rapidly undergoes group transfer to both electrophilic and nucleophilic substrates.

Encouraged by this success, we attempted the synthesis of late transition metal complexes with other divalent heteroatom-based ligands, such as a terminal oxo moiety. Terminal oxo complexes of late metals are rare. Thus far, the only published examples of terminal oxo complexes with more than six d-electrons are a rhenium(I) oxo complex described by Mayer and Cundari[1] and platinum(IV) and palladium(IV) oxo complexes reported by Neiwert and Hill.[2] We found that attempts to synthesize metal-oxo precursors containing **1** (such as metal-hydroxide complexes or metal-siloxide complexes) instead led to deligation and metal precipitation.

Figure 1. The structure of IMes



IMes

To circumvent the dissociation of the supporting ligand, we explored the use of N-heterocylic carbene (NHC) ligands in place of substituted 1,10-phenenanthroline ligands. Because NHC ligands display a low tendency toward dissociation,[3,5a] we hoped to use two untethered NHCs rather than a chelate. This strategy could confer benefits beyond synthetic simplicity. Untethered ligands are flexible and more accommodating of

steric congestion about the metal center. Also, untethered ligands can accommodate various bite angles of ligand binding. Sharp and coworkers have demonstrated that bite angle can have a dramatic effect on stability and reactivity of metal(imido) and metal(oxo) complexes.[4] N-Heterocyclic carbene ligands are also strong σ-donors.[5] Strong σ-donation into d-orbitals of π-symmetry can greatly stabilize metal-ligand multiple bonds.[6] Finally, NHC supporting ligands stabilize very polar bonds. For instance, the synthesis of the first isolable Au(I) fluoride complex used an NHC-supporting ligand.[7] Natural bond order calculations of a model complex suggest a large ionic component to the Au–F bond, with a charge of –0.77 on fluorine. The NHC ligand, in contrast to phosphines, stabilizes the otherwise-destabilizing pπ/dπ-interaction.

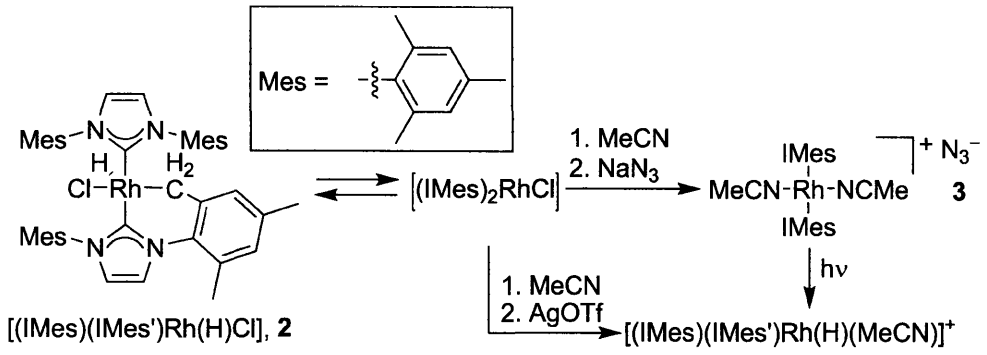
A rhodium(I) complex containing NHC supporting ligands could be a synthetic entryway to a rhodium(III) oxo complex. Nolan and coworkers reported that the attempted preparation of a rhodium(I) compound of IMes (Figure 1) instead led to the formation of the rhodium(III) hydride complex, (IMes)(IMes')Rh(H)Cl (**2**, Scheme 1),[8] formed through the oxidative addition of a benzylic C–H bond of IMes. They also found that addition of carbon monoxide to **2** induced reductive elimination to form $(IMes)_2Rh(CO)Cl$. We were inspired by this result to further investigate the factors that control the reversible cyclometallation of (IMes)rhodium compounds, and to explore its relevance to the pursuit of rhodium oxo complexes.

Results and Discussion

Upon treatment with acetonitrile, **2** rapidly undergoes reductive elimination to form an acetonitrile adduct of a rhodium(I) complex, $(IMes)_2Rh(NCMe)Cl$. Displacement of chloride by the azide ion would afford a rhodium(I) azide complex, potentially the precursor to a rhodium(III) nitride complex. Unfortunately, treatment of $(IMes)_2Rh(NCMe)Cl$ with sodium azide in acetonitrile solution resulted in the formation of

the ionic complex, $[(IMes)_2Rh(NCMe)_2][N_3]$ (**3**) instead. A study by X-ray diffraction revealed *trans*-orientation of IMes ligands about the planar rhodium center (Figure 2), and the presence of an unbound azide anion. In the ^1H NMR spectrum of **3**, the peak resonances of the bound acetonitrile are significantly shifted from that of free acetonitrile. In the absence of light, the bound acetonitrile molecules do not exchange with acetonitrile-d_3 after 20 h.

Scheme 1. The synthesis of a cationic azide complex (**3**).



A ^1H NMR spectrum of **3** after exposure to UV light contained multiple-ligand resonances and a doublet at δ –18.62 ppm, both consistent with $[(IMes)(IMes')Rh(H)(NCMe)]^+$ formation (Scheme 1).[9] An identical product is formed when **2** is treated with silver trifluoromethanesulfonate (AgOTf) in acetonitrile. It appears that the cationic rhodium(I) complex containing IMes supporting ligands can be kinetically stabilized by coordination of acetonitrile ligands, but is thermodynamically unstable to oxidative addition of a benzylic C–H bond of IMes to form an orthometallated rhodium(III) hydride complex.

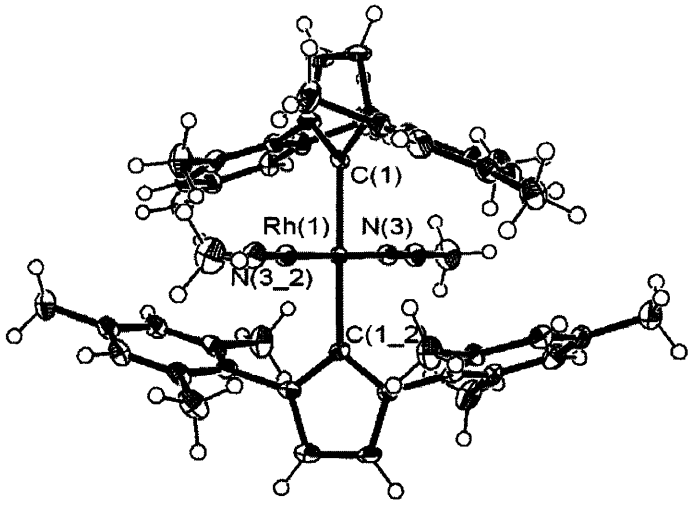


Figure 2. Representation of $[(IMes)_2Rh(NCMe)_2][N_3]$, shown as 50% ellipsoids. The $(N_3)^-$ ion has been omitted for clarity. Selected interatomic distances (Å) and bond angles (°): Rh–N(3) 1.9770(15), Rh–C(1) 2.0406(16), C(1)–Rh–N(3) 89.68(7).

Encouraged by the ease which **2** undergoes reductive elimination, we investigated the chemistry of **2** in less coordinating solvents. In particular, we wondered whether the rhodium(III) hydride complex **2** would serve as the synthetic equivalent of its rhodium(I) isomer, $(IMes)_2RhCl$.[10] Indeed, treatment of **2** with dioxygen in benzene led to slow formation of a light blue complex, $(IMes)_2Rh(O_2)Cl$ (Scheme 2). Presumably, this complex is a result of reductive elimination of **2**, followed by reaction of the resulting rhodium(I) center with dioxygen. The X-ray crystal structure of the product contains some disorder; however, general connectivity can be identified (Figure 3). The coordination geometry about rhodium is roughly trigonal bipyramidal with IMes ligands in the axial positions.

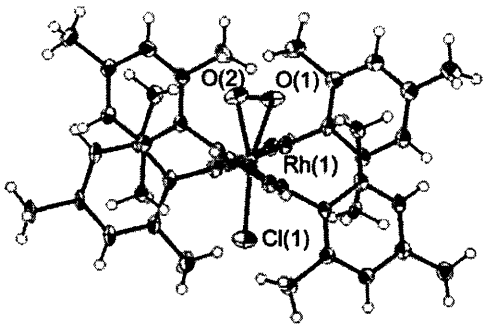
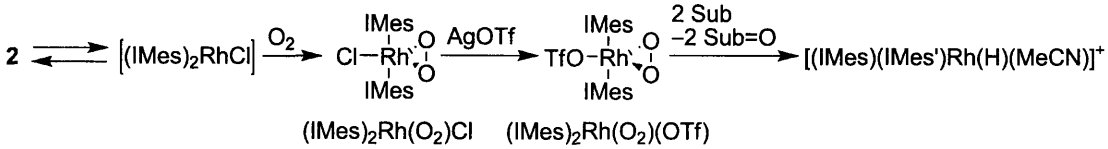


Figure 3. Representation of $(IMes)_2Rh(O_2)Cl$, shown as 50% ellipsoids. Significant disorder has precluded accurate identification of bond lengths and angles. Structure shows general connectivity.

We next attempted the removal of an oxygen atom from the peroxide complex to form an oxo complex. We found that the reaction of $(IMes)_2Rh(O_2)Cl$ with monooxygen acceptors proceeded sluggishly. For instance, treatment of $(IMes)_2Rh(O_2)Cl$ with $P(OMe)_3$ resulted in no reaction, even at 60 °C for 2 days. We reasoned that a cationic peroxide complex of rhodium would be more capable of monooxygen transfer. Indeed, treatment of $(IMes)_2Rh(O_2)Cl$ with AgOTf resulted in a complex that oxidizes $P(OMe)_3$ to $OP(OMe)_3$ at elevated temperatures (60 °C). When $(IMes)_2Rh(O_2)(OTf)$ was treated with a single equivalent of $P(OMe)_3$ in acetonitrile, a 1:1 mixture of $(IMes)_2Rh(O_2)(OTf)$ and [(IMes)(IMes')Rh(H)(NCMe)][OTf] resulted. Presumably, the transiently formed $(IMes)_2Rh(O)(OTf)$ was deoxygenated more rapidly than $(IMes)_2Rh(O_2)(OTf)$.

Scheme 2. Complex **2** as a synthetic equivalent to a (IMes)Rh(I) complex. Synthesis of peroxide complexes. Sub is $P(OMe)_3$ and *trans*-stilbene; Sub=O is $OP(OMe)_3$ and *trans*-stilbene oxide.



In lieu of formation a terminal oxo complex of rhodium(III), we investigated oxygen-transfer from the cationic peroxide complex. Treatment of $(IMes)_2Rh(O_2)(OTf)$ with an excess of *trans*-stilbene results in formation of 1.5 equivalents of *trans*-stilbene oxide after 24 h at 60 °C.[11,12] In the absence of air, [(IMes)(IMes')Rh(H)(NCMe)][OTf]

forms after oxygen transfer; however, in the presence of air, $(IMes)_2Rh(O_2)(OTf)$ is regenerated after oxygen transfer (as judged by ^1H NMR). The development of a practical system must await the exploration of other ligands and reactions conditions. However, the fundamental steps of oxygen activation and oxygen transfer have been demonstrated, and the regeneration of $(IMes)_2Rh(O_2)(OTf)$ through oxygen atom transfer suggest that catalysis should be possible.

Conclusions

We have investigated the reaction chemistry of reversibly cyclometallated (IMes)rhodium complexes. Treatment of a rhodium(I)-chloride complex with sodium azide in acetonitrile led to the formation of a bis(acetonitrile) rhodium(I) azide complex. Upon exposure to UV light, a cationic orthometalated rhodium(III) hydride complex formed. Also, a neutral orthometalated rhodium(III) hydride complex reacted with dioxygen to form a neutral rhodium(III) peroxide complex. The neutral rhodium(III) peroxide complex had a low propensity for monooxygen transfer, however a cationic rhodium(III)-peroxide complex oxidized $P(OMe)_3$ to form $OP(OMe)_3$ and *trans*-stilbene to form *trans*-stilbene oxide.

Experimental:

General Considerations. Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA, or Desert Analytics, Tucson, AZ. Anhydrous hexanes and diethyl ether were purchased from Aldrich in 18-L Pure-Pac^{TM} solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for diethyl ether) or through neutral

alumina and copper(II) oxide (for hexanes). 3 Å molecular sieves were activated by heating in a 190 °C oven for several days. Acetonitrile (Aldrich), α,α,α-trifluorotoluene ($PhCF_3$, Aldrich) and benzene (Aldrich) were purchased anhydrously and stored over 3 Å molecular sieves. IR spectra were recorded on a Nicolet Impact 410 spectrometer as KBr pellets. NMR solvents were dried as follows: acetonitrile-d_3 (Cambridge Isotope Laboratories) over calcium hydride, benzene-d_6 (Cambridge Isotope Laboratories) over sodium benzophenone ketal. All NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ^{1}H NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. ^{19}F NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm). ^{13}C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak. The starting material **2** was synthesized by a previously reported procedure.[8] The starting materials silver trifluoromethanesulfonate (Strem), and sodium azide (Alfa Aesar) were used as received.

$[(IMes)_2Rh(NCMe)_2][N_3]$

In an oven-dried vial wrapped in aluminum foil, complex **2** (0.075 g, 0.10 mmol) was dissolved in acetonitrile (3 mL). Sodium azide (0.020 g, 0.31 mmol) was added, and the suspension was stirred for 14 h. The suspension was filtered through a dry Celite plug, which was washed with acetonitrile (2 x 1 mL). Diethyl ether (12 mL) was added to the combined filtrates. The resulting solution was layered with hexane (12 mL). After 12 h, orange, plate-like crystals had formed. The solid product was collected by filtration, washed with hexanes (2 x 2 mL) and dried *in vacuo*, affording the title complex (0.035 g, 44%). ^{1}H NMR (300.1 MHz, acetonitrile-d_3): δ 7.03 (s, 8 H), 7.00 (s, 4 H), 2.47 (s, 12 H), 1.837 (s, 24 H), 1.73 (s, 6 H) ^{13}C NMR (128 MHz, acetonitrile-d_3): 189.2 (d, J =

41 Hz), 138.6, 137.7, 136.0, 129.7, 123.2, 119.4 (d, J = 16 Hz), 21.3, 18.7, 4.2. IR (KBr, cm^{-1}): 2254, 1997, 1611, 1553, 1488, 1397, 1371, 1307, 1264, 1034, 924, 848, 742. Attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.

$(IMes)_2Rh(O_2)Cl$

A Schlenk tube was charged with **2** (0.500 g, 0.669 mmol) and benzene (8 mL). The solvent was frozen, the tube was evacuated, and an atmosphere of dry air was admitted. The solution was allowed to stir for 15 h. The solvent was removed on a rotary evaporator. The solid was collected on a fritted funnel, washed with hexanes (3 x 5 mL), and further dried *in vacuo* to yield a blue powder (0.410 g, 79%). ^{1}H NMR (300.1 MHz, benzene-d_6): δ 6.86 (s, 8 H), 6.20 (s, 4 H), 2.37 (s, 12 H), 2.04 (s, 24 H). ^{13}C NMR (128 MHz, benzene-d_6): δ 181.5 (d, J = 38 Hz), 137.5, 137.3, 129.0, 128.7, 122.5, 21.7, 19.0. IR (KBr, cm^{-1}): 2095, 1609, 1407, 1328, 1271, 1230, 1033, 928, 852, 844. Anal. calcd For $C_{42}H_{48}ClN_4O_2Rh$: C, 64.74; H, 6.21; N,.7.19. Found: C, 64.89; H, 5.82; N, 7.07.

$(IMes)_2Rh(O_2)OTf$

In the absence of light, $(IMes)_2Rh(O_2)Cl$ (0.250 g, 0.321 mmol) and silver trifluoromethanesulfonate (0.082 g, 0.321 mmol) were added to an oven-dried vial equipped with a Teflon-coated magnetic stir bar in the box. $PhCF_3$ (5 mL) was added, and the suspension was allowed to stir for 8 h. The suspension was filtered through a dry Celite plug. The plug was extracted with $PhCF_3$ (3 x 3 mL). The solvent was removed *in vacuo* on a rotary evaporator. The red solid was collected on a fritted funnel, washed with hexanes (2 x 2 mL) and further dried in vacuo (0.203 g, 71 %). ^{1}H NMR (300.1 MHz, acetonitrile-d_3): δ 7.24 (s, 2 H), 7.24 (s, 2 H), 6.98 (s, 8), 2.43 (s, 12 H), 1.72 (s, 24 H). ^{19}H NMR (300.1 MHz, acetonitrile-d_3): δ –78.8 (s, 3 F). ^{13}C NMR (128 MHz,

benzene-d_6): δ 140.0, 135.3, 129.7, 123.8, 21.0, 17.1.[13] IR (KBr, cm^{-1}): 1488, 1409, 1260, 1225, 1158, 1032, 855, 699, 638. Attempts at elemental analysis failed to give satisfactory results; ^1H and ^{13}C NMR spectra for this compound are included to attest to its purity.

X-Ray Crystallography

General considerations. Crystals of **3** and $(IMes)_2Rh(O_2)Cl$ were transferred onto a microscope slide from a scintillation vial and coated with STP. A crystal was selected, mounted on a glass fiber, and optically centered. The data were collected on a Siemens platform goniometer with a CCD detector. The structures were solved by direct methods in conjunction with standard difference Fourier techniques (SHELXTL v5.1, Sheldrick, G. M. and Siemens Industrial Automation, 1997). Non-hydrogen atoms were treated anisotropically, and hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 Å).

$[(IMes)_2Rh(NCMe)_2][N_3]$, (3):

Single crystals suitable for X-ray diffraction were grown by slow diffusion of hexanes into a saturated solution of **3** (0.03 g) in acetonitrile (1.5 mL) and diethyl ether (1.5 mL) in the dark.

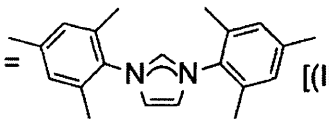
$(IMes)_2Rh(O_2)Cl$

Single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a saturated solution of $(IMes)_2Rh(O_2)Cl$ (0.015 g) in benzene (1 mL). Significant disorder precluded anisotropic refinement. The structure is presented to establish general connectivity.

Table 1. Crystallographic data for **3**

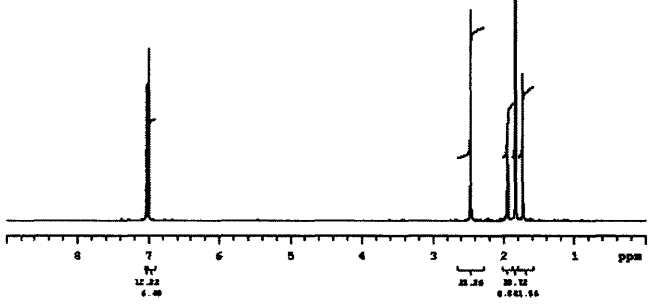
	3
Empirical formula	$C_{46}H_{54}N_9Rh$
FW	835.89
T, K	100(2)
Crystal syst,	Orthorhombic
Space group	Aba2
a, Å	15.312(6)
b, Å	14.907(5)
c, Å	19.034(7)
α, deg	90
β, deg	90
λ,deg	90
V, $Å^3$	4345(3)
ρ, g/cm^{-1}	1.278
Z	4
μ, mm^{-1}	0.435
F(000)	1752
Cryst size, mm^3	0.50 x 0.50 x 0.04
θ-range, deg	2.14 to 29.57
Total no. of reflns	45201
GOF on F^2	1.049
Final *R* indices [I>2σ(I)]	0.0255
	0.0649
R indices (all data)	0.0314
	0.0694

NMR Spectra:

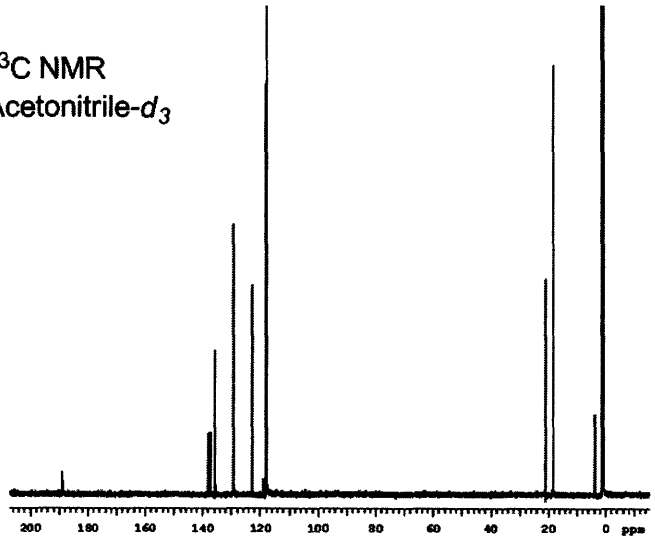
Imes = 

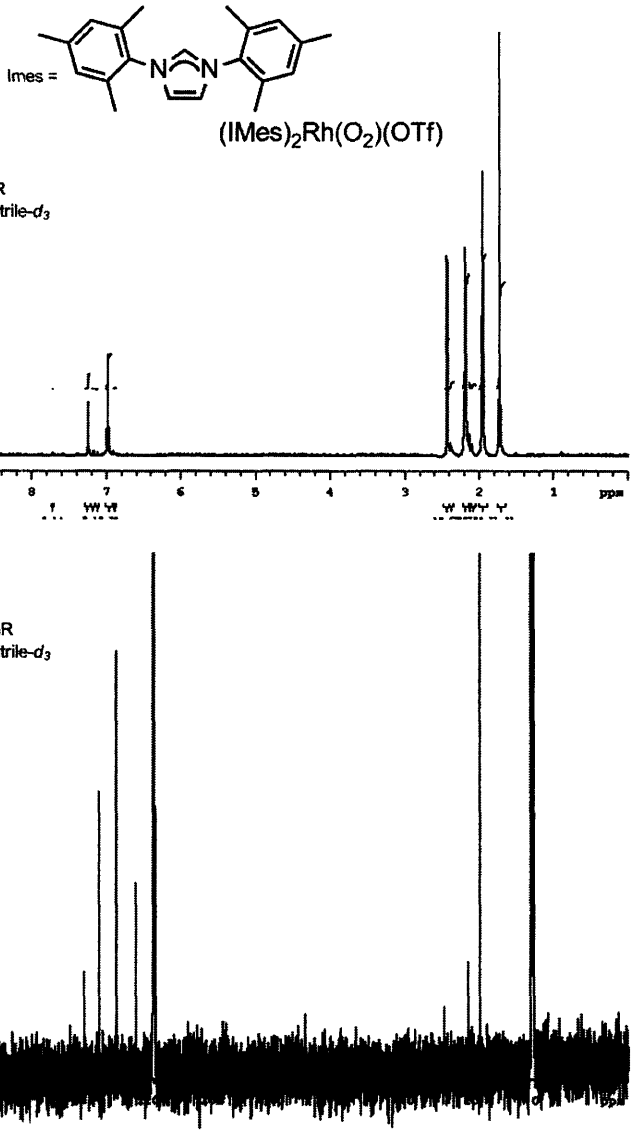
$[(IMes)_2Rh(NCMe)_2][N_3]$

^1H NMR
Acetonitrile-d_3



^{13}C NMR
Acetonitrile-d_3




Imes =
(IMes)2Rh(O2)(OTf)
1H NMR
Acetonitrile-d3
13C NMR
Acetonitrile-d3

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[13] The poor solubility of this compound precluded identification of ^{13}C NMR signals of $O_3S\underline{C}F_3$ and $N_2\underline{C}Rh$.

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Graduate Student — August 2001–Present

Education

Massachusetts Institute of Technology — Cambridge, MA
Ph.D. Candidate in Inorganic Chemistry — August 2001–present
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Texas A&M University — College Station, Tx
B.S. *Magna Cum Laude* — September 1997–June 2001

Research Experience

Massachusetts Institute of Technology — Cambridge, MA
Position: Research Assistant — (November 2001–Present)
Research Advisor: Professor Joseph Sadighi

Graduate research focused on the synthesis of monomeric, late transition metal complexes containing divalent, heteroatom-based ligands. A sterically encumbering, oxidation-resistant 2,9-diaryl-1,10-phenanthroline supporting ligand was prepared to stabilize complexes of this type. By deprotonation of a cationic palladium (II) sulfonamido complex, the first monomeric palladium sulfonimido complex was synthesized. The sulfonimido complex can function as either an electrophilic or nucleophilic group-transfer reagent. Also, a copper (I) complex of this supporting ligand catalyzes oxidative C–N bond formation by nitrene transfer to arene C–H bonds, using iminoiodinanes or sulfonyl azides as the nitrene source. Current research pursues the isolation of terminal oxo complexes of late transition metals, using N-heterocyclic carbene (NHC) supporting ligands.

Argonne National Laboratory — **Argonne, Il**
Position: Research Assistant — (May 2000 – August 2000)
Research Advisor: Dr. Christopher Marshall

A summer internship focused on the development of a high-throughput assay to monitor benzene oxidation to phenol using hydrogen peroxide or oxygen as the oxidant. Over sixty-five catalysts were tested including supported metal frameworks.

Texas A&M University (Cyclotron Institute) — College Station, Tx
Position: Research Assistant — (January 1998–August 2001)
Research Advisor: Professor Joseph Natowitz

Undergraduate research focused on the construction and modification of a particle-detector array. This detector array is currently used to identify products from nuclear reactions. A modification

was made to the array for *in situ* calibration using cosmic radiation. Data analysis and simulations were performed using c++ programming language.

Awards

IUCCP - A.E. Martell Scholar
CRC Outstanding Chemistry Majors
Chemistry Department Achievement Award

Publications

Hamilton, C. W.; Laitar, D. S.; Sadighi, J. P. "Synthesis and reactivity of monomeric sulfonylamido and sulfonylimido complexes of palladium." Manuscript in preparation.

Akana, J. A.; Hamilton, C. W.; Laitar, D. S.; Sadighi, J. P. "Copper(I)-Catalyzed Nitrene Transfer from Sulfonyl Azides to C–H Bonds." To be submitted to *Inorg. Chem.*

Hamilton, C. W.; Laitar, D. S.; Sadighi, J. P. "Oxidation-resistant, sterically demanding phenanthrolines as supporting ligands for copper(I) nitrene transfer catalysts." *Chem. Commun.*, **2004**, 1628–1629.

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Presentations

Hamilton, C. W.; Sadighi, Joseph P.; Laitar, David S. "Synthesis and reactivity of monomeric sulfonylamido and sulfonylimido complexes of palladium." Oral presentation, 230th ACS National Meeting, Washington, DC, United States, Aug. 28-Sept. 1, 2005 (2005), INOR-323.

Hamilton, C; Gardner, E; Marshall, C; Iton, L. "Combinatorial screening for the direct catalytic oxidation of benzene to phenol." Poster presentation, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), CHED-347.

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