

Diverse Reactivity of a Rhenium(V) Oxo Imido Complex: [2 + 2] Cycloadditions, Chalcogen Metathesis, Oxygen Atom Transfer, and Protic and Hydridic 1,2-Additions

Trevor D. Lohrey, Emmanuel A. Cortes, Jade I. Fostvedt, Alexander K. Oanta, Anukta Jain, Robert G. Bergman, and John Arnold*

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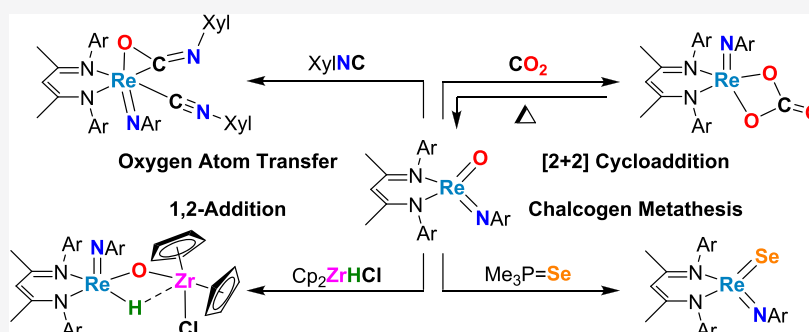
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ABSTRACT: We present a wide range of reactivity studies focused on the rhenium(V) oxo imido complex (DippN)(O)Re(BDI) (**1**, Dipp = 2,6-diisopropylphenyl and BDI = *N,N'*-bis(2,6-diisopropylphenyl)-3,5-dimethyl- β -diketiminate). This complex, which was previously shown to possess a highly polarized Re oxo moiety, has proven to be a potent nucleophile and a valuable precursor to a variety of rare structural motifs in rhenium coordination complexes. For example, the Re oxo moiety of **1** undergoes [2 + 2] cycloadditions with carbodiimides, isocyanates, carbon dioxide, and isothiocyanates at room temperature. In the case of CO₂, the cycloadduct with **1** (a carbonate complex) undergoes the facile ejection of CO₂, demonstrating that this binding process is reversible. In the case of isothiocyanate, chalcogen metathesis with **1** takes place readily as the inclusion of a second equivalent of substrate in the reaction mixture rapidly yields a dithiocarbamate complex. This metathesis process was extended to the reactivity of **1** with phosphine chalcogenides, leading to the isolation of terminal sulfido imido and selenido imido complexes. Attempts to complete this series and generate the analogous terminal telluride led to the formation of a bidentate tritelluride (Te₃²⁻) complex. Triethylphosphine could only undergo oxygen atom transfer (OAT) with **1** under pressing thermal conditions that also led to C–N cleavage of the BDI ligand. In contrast, OAT between **1** and CO or 2,6-xylylisocyanide (XylINC) was found to be much more facile, proceeding within seconds at room temperature. While the addition of excess CO led to a rhenium(III) imido dicarbonyl complex, we found that the addition of 2 equiv of XylINC was necessary to promote OAT, resulting in the isolation of a rare example of a stable metal isocyanate complex. Our experimental observations of CO and XylINC and their OAT reactions with **1** inspired a mechanistic computational study to probe the intermediates and kinetic barriers along these reaction pathways. Finally, we describe 1,2-additions of both protic and hydridic substrates with the Re oxo moiety of **1**, which most notably led to the syntheses of an uncommon example of a terminal rhenium hydroxide complex and an oxo-bridged Re–O–Zr hetero-bi-metallic complex that was generated using Schwartz's reagent (Cp₂ZrHCl). A brief discussion of a potential alternative route to **1** is also presented.

INTRODUCTION

The most common multiply bonded ligand in transition metal chemistry is undoubtedly the metal oxo, which, owing to the ubiquity of water and dioxygen in our environment, is of inescapable relevance to both bioinorganic and synthetic chemistry.^{1,2} While many research groups have focused on the synthesis and characterization of highly reactive and often transient first row transition metal oxo species, which often display a radical character,^{3–9} others have probed the chemistry of metal oxo complexes of the 4d and 5d transition metals, which

form stronger metal–ligand π -bonds and do not tend to display a radical character in their electronic structures or reactivity patterns.^{10–17} Transition metal oxo complexes of both types

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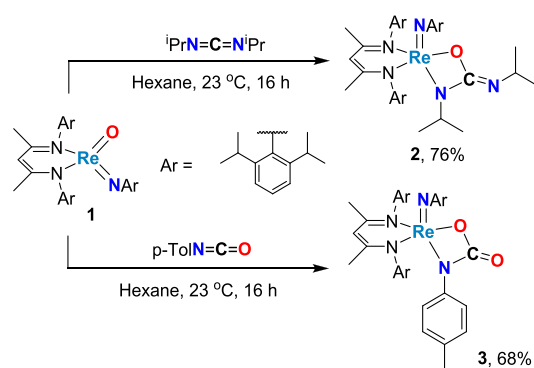
have shown a wide range of electronic structures and reactivities, and a number of reviews and textbooks have been dedicated to covering the subject.^{1,2,18–21}

Our group has taken an interest in the intersection of rhenium oxo chemistry and an established π -loading strategy, whereby the presence of two or more multiply bound ligands in a transition metal complex leads to the enhanced polarity and reactivity of the metal–ligand π -system. Recently, we have shown that the combination of a terminal oxo and a terminal imido ligand in a sterically constrained 4-coordinate rhenium(V) complex can lead to an advantageous weakening of the rhenium–oxo bond, specifically due to the more extensive π -bonding of the metal to the imido ligand.²² The enhanced polarity of the Re–oxo bond in this oxo imido system was established by density functional theory (DFT) calculations as well as the observation of the rapid activation of triarylboranes via B–C bond cleavage. This nucleophilic reactivity is in stark contrast to known examples of rhenium(VII) oxo imido complexes, which display an electrophilic character at the oxo ligand.²³ Here, we report continued reactivity studies of the oxo imido complex (DippN)(O)Re(BDI) (**1**), which have proven that our approach to enhancing the polarity of the rhenium oxo moiety can lead to a variety of new chemistry derived from this multiply bound fragment.

RESULTS AND DISCUSSION

[2 + 2] Cycloadditions and Subsequent Chalcogen Metathesis Reactions. Considering that initial reactivity studies of **1** showed that the high degree of Re oxo polarization in this system is capable of promoting the cleavage of B–C bonds in triarylboranes, additional reactions that highlight this nucleophilic behavior, namely [2 + 2] cycloaddition with unsaturated organic molecules, were investigated.⁶ The combination of **1** with *N,N'*-diisopropylcarbodiimide (DIC) or *p*-tolylisocyanate (TolNCO) rapidly yielded a dark orange-brown solution from which similarly colored products could be crystallized (Scheme 1). X-ray diffraction studies of these two

Scheme 1. Syntheses of **2** and **3**



complexes (Figure 1), in combination with their sharp and asymmetric NMR spectra, showed unambiguously that the Re oxo moiety of **1** had undergone a cycloaddition with a C=N double bond in each of these substrates, yielding the ureate complex **2** (from DIC) or the carbamate complex **3** (from TolNCO). Both **2** and **3** are relatively inert, showing no signs of reactivity when heated in benzene at 100 °C. To our knowledge, **2** represents the first example of an isolated cycloaddition product of a metal oxo with a carbodiimide (however, similar complexes have been accessed by the cycloaddition of the C=O

bond of isocyanates with terminal metal imido groups).^{24–27} The carbamate fragment in **3** is also a known motif, albeit infrequently encountered in structurally characterized transition metal complexes; previous examples possessing this ligand have been formed via the cycloaddition of isocyanates with metal oxos^{28–30} as well as via cycloadditions of CO₂ with metal imidos.^{31–33} Akin to the aforementioned examples, complex **3** highlights a thermodynamic favorability for the cycloaddition of the C=N bond of TolNCO over the C=O bond.

The addition of ca. 1 atm of CO₂ to a solution of **1** led to the formation of a new species, which was isolated from toluene as dark green crystals. X-ray crystallography and NMR spectroscopy confirmed the identity of this complex as the bidentate carbonate complex **4** (Scheme 2). Transition metal carbonate complexes are well known, and while some have been formed by CO₂ cycloadditions akin to the example presented here^{34–38} other examples have been accessed by the oxidation of metal carbonyls with O₂^{39,40} or most often by salt metathesis reactions to install the carbonate directly.^{41,42} While **4** is structurally analogous to **2** and **3**, it will eject CO₂ when left in solution under a N₂ atmosphere (either slowly over the course of days at room temperature or within 2 min at 100 °C). We independently confirmed that **1** and **4** can be easily interconverted by the addition or removal of a CO₂ atmosphere. Heating **4** under a CO₂ atmosphere for several hours, however, led to the decomposition of the compound to a convoluted mixture. Density functional theory (CAM-B3LYP-D3BJ and a mixed def2 basis set, Supporting Information) calculations on truncated models of **1** and **4**, namely **1*** and **4***, where the 2,6-diisopropylphenyl groups have been simplified to phenyl substituents indicate that the binding energy of CO₂ to **1*** to form the carbonate species **4*** is ca. 2.2 kcal/mol. This value is in line with the experimental observation that the binding of CO₂ to **1** is favorable but reversible. Similarly, the binding of CO₂ by molybdate (MoO₄²⁻) was found to be reversible, with CO₂ binding energies on the same order as that computed for **1***.³⁵ A nucleophilic Ti terminal oxo complex has also been shown to undergo the reversible [2 + 2] cycloaddition of CO₂ to the Ti=O moiety at room temperature.³⁶

The reaction of **1** with a single equivalent of 2,4,6-trimethylphenylisothiocyanate (MesNCS) led to the formation of a mixture of products. Further studies revealed that the addition of 2 equiv of MesNCS to **1** led to the formation of a single isolable product, the dithiocarbamate complex **5** (Scheme 3). The related thiocarbamate complex **6**, the product of a single cycloaddition of MesNCS to **1**, could only be accessed in a pure state when isolated as a precipitate after a brief reaction time in hexane. Thiocarbamate ligands, such as those found in **6**, are not commonly encountered in structurally characterized transition metal complexes.^{43,44} The fact that **5** forms by a mechanism in which **6** is an intermediate supports the possibility that a terminal Re sulfide is generated by the ejection of isocyanate from **6**, which is then trapped by a second equivalent of MesNCS. Since a mixture of **5** and **6** was observed when only one equivalent of MesNCS was added to the reaction mixture, it appears that the ejection of isocyanate to form this putative terminal sulfide is relatively fast.

In an effort to isolate this putative terminal sulfido species, we turned to studying the reactivity of **1** with phosphine sulfides, which have some ability to exchange reactive metal oxo groups for terminal metal sulfides.^{45,46} The reaction of **1** with trimethylphosphine sulfide (S=PMe₃) proceeds within minutes at room temperature, and the desired product, the

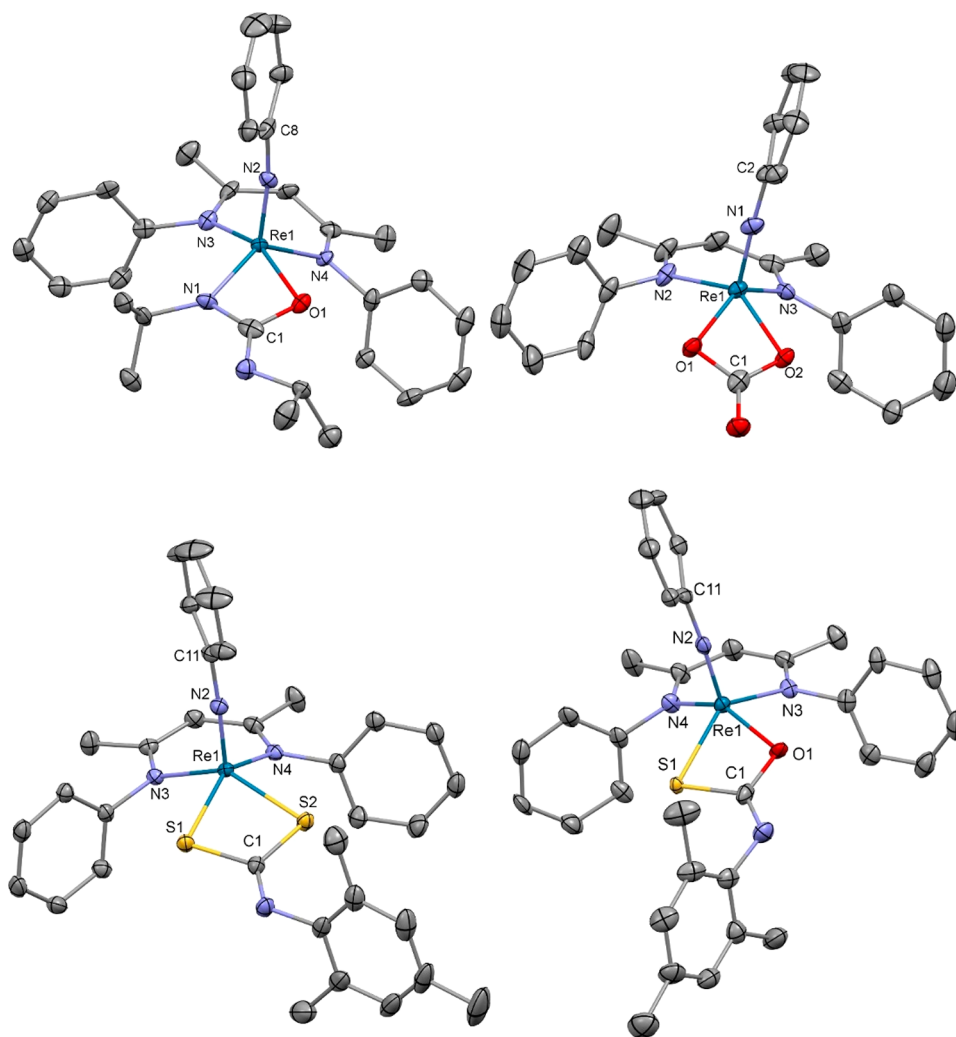
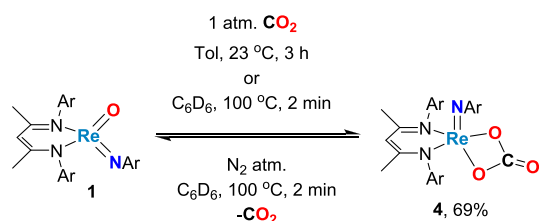
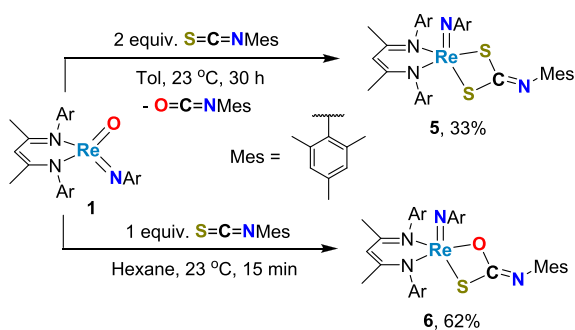


Figure 1. X-ray crystal structures of **2** (top left), **4** (top right), **5** (bottom left), and **6** (bottom right) with 50% probability ellipsoids. Hydrogen atoms, Dipp isopropyl groups, solvent (where applicable), and disordered fragments (where applicable) are excluded for clarity. Selected metrics for all structures may be found in the [Supporting Information](#).

Scheme 2. Reversible CO₂ Binding by **1** to Form **4**

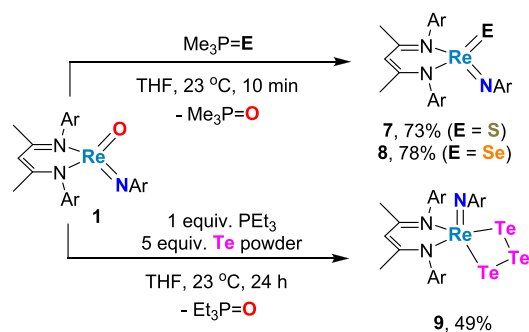


Scheme 3. Syntheses of **5** and **6**



terminal sulfido imido complex **7**, can be readily crystallized from pentane (Scheme 4). Trimethylphosphine selenide (Se=

Scheme 4. Syntheses of **7**, **8**, and **9**



PMe₃) also provides rapid access to the terminal selenido imido complex **8**, which we believe to be the first example of a structurally characterized rhenium terminal selenide. The crystal structures of both **7** and **8** indicate the presence of disulfide and diselenide fragments as co-crystallized impurities (Figure 2). A number of efforts were required to obtain satisfactory X-ray

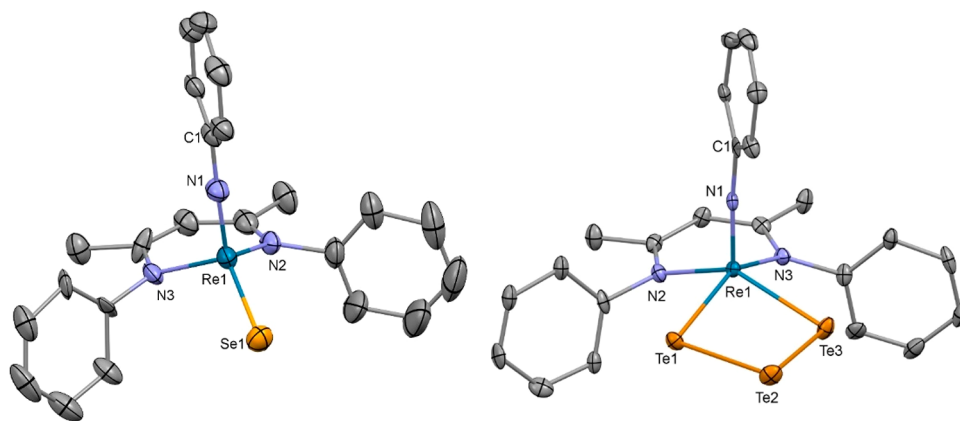


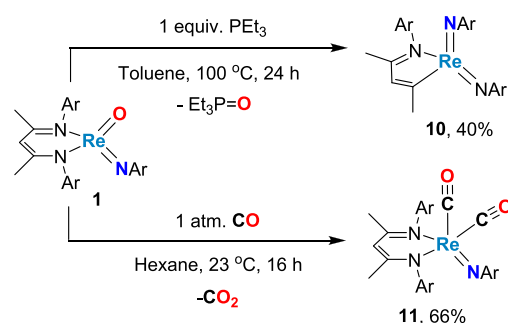
Figure 2. X-ray crystal structures of **8** (left) and **9** (right) with 50% probability ellipsoids. Hydrogen atoms, Dipp isopropyl groups, and disordered fragments (where applicable) are excluded for clarity.

diffraction data for these species, and we found that these impurities were present in every case.

Attempts were made to generate a terminal tellurido imido complex from **1**. However, **1** was found to be unreactive toward tricyclohexylphosphine telluride ($\text{Te}=\text{PCy}_3$), an atypical example of a stable phosphine telluride,⁴⁷ even when heated at 120 °C in benzene for prolonged periods. It is likely that the larger size of this reagent in comparison to the trimethylphosphine chalcogenides prevents the desired reaction from proceeding. In an attempt to accommodate the steric constraints of this system, **1** was combined with a stoichiometric amount of triethylphosphine (PEt_3) and 5 equiv of Te powder. These conditions resulted in an observable reaction over the course of 24 h; however, upon workup the isolated product was not a terminal telluride but instead a bidentate tritelluride (Te_3^{2-}) complex (**9**). It is unclear if any terminal telluride intermediate is formed under these reaction conditions, though it is apparent that some form of phosphine telluride species is responsible for the observed metathesis reaction to form **9**. Similar reactions to form zirconium trichalcogenide complexes have been previously observed.^{48,49}

Experimental and Computational Studies of Oxygen Atom Transfer to Phosphines, CO, and XylNC. The reactivity of **1** with phosphine chalcogenides led to the hypothesis that the oxo moiety of **1** could participate not only in nonvalent metathesis reactions but in reductive oxygen atom transfer (OAT) reactions, wherein the oxo ligand is removed to generate a rhenium(III) imido complex. Based on the synthesis of **9**, it was apparent that **1** and PEt_3 did not react at room temperature despite the fact that PEt_3 can be a potent oxygen atom acceptor.²¹ Further investigation revealed that OAT between **1** and PEt_3 only took place at elevated temperatures (100 °C), leading to the formation of a dark purple product that was problematic to isolate due to its high solubility in hydrocarbons and hexamethyldisiloxane (HMDSO) (Scheme 5). Eventually, this product was identified as the rhenium(V) bis(imido) complex **10**, which presumably formed by OAT between **1** and PEt_3 followed by nitrene transfer from the BDI ligand to form a monoazadiene (MAD) ligand, specifically 4-((2,6-diisopropylphenyl)imino)pent-2-enide). This mode of BDI cleavage has been well documented by our group (in both group 5 and Re BDI chemistry) and many others, and typically occurs in low-valent coordinately unsaturated BDI complexes.^{50,51}

Scheme 5. Syntheses of **10** and **11**



We have previously described the reactivity of a rhenium(III) terminal oxo complex that was inert toward trialkylphosphines but rapidly underwent OAT with carbon monoxide (CO) and isocyanides, owing to the nucleophilic character of its metal oxo moiety.⁵² Considering that the high nucleophilicity of the oxo ligand in **1** has already been demonstrated, it was hypothesized that **1** would undergo facile OAT with CO and 2,6-xylylisocyanide (XylNC). The addition of ca. 1 atm of CO to a solution of **1** led to an almost instantaneous darkening of the reaction mixture. Crystallization of the product from HMDSO allowed for its definitive assignment as the rhenium(III) imido dicarbonyl complex **11** (Figure 3). Compound **11** displays two sharp CO stretches in its IR absorbance spectrum at 1965 and 1845 cm^{-1} . We previously reported an analogous niobium(III) imido BDI dicarbonyl complex; however, this compound was generated by the addition of CO to a niobium(V) dimethyl complex to eject acetone and formally reduce the Nb center.⁵³ This Nb dicarbonyl proved to be a valuable synthetic precursor and precatalyst for alkyne semi-hydrogenation.⁵⁴

Subsequent reactivity studies with XylNC provided valuable insight into the mechanism of OAT from **1**. The addition of 1 equiv of XylNC to **1** led to the formation of a stable adduct, **12** (Scheme 6). This emerald green species displays a distinct isocyanide stretching feature in its IR absorbance spectrum at 2079 cm^{-1} , which, in comparison to that observed for free XylNC (2116 cm^{-1}),⁵⁵ indicates that a substantial amount of π -backbonding is occurring in **12**. The addition of 2 equiv of XylNC to **1** led to a dark brown product, which contained two xyllyl groups to every BDI ligand as indicated by the NMR spectra. X-ray diffraction studies revealed that the product of this reaction was the rhenium(III) imido $\eta^2\text{-C,O}$ -isocyanate complex **13**. First, this result experimentally demonstrated that OAT

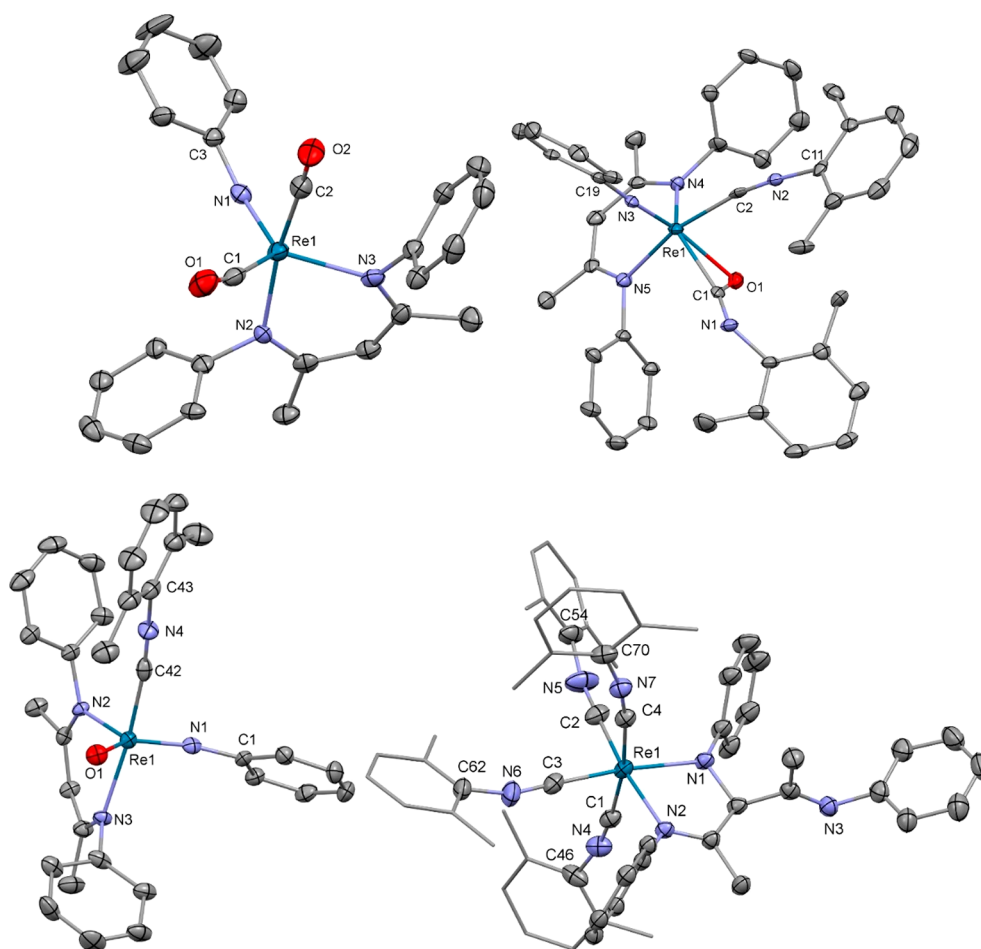
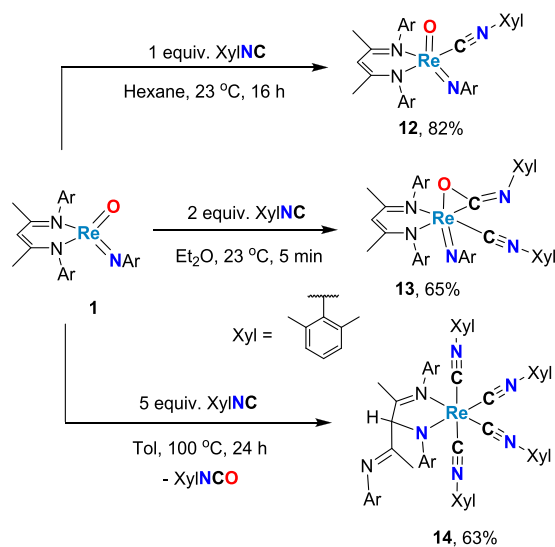


Figure 3. X-ray crystal structures of **11** (top left), **13** (top right), **12** (bottom left), and **14** (bottom right) with 50% probability ellipsoids. Hydrogen atoms, Dipp isopropyl groups, solvent (where applicable), and disordered fragments (where applicable) are excluded for clarity.

Scheme 6. Syntheses of **12**, **13**, and **14**



from **1** does not appear to occur from **1** itself but rather its adducts, meaning that 2 equiv of reagent are required to achieve OAT. A very similar reaction was observed in a series of Mo and W oxo complexes that were observed to undergo reversible OAT with CO and *t*-BuNC, in which 2 equiv of the OAT acceptor appeared to participate in the reaction.⁵⁶ Second, **13** is likely

representative of an intermediate formed in the OAT from **1** to CO (containing an η^2 -CO₂ ligand and one CO ligand); however, in that case the CO₂ generated in the reaction is rapidly displaced by the additional CO. Third, **13** is a rare example of a structurally characterized metal isocyanate complex.^{56–58}

Further reactivity studies demonstrated that **13** is inert to additional equivalents of XylINC at room temperature, whether it be from the addition of excess XylINC to a solution of **1** or by the addition of XylINC to isolated **13**. Heating reaction mixtures containing **13** and 1 equiv of either XylINC or **1** and 3 equiv of XylINC led to some conversion at 100 °C over the course of 24 h; however, these reactions appeared to stall after a time. The reaction of **1** with excess XylINC (>5 equiv) at 100 °C was observed to proceed to completion, with **13** being converted to a new and unknown product. Further efforts yielded the unknown compound as a dark red crystalline product, which proved to be the rhenium(I) tetrakis(XylINC) complex **14**. Unexpectedly, while the reduction of Re(V) to Re(III) assuredly proceeds by OAT and the loss of isocyanate, the reduction of Re(III) to Re(I) as observed in **14** proceeds by the formation of a C–N bond between the imido nitrogen and the backbone CH group of the BDI ligand. Consequently, this functionalized BDI ligand is monoanionic at the former imido nitrogen, which remains bound to the Re center, while one of the BDI imine groups is unbound from the metal. While it is likely that the presence of multiple XylINC groups affects the behavior of this system, we do not believe that another example of formal C–N reductive

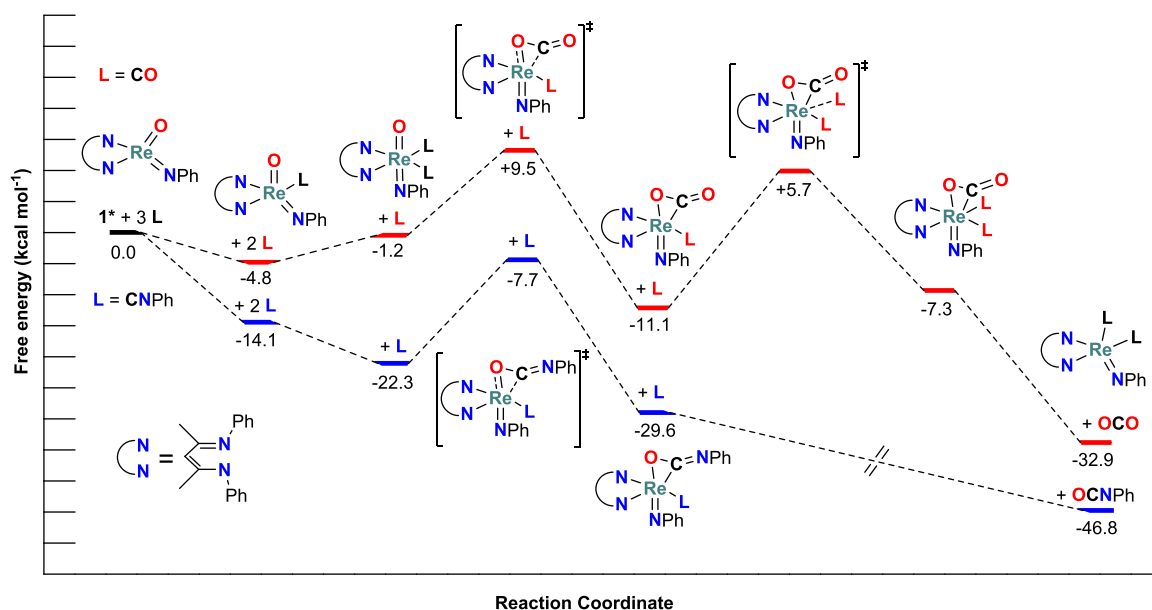


Figure 4. DFT-calculated reaction pathways for OAT from 1^* to CO and phenyl isocyanide (PhNC). The CAM-B3LYP-D3BJ functional and a mixed def2 basis set were employed.

elimination from a Re(III) center, or of a C–N bond-forming process taking place at a rhenium imido group in general, exists. The coupling between the imido and BDI ligands under these conditions is intriguing given that isocyanides have been shown to act as nitrene acceptors to form carbodiimides in a number of reactive metal imido systems.^{59–61}

The OAT reactivity studies of **1** were used as a guide for modeling a potential mechanistic pathway between **1** and **11** using density functional theory (DFT) calculations. Again, to simplify the computations the BDI ligand and the imido group were truncated such that the 2,6-diisopropylphenyl groups were represented as phenyl groups (1^* in Figure 4). The DFT results suggest that OAT from 1^* to CO proceeds first by the reversible binding of two CO ligands to 1^* , forming a pseudo-octahedral dicarbonyl species in which the oxo and imido ligands are *trans* to one another. The key OAT step then takes place by the insertion of a CO ligand into the Re oxo bond, with a free energy barrier of ca. 14.3 kcal/mol (from the monocarbonyl intermediate), forming an intermediate η^2 -CO₂ carbonyl species (analogous to the isolated isocyanate complex **13**). This mode of OAT, whereby the acceptor migrates from a metal site, is distinct from classical OAT reactions that occur between external OAT acceptors (such as phosphines) and attack the oxo ligand directly.⁶² The reverse of the OAT process described here has been observed in Mo and W systems that activate CO₂ to yield oxo carbonyl products.^{63,64} Given the terminology used in these previous reports, the OAT process we describe here may be better identified as a reductive elimination, considering that the bond formation process occurs between two metal-bound atoms rather than by the attack of an external OAT acceptor to the oxo ligand.

Both rigorously associative and dissociative mechanisms were modeled for the displacement of CO₂ by CO to ultimately generate the final product, a truncated model of **11**. The DFT results suggest that the association of CO to the intermediate η^2 -CO₂ complex is slightly endergonic, with a kinetic barrier of ca. 16.8 kcal/mol. The dissociation of CO₂ prior to CO binding leads to an intermediate only ca. 0.4 kcal/mol lower in energy than the starting materials (Supporting Information). The

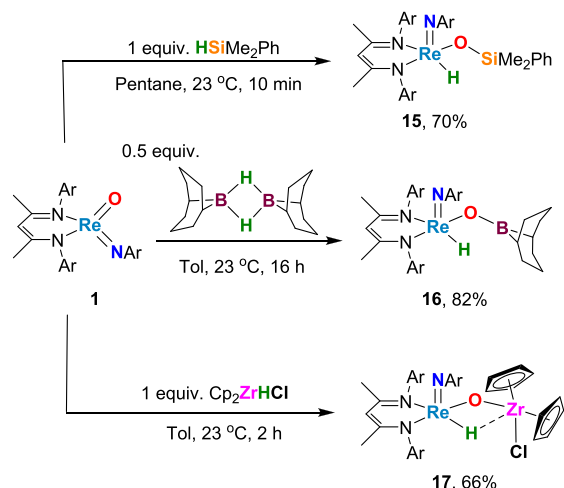
overall exchange of CO for CO₂ is thus predicted to be highly favorable, which, given the DFT results, we posit to proceed by some form of an interchange mechanism.

The free energy profile of the conversion of 1^* to a similarly truncated model of **13** (where BDI, imido, and isocyanide aryl groups were simplified to phenyl) was also modeled by DFT calculations, which suggested that OAT in this system likely proceeds in the same manner despite some key differences in the relative energies of the intermediates and transition states. Specifically, the binding of 2 equiv of PhNC to 1^* was highly favorable, with the bis(isocyanide) species lying ca. 22 kcal/mol lower in energy (whereas the dicarbonyl is only ca. 1.2 kcal/mol lower in the CO case). Unlike the models with CO, the binding of a second equivalent of PhNC was overall favorable compared to the binding of a single equivalent. The migration of PhNC to the oxo ligand of the model system was found to have a free energy barrier of ca. 14.6 kcal/mol, although the energy of this transition state is ca. 7.7 kcal/mol lower in energy than those of the starting materials. The formation of the final η^2 -PhNCO isocyanide complex is overall favorable to a greater extent than that observed in the CO model system. A structure of a truncated bis(PhNC) analog of **11** was optimized, highlighting that the transformation of the η^2 -PhNCO complex to a bis(PhNC) complex would be significantly downhill in energy. It is possible that the steric profile of an aryl isocyanide ligand may prevent this simple ligand exchange reaction from taking place. The fact that no such bis(isocyanide) complex derived from **13** could be observed or isolated indicates that beyond the OAT step the free energy profiles in the CO and PhNC systems diverge greatly. In summary, while the energy profile of this reaction can differ greatly on the basis of the oxygen atom acceptor, the DFT results suggest that the same overall mechanism for the OAT process itself remains plausible.

1,2-Addition Reactions: A Re–Zr Bimetallic and the Evaluation of Glycol Deoxygenation Reactivity. One of the best known examples of a reactive rhenium(V) oxo complex is the air-stable dioxo species O₂ReI(PPh)₃.⁶⁵ The catalytic and stoichiometric reactivity of this compound have been the subject of a number of studies, with a particular emphasis on

hydrosilylation and other reductions of organic substrates.^{66,67} One hallmark of this chemistry is the ability to isolate stable rhenium hydride species derived from the 1,2-addition of a Si–H or B–H bond across the Re oxo. Given this established precedent, we hypothesized that an analogous hydride species could be derived from the oxo imido complex **1**. The addition of phenylsilane (PhSiH₃) to **1** led to a rapid reaction, which yielded a complex mixture of products based on an NMR spectrum of the crude reaction mixture. The reaction of **1** with a bulkier silane, phenyldimethylsilane (PhMe₂SiH), led exclusively to the formation of the siloxide hydride complex **15** (Scheme 7). The

Scheme 7. Syntheses of **15**, **16**, and **17**



hydride ligand of this species is observable in both the ¹H NMR spectrum at 1.90 ppm and the IR absorbance spectrum as a small yet sharp peak at 1953 cm⁻¹. The hydride ligand of **15** was also located and freely refined in the X-ray crystal structure of this complex (Figure 5). In a related experiment, the analogous borinate hydride complex **16** could be obtained from the reaction of **1** with the 9-borabicyclo[3.3.1]nonane (9-BBN) dimer. While a crystal structure of **16** could not be obtained, the hydride ligand was readily observed in the ¹H NMR and IR absorbance spectra of this product, with chemical shift and IR

absorbance values similar to those measured for the hydride ligand in **15**.

Beyond establishing that **1** can promote the same kind of 1,2-additions that have been reported with O₂ReI(PPh)₃, this mode of reactivity was employed to construct an oxo-bridged heterobimetallic complex; Schwartz's reagent, zirconocene hydrochloride (Cp₂ZrHCl), readily hydrozirconates the Re oxo moiety of **1** to form the isolable bimetallic complex **17**. The X-ray crystal structure of **17** shows that while the hydride ligand is undoubtedly bound to the Re center there is still a close contact being maintained between the hydride (or more precisely, the Re–H bond) and the Zr center. Evidence of this interaction is found in the spectroscopic data for **17**. The hydride chemical shift is found at 0.27 ppm in the ¹H NMR spectrum (notably shifted from those recorded for the hydrides in **15** and **16**, which appear at ca. 2 ppm), and the hydride stretching feature in the IR absorbance spectrum is significantly broadened in comparison to those observed in the spectra of **15** and **16**. While a number of hetero-multi-metallic transition metal complexes containing bridging oxo linkages to zirconium have been reported, we believe that the reaction to form **17** represents a novel means of constructing this moiety.^{68–70} Additionally, previous examples of oxo-bridged Re–Zr multi-metallic complexes invariably involve the binding of a perrhenate anion (ReO₄⁻) to a ligated Zr center.⁷¹ The derivatization of **17** to form a Zr–alkyl linkage by the displacement of the chloride ligand was attempted several times. The inclusion of a strongly basic group was hypothesized to possibly lead to the deprotonation of the Re hydride, formally reducing this bimetallic system and facilitating the formation of Re–Zr bonds. The reactions of **17** with either methyl lithium or (trimethylsilyl)methyl lithium did not lead to the formation of a single isolable product. Significant quantities of **17** were observed to persist in all of these attempted reactions, indicating that this bimetallic complex is somewhat sterically hindered and resistant to salt metathesis. Heating these reaction mixtures demonstrated that **17** is not entirely stable and will begin to decompose upon heating in benzene.

Reactions of **1** with protic substrates were also carried out to determine if the inherent Brønsted basicity and polarization of the Re oxo ligand in this compound could provide a driving force

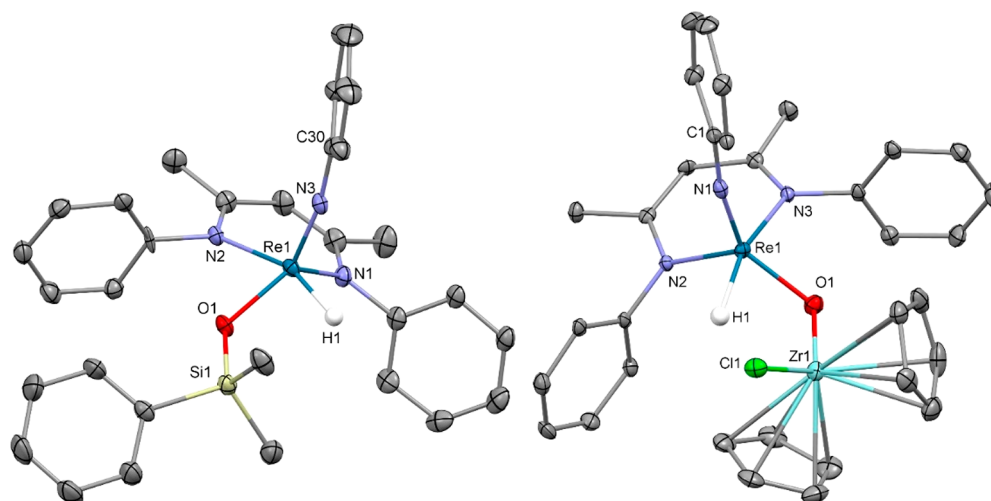
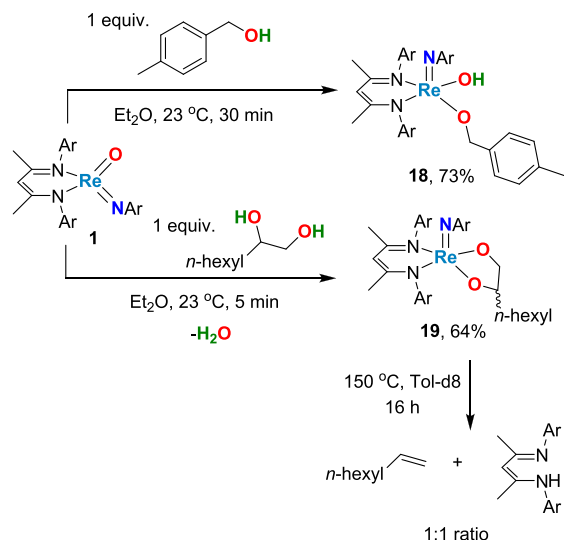


Figure 5. X-ray crystal structures of **15** (left) and **17** (right) with 50% probability ellipsoids. Hydrogen atoms, Dipp isopropyl groups, and solvent (where applicable) are excluded for clarity.

for 1,2-additions. The addition of 4-methylbenzyl alcohol to **1** rapidly yielded the orange hydroxide complex **18** (Scheme 8).

Scheme 8. Syntheses of **18** and **19** and the Degradative Thermolysis of **19**



The hydroxide proton of this complex is readily observed in the X-ray crystal structure as well as in a sharp peak in the ^1H NMR spectrum at 8.94 ppm (Figure 6). A number of other structurally characterized terminal rhenium hydroxide complexes have been reported in the literature.^{72–74}

While **18** was unreactive toward additional equivalents of 4-methylbenzyl alcohol, we examined the possibility that **1** could behave akin to the proposed intermediates of Re-catalyzed glycol deoxygenation (like MeReO_2 , Cp^*ReO_2 , or analogs thereof), which rapidly condense with glycols to form isolable complexes.^{75–78} This hypothesis was confirmed upon the isolation of the glycolate complex **19** from the reaction of **1** with 1 equiv of 1,2-octanediol. While a single crystal of this complex was found to contain a single diastereomer of **19** when subjected to X-ray diffraction studies, the ^1H NMR spectrum of

the bulk product indicated that the use of a racemic glycol (with C2 as a chiral center) led to the formation of two isolable diastereomers of **19** in an approximately 1.0:0.6 ratio. Complex **19** was subjected to thermolysis conditions with frequent monitoring for the formation of 1-octene and a new oxidized rhenium BDI species. Such a process is a key step in the deoxygenation catalysis mentioned above and would demonstrate the competence of **1** as a potential new catalyst for this application. While the thermolysis of **19** in toluene overnight at 150 °C does in fact lead to the formation of 1-octene, as observed in the crude ^1H NMR spectrum, it also leads to the formation of an equal quantity of free protonated BDI. Thus, we believe that while the proposed deoxygenation does take place, this process is directly associated with decomposition of the Re BDI complex. To date, whether from this work or prior studies, there are no examples of isolated rhenium(VII) BDI complexes; one possible reason for this is that Re(VII) compounds most often contain three oxo or imido ligands in a facial arrangement. Unlike Cp and methyl ligands, which are found in well-known Re deoxygenation catalysts, the steric bulk of the BDI ligand, as well as its geometrically constrained bidentate binding mode (though some monodentate BDI complexes have been reported),^{79,80} appears unsuitable for accommodating the necessary facial arrangement of three highly donating multiply bound ligands bound to a Re(VII) center. Despite the fact that **1** appears to be ill-suited to act as a deoxygenation catalyst, its reactivity studies demonstrated that the polarized metal oxo group of this complex can serve to cleave both protic and hydric element–hydrogen bonds.

Throughout these reactivity studies, an alternative synthetic route to **1** was also investigated. We hypothesized that the reaction of $\text{OReCl}_2(\text{BDI})$ with 2 equiv of potassium(2,6-diisopropylanilide) (KNHDipp) would yield **1** in a single step via salt metathesis followed by the α -elimination of 2,6-diisopropylaniline, overall removing both chloride ligands from the starting material and installing an imido group in their place. The reaction of $\text{OReCl}_2(\text{BDI})$ with KNHDipp in hexane gave a dark purple solution from which a similarly colored product could be crystallized in modest yield (Scheme 9). Crystallographic studies of this product showed it to be the

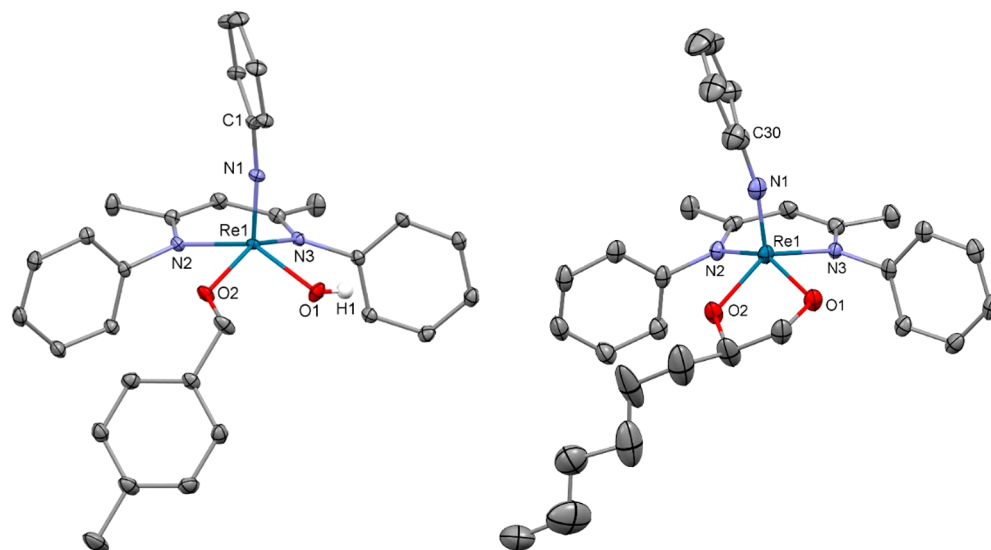
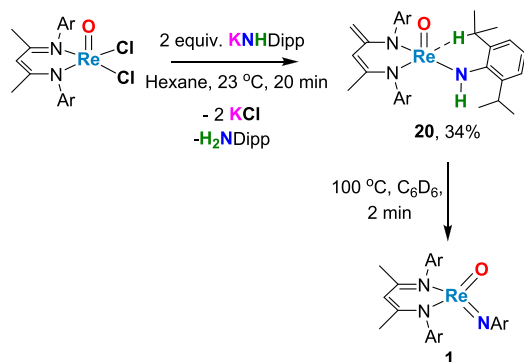


Figure 6. X-ray crystal structures of **18** (left) and **19** (right) with 50% probability ellipsoids. Hydrogen atoms and Dipp isopropyl groups are excluded for clarity.

Scheme 9. Synthesis of **20** and its Conversion to **1**

rhenium oxo amide complex **20**, which contains a dianionic doubly deprotonated BDI ligand that has been observed in a number of other studies of metal BDI complexes (Figure 7).^{50,81}

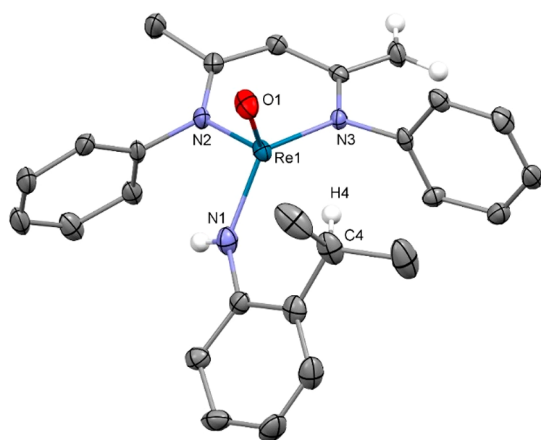


Figure 7. X-ray crystal structure of **20** with 50% probability ellipsoids. Hydrogen atoms (except for those on the amide N atom and the =CH₂ group and that involved in a close interaction with Re) and Dipp isopropyl groups (except for that in close contact with Re) are excluded for clarity.

It appeared that the steric profile of the bulky anilide ligand was too large for two equivalents to enter the coordination sphere of Re; thus, while one equivalent was able to bind, the second acted as a base toward a BDI methyl group. The X-ray crystal structure of **20** shows that while it is formally 4-coordinate, the geometry around Re more closely resembles trigonal bipyramidal because an agostic interaction is apparent between an axial site on the Re center and an isopropyl methine group in the amide ligand. The persistence of this interaction in solution could not be determined by NMR spectroscopy, as the resonances associated with the methine groups in question are highly broadened and not observable at room temperature.

During the initial characterization of **20**, it was apparent that **1** was present as a significant impurity. Heating **20** in benzene at 100 °C revealed that this amide species converted completely to **1** within 2 min. This result was intriguing, as we have shown in the past that niobium(V) bis(imido) BDI complexes will readily undergo the opposite transformation, forming amide complexes with doubly deprotonated BDI ligands as the more stable tautomers.⁸¹ In the Re system under study, it is clear the opposite is true and the oxo imido complex is the more stable species. With this knowledge, a larger scale synthesis of **1** directly from OReCl₂(BDI) and KNHDipp was attempted with heating

of the reaction mixture. Unfortunately, the conversion of **20** to **1** in this manner was much less efficient, likely owing to the presence of free 2,6-diisopropylaniline. While a dark red-brown solution was obtained from this reaction, the product appeared quite oily and no pure **1** could be obtained by crystallization. Considering that the current reported route to **1** involves two efficient and optimized steps from OReCl₂(BDI), we believe that the established synthesis remains the ideal route for accessing this compound or its analogs.^{22,82}

CONCLUSIONS

We have carried out a wide array of reactivity studies centered on the oxo imido complex **1**, which contains a highly polarized Re oxo moiety. A number of the reactions described in this work, including the [2 + 2] cycloaddition of heteroallenes to form isolable complexes, oxygen atom transfer to isocyanide to form a stable isocyanate complex, and the hydrozirconation of a terminal oxo ligand, have not previously been demonstrated with Re oxo complexes and, in some cases, with transition metal oxo complexes in general. Future studies will target the implementation of these transformations in catalytic reactions involving **1** or an analog thereof as well as reactivity studies of several of the new compounds described in this work, such as the carbonate complex **4**, the terminal sulfido and selenido species **7** and **8**, the rhenium(III) imido complex **11**, and the bimetallic complex **17**.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01589>.

General considerations, synthetic procedures, NMR spectra, IR absorbance spectra, crystallographic information, and computational details (PDF)

Output coordinates from DFT calculations (ZIP)

Accession Codes

CCDC 1993795–1993812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

John Arnold – Department of Chemistry, University of California, Berkeley, California 94720, United States; Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0001-9671-227X; Email: arnold@berkeley.edu

Authors

Trevor D. Lohrey – Department of Chemistry, University of California, Berkeley, California 94720, United States; Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; orcid.org/0000-0003-3568-7861

Emmanuel A. Cortes – Department of Chemistry, University of California, Berkeley, California 94720, United States

Jade I. Fostvedt – Department of Chemistry, University of California, Berkeley, California 94720, United States

Alexander K. Oanta – Department of Chemistry, University of California, Berkeley, California 94720, United States
Anukta Jain – Department of Chemistry, University of California, Berkeley, California 94720, United States
Robert G. Bergman – Department of Chemistry, University of California, Berkeley, California 94720, United States;
orcid.org/0000-0002-3105-8366

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.inorgchem.0c01589>

Notes

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