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Synthesis and Reactivity of Tris(imido)rhenium Complexes Containing Rhenium–Main Group Element Bonds. Silicon–Carbon Bond Activations of $PhSiH_3$ by Silyl Complexes

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The synthesis and reactivity of a series of complexes of the $(DippN{=})_3Re$ (Dipp $=$ 2,6-$^iPr_2C_6H_3$) fragment are reported. The anionic, Re(V) complex $(THF)_2Li(\mu,\mu\text{-}NDipp)_2Re({=}NDipp)$ (**1**), prepared by the reaction of $(DippN{=})_3ReCl$ with $(THF)_3LiSi(SiMe_3)_3$ or ^tBuLi (2 equiv) in the presence of THF (4 equiv), served as an important starting material for the synthesis of rhenium–element-bonded complexes. For example, treatment of **1** with $ClSiR_3$ gave the corresponding silyl complexes $(DippN{=})_3ReSiR_3$ ($SiR_3 = SiMe_3$ (**2a**), $SiHPh_2$ (**2b**), SiH_2Ph (**2c**)). Complexes **2a**–**c** are thought to exist in equilibrium between the Re(VII) $(DippN{=})_3ReSiR_3$ and Re(V) $(DippN{=})_2ReN(SiR_3)$-Dipp isomers. Complexes **2a**,**b** reacted with $PhSiH_3$ to give reaction mixtures that included **2c**, Ph_2SiH_2, SiH_4, and C_6H_6. The silane and organic products arise from Si–C bond formation and cleavage. Treatment of **2a** with CO gave $(DippN{=})_2Re[N(SiMe_3)Dipp](CO)$ (**3**), which appears to result from trapping of the reactive Re(V) isomer of **2a** by CO. Complex **1** reacted with the main group halides MeI, Ph_3GeCl, Me_3SnCl, Ph_2PCl, and PhSeCl to give the corresponding rhenium complexes $(DippN{=})_3ReER_n$ (ER_n = Me (**4**), $GePh_3$ (**5**), $SnMe_3$ (**6**), PPh_2 (**7**), SePh (**8**)) in high yields. X-ray diffraction data for **5** indicate that the germyl ligand is bonded to rhenium, but positional disorder of the phenyl and Dipp groups prevented refinement of accurate metric parameters.

Introduction

The chemistry of compounds containing a bond between a d^0 transition metal and a heavy main group element (from the third period and beyond) is relatively unexplored.[1−7] Such compounds are of interest for their potential to display new structures and bonding modes and because they are expected to be highly reactive.[8] For example, thermochemical data reported by Marks and co-workers indicate that σ-bonds between lanthanides and main group element ligands are relatively weak[9,10] and should readily participate in reactions such as σ-bond metathesis.[11] While d^0 transition metal−silicon chemistry has been extensively studied (especially for reactions such as σ-bond metathesis),[1,12] comparatively fewer complexes containing germyl,[3,13,14] stannyl,[3,4,14−16] phosphido,[17,18] and selenido[2] ligands have been described.

In a search for new reactivity for σ-bonds involving d^0 transition metals, we have investigated complexes containing silyl[12,14,19] and stannyl[14,15] ligands. Much of this chemistry is derived from complexes containing a bis(cyclopentadienyl)

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ancillary ligand framework. Given the formal 1σ, 2π donor analogy between cyclopentadienyl and imido ligands,[20,21] and the robust nature of the early metal imido bond,[22,23] complexes that possess both imido and main group element ligands are interesting candidates for exploration. Generally, however, complexes containing both imido ligands and reactive σ-bonds are rare. Examples of d^0 silyl complexes that contain imido ligands have been reported for hafnium,[24] niobium,[25−28] tantalum,[26−36] molybdenum,[37,38] and tungsten.[37]

Few d^0 complexes containing both imido ligands and reactive σ-bonds (e.g., M−H and M−Si) have been reported for rhenium, although the chemistry of rhenium imido complexes has been extensively investigated.[39] In 1981, La Monica et al. reported the Re(V) (d^2) complexes (p-$MeC_6H_4N{=})Re(PPh_3)_2(H)(Cl)(X)$ (X = Cl, OMe, OEt), the first examples of compounds containing both imido and hydride ligands.[40] More recently, Schrock and co-workers described the Re(V) imido hydride complex $(DippN{=})_2ReH(PMe_2Ph)_2$ (Dipp = 2,6-$^iPr_2C_6H_3$) and the high oxidation state (Re(VII)) complex $(DippN{=})_3ReH$, though some uncertainty remains regarding the structure of the latter compound.[41] Herein we report complexes of the $(DippN{=})_3Re$ fragment containing silyl and other main group element ligands and the reactivity of the silyl complexes toward silane substrates.

Results and Discussion

Preparation of an Anionic Re(V) Complex. The tris(imido)rhenium chloride complex $(DippN{=})_3ReCl$ (Dipp = 2,6-$^iPr_2C_6H_3$), reported by Schrock and Williams,[41] appeared to be a convenient starting material for the preparation of imido silyl complexes. Initial efforts focused on the synthesis of silyl derivatives via salt metathesis reactions of this compound. However, when $(DippN{=})_3ReCl$ was treated with $(THF)_3LiSi(SiMe_3)_3$, $(THF)_2LiSi(^tBu)Ph_2$, or $(THF)_2LiSiHMes_2$, the corresponding silyl complexes were not obtained. Instead, the reduced Re(V) compound $(THF)_2Li(\mu,\mu\text{-}NDipp)_2Re({=}NDipp)$ (**1**) was formed in high yield (74% isolated yield for the reaction with $(THF)_3LiSi(SiMe_3)_3$) along with the corresponding chlorosilane (eq 1). In an NMR tube scale reaction of $(DippN{=})_3ReCl$ with $KSi(SiMe_3)_3$ (benzene-d_6, room temperature, <1 min), an insoluble precipitate was obtained and $ClSi(SiMe_3)_3$ was the only product observed by ^1H NMR spectroscopy. Thus, the precipitate in the reaction mixture is likely due to an insoluble, reduced complex that might be the potassium analogue of **1**. When THF-d_8 was used as the reaction solvent, multiple products were observed in the reaction mixture (by ^1H NMR spectroscopy), indicating that the reduced potassium complex did not form cleanly.

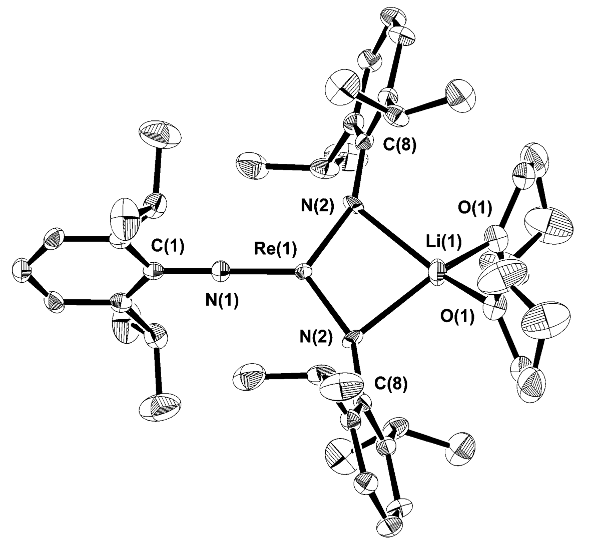
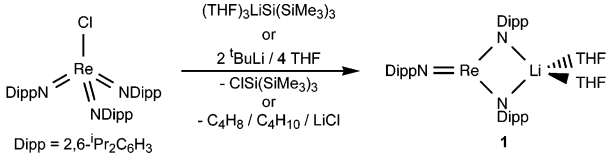


Figure 1. ORTEP diagram of $(THF)_2Li(\mu,\mu\text{-}NDipp)_2Re({=}NDipp)$ (**1**).



(1)

While reactions with silyl anions did not yield the desired products containing Re−Si bonds, complex **1** was envisioned as a precursor to silyl complexes via salt metathesis reactions with halosilanes. Therefore, a more readily available reducing agent was desired for the preparation of **1**. Fortunately, $(DippN{=})_3ReCl$ was found to react with ^tBuLi (2 equiv) in the presence of THF (4 equiv) in toluene to afford **1** in 70% yield (eq 1). Thus, this reaction is approximately as efficient as the analogous reaction with $(THF)_3LiSi(SiMe_3)_3$, but ^tBuLi is much preferred as the reagent to employ in the synthesis of **1**, as it is commercially available.

X-ray-quality crystals of **1** were obtained by cooling a concentrated pentane solution of complex **1** to −35 °C. The molecular structure is shown in Figure 1, and important bond distances and angles are listed in Table 1. One of the imido

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for $(THF)_2Li(\mu,\mu\text{-}NDipp)_2Re({=}NDipp)$ (**1**)

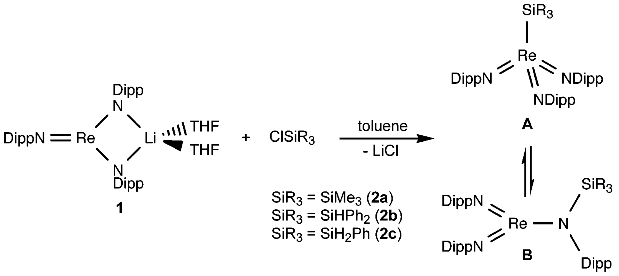
Bond Lengths			
Re(1)−N(1)	1.737(5)	N(1)−C(1)	1.410(8)
Re(1)−N(2)	1.794(3)	N(2)−C(8)	1.397(5)
Re(1)···Li(1)	2.81(1)	N(2)−Li(1)	2.297(10)
Li(1)−O(1)	1.978(8)		

Bond Angles			
Re(1)−N(1)−C(1)	180.0	Li(1)−N(2)−C(8)	120.6(3)
Re(1)−N(2)−C(8)	153.4(3)	N(2)−Li(1)−N(2)	79.0(4)
N(1)−Re(1)−N(2)	125.5(1)	O(1)−Li(1)−O(1)	103.8(6)
N(2)−Re(1)−N(2)	109.0(2)	O(1)−Li(1)−N(2)	98.0(2)
Re(1)−N(2)−Li(1)	86.0(2)	O(1)−Li(1)−N(2)	144.4(2)

ligands is terminal, with a Re═N bond length of 1.737(5) Å and a Re(1)−N(1)−C(1) bond angle of 180.0°. Two of the imido ligands bridge the Re and Li atoms, the latter of which is bonded to two THF ligands. This structure type has previously been observed for the rhenium imido complex $(tmeda)Li(\mu,\mu\text{-}N^tBu)_2Re({=}N^tBu)_2$ (tmeda = tetramethylethylenediamine).[42] In contrast, the related complex $[N(PPh_3)_2][Re({=}NDipp)_3]$ contains well-separated ion pairs.[41]

Even though the X-ray crystal structure of **1** reveals imido ligands that bridge a $Li(THF)_2$ group, only one set of imido ligand resonances were found in the ^1H NMR spectrum of **1**, indicating approximate C_{3v} symmetry. This observation suggests the presence of separated ion pairs in solution, or a rapid exchange between equivalent structures via migration of the $Li(THF)_2$ group between equivalent pairs of imido ligands. However, cooling a pentane-d_{12} solution to −105 °C revealed only one set of broadened imido ligand resonances, implying that the exchange process is still rapid at −105 °C. While the ^1H NMR spectrum of the analogous complex $(tmeda)Li(\mu,\mu\text{-}N^tBu)_2Re({=}N^tBu)_2$ also contains only one set of ligand resonances at room temperature, cooling a toluene-d_8 solution of this compound to −50 °C revealed two distinct sets of resonances for the bridging and terminal imido groups.[43]

Synthesis and Reactivity of Silyl Complexes. Since reactions of lithium and potassium silyl reagents with $(DippN{=})_3ReCl$ did not provide the desired complexes containing Re−Si bonds, silyl complexes were prepared via salt metathesis reactions of **1** with chlorosilanes. Compound **1** cleanly reacted with $ClSiMe_3$, $ClSiHPh_2$, and $ClSiH_2Ph$ in toluene to provide the corresponding silyl complexes $(DippN{=})_3ReSiR_3$ ($SiR_3 = SiMe_3$ (**2a**), $SiHPh_2$ (**2b**), SiH_2Ph (**2c**)) in 99%, 61%, and 59% yields, respectively (eq 2). Alternatively, $Me_3Si(OSO_2CF_3)$ can be used to synthesize **2a**. The ^1H NMR spectra for all three compounds **2a**−**c** contain only one set of imido ligand resonances, indicating pseudo-3-fold symmetry. The ^{29}Si NMR resonances for **2a**−**c** appear at 34.31, 14.97, and −16.52 ppm, respectively, and compounds **2b**,**c** possess $^1J_{SiH}$ values of 199 and 201 Hz. No reaction was observed between **1** and the more hindered chlorosilanes $ClSiPh_3$ (5 days) and $ClSiHMes_2$ (2 days) in benzene-d_6 at room temperature.



(2)

Cooling a toluene-d_8 solution of **2a** to −95 °C revealed only one set of broadened imido ligand resonances by ^1H NMR spectroscopy, which suggests the presence of a rhenium-bound silyl ligand (**A**, eq 2). However, given the observed behavior of **1**, it is also possible that **2a** is highly fluxional, with the silyl group migrating rapidly between the nitrogen atoms. In this case, complex **2a** might be described as having a ground-state structure with a nitrogen-bound silyl group and a Re(V) metal center (**B**). A third possibility involves an equilibrium between structures **A** and **B** in which the silyl group rapidly migrates between the rhenium and nitrogen atoms. This type of transformation is thought to occur as the initial step in the thermal decomposition of $Cp^*(DippN{=})Ta[Si(SiMe_3)_3]H$ to $Cp^*(DippN{=})Ta[CH_2Si(SiMe_3)_2SiMe_2H]H$,[31] in which the hydride ligand migrates to the imido nitrogen to give the Ta(III) compound $Cp^*Ta[N(H)Dipp]Si(SiMe_3)_3$. Schrock and Williams have suggested a related dynamic process for the hydride complex $(DippN{=})_3ReH$.[41] The latter compound features a ^1H NMR resonance at 7.22 ppm (which is reasonable for either a Re−H or N−H group), but no ν_{ReH} or ν_{NH} stretches were observed in the IR spectrum. Attempts to obtain X-ray-quality crystals of **2a** have been complicated by the high solubility of this compound in common organic solvents and the associated difficulty in growing single crystals. However, the X-ray crystal structures of $(DippN{=})_3ReMe$[44] and $(DippN{=})_3ReGePh_3$ (**5**, vide infra) reveal rhenium-bound one-electron ligands, and this suggests that **2a**−**c** possess ground-state structures with Re−Si bonds (structure **A**).

The ^{29}Si NMR data for complexes **2a**−**c** do not allow a distinction between either structure type. While the ^{29}Si NMR shift of **2a** (34.31 ppm) is somewhat downfield from the values for the nitrogen-bound silyl groups in $(DippN{=})_2Re[N(SiMe_3)Dipp](CO)$ (24.36 ppm, **3**, vide infra), $DippN(SiMe_3)H$ (3.70 ppm), and $[DippN(SiMe_3)Li]_2$ (−11.52 ppm), these differences do not appear to be significant enough to draw a meaningful conclusion regarding the ground-state structure of **2a**. Furthermore, the ^{29}Si NMR chemical shift of complex **2b** (14.97 ppm) appears in the range of complexes that contain nitrogen-bound silyl groups, and the value for **2c** (−16.52 ppm) appears upfield of all the values listed.

In some cases, chemical reactivity may provide a useful indication of structure. For example, a compound of structure type **A** is expected to possess a nucleophilic silyl group with

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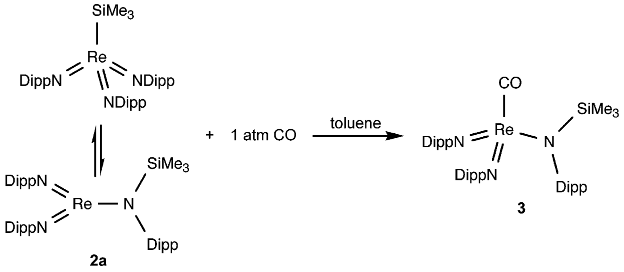
silyl anion character.[45-47] Such compounds should react with an alcohol to yield the corresponding silane $HSiR_3$ and a rhenium alkoxide. However, a compound of structure type **B** would be expected to contain an electrophilic silyl group, which should react with an alcohol to yield a silyl ether as the organic product. Treatment of **2a** with MeOH (1 equiv) in benzene-d_6 (room temperature, 30 min) gave rise to a complex reaction mixture that contained $MeOSiMe_3$ by ^1H NMR spectroscopy and GCMS. The formation of $MeOSiMe_3$ suggests the presence of an electrophilic silyl group in **2a**, which is consistent with a ground-state, nitrogen-bound structure (**B**) or with the rapid equilibrium of eq 2, where isomer **B** is much more reactive than **A** toward MeOH. Given the spectroscopic, reactivity, and structural data described above, we favor the latter possibility.

Compound **2a** reacted cleanly with CO (1 atm) at room temperature to provide the Re(V) complex (DippN=)$_2$Re[N(SiMe$_3$)Dipp](CO) (**3**) as a red-brown crystalline solid in 69% yield (eq 3). The ν_{CO} stretch at 1927 cm^{-1} and ^{13}C NMR resonance at 260.6 ppm are consistent with a rhenium-bound carbonyl ligand, and multiple Dipp resonances indicate the loss of apparent C_{3v} symmetry. The result of this reaction with CO is consistent with both structures **A** and **B** for the starting rhenium complex, assuming an equilibrium between the rhenium- and nitrogen-bound silyl group structures. A complex reaction mixture was obtained upon treating a benzene-d_6 solution of **2a** with (2,6-Me$_2$C$_6$H$_3$)N≡C (room temperature, 25 min) or DMAP (room temperature, 6 days). No reaction was observed with the donor ligands PPh$_3$, O=PPh$_3$, and 4-^{t}BuC$_5$H$_4$N (benzene-d_6, 55 °C, 4 h).



(3)

X-ray-quality crystals were obtained by cooling a concentrated pentane solution of complex **3** to −35 °C. The molecular structure is shown in Figure 2, and important bond distances and angles are listed in Table 2. Due to the steric demands of the imido and amido ligands, the compound adopts an approximate tetrahedral geometry that is highly distorted toward a trigonal pyramid. The Re(1)−N(2) and Re(1)−N(3) bond lengths of 1.759(4) and 1.781(4) Å, respectively, are well within the expected region for rhenium imido bonds.[22,23,48,49] The Re(1)−N(1) bond length of 2.004(4) and the sum of the angles around the amido nitrogen (N(1), 360°) are reasonable for a rhenium amido complex.[22,23,48,49]

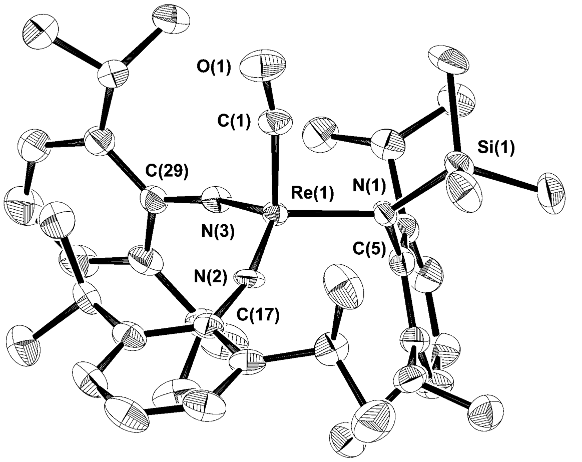


Figure 2. ORTEP diagram of (DippN=)$_2$Re[N(SiMe$_3$)Dipp](CO) (**3**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (DippN=)$_2$Re(DippNSiMe$_3$)(CO) (**3**)

Bond Lengths			
Re(1)−N(1)	2.004(4)	Re(1)−C(1)	1.905(5)
Re(1)−N(2)	1.759(4)	O(1)−C(1)	1.174(6)
Re(1)−N(3)	1.781(4)	N(1)−Si(1)	1.741(4)
N(2)−C(17)	1.391(6)	N(1)−C(5)	1.450(6)
N(3)−C(29)	1.371(6)		
Bond Angles			
Re(1)−N(1)−Si(1)	126.5(2)	N(1)−Re(1)−N(2)	116.4(2)
Re(1)−N(1)−C(5)	114.7(3)	N(1)−Re(1)−N(3)	109.4(2)
Re(1)−N(2)−C(17)	164.0(4)	N(2)−Re(1)−N(3)	121.2(2)
Re(1)−N(3)−C(29)	161.0(4)	C(1)−Re(1)−N(1)	98.5(2)
Re(1)−C(1)−O(1)	169.0(5)	C(1)−Re(1)−N(2)	99.3(2)
Si(1)−N(1)−C(5)	118.8(3)	C(1)−Re(1)−N(3)	108.5(2)

The reactivity of complexes **2a**,**b** toward substrates containing H−H and Si−H bonds was evaluated by exposing these complexes to H_2 and $PhSiH_3$. A Re(VII) silyl complex (**A**) might be expected to react with H_2 through a concerted, four-membered transition state to give $HSiMe_3$ and (DippN=)$_3$ReH.[50,51] A Re(V) silylamido complex (**B**), on the other hand, should add H_2 to give the dihydride (DippN=)$_2$Re[N(SiR$_3$)Dipp](H)$_2$. This compound could be a stable product of the reaction, or could eliminate $HSiMe_3$ to yield (DippN=)$_3$ReH. Tilley and Gountchev have observed a related silane elimination that forms a Ta(V) imido complex.[33] However, no reaction was observed between **2a** and H_2 (1 atm) at room temperature (benzene-d_6), and heating to 50 °C (12 days) resulted only in the thermal decomposition of **2a**. Hydrogen was not involved in the reaction, as indicated by the observation of identical ^1H NMR resonances when **2a** was heated to 50 °C in the absence of H_2 (benzene-d_6, 12 days). Similarly, no reaction was observed between **2b** and H_2 (1 atm) at 60 °C (5 h, benzene-d_6), and heating to 100 °C resulted in a complex reaction mixture.

Treatment of **2a** with $PhSiH_3$ (1 equiv) in benzene-d_6 (46 h) gave rise to $HSiMe_3$ (0.70 equiv) and (DippN=)$_3$Re-SiH$_2$Ph (**2c**, 0.58 equiv). Only a trace amount of unreacted $PhSiH_3$ was observed in the reaction mixture. In cyclohexane-

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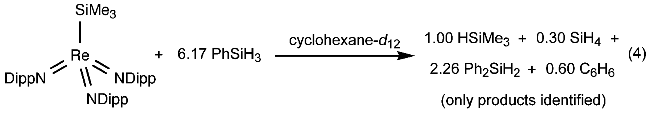
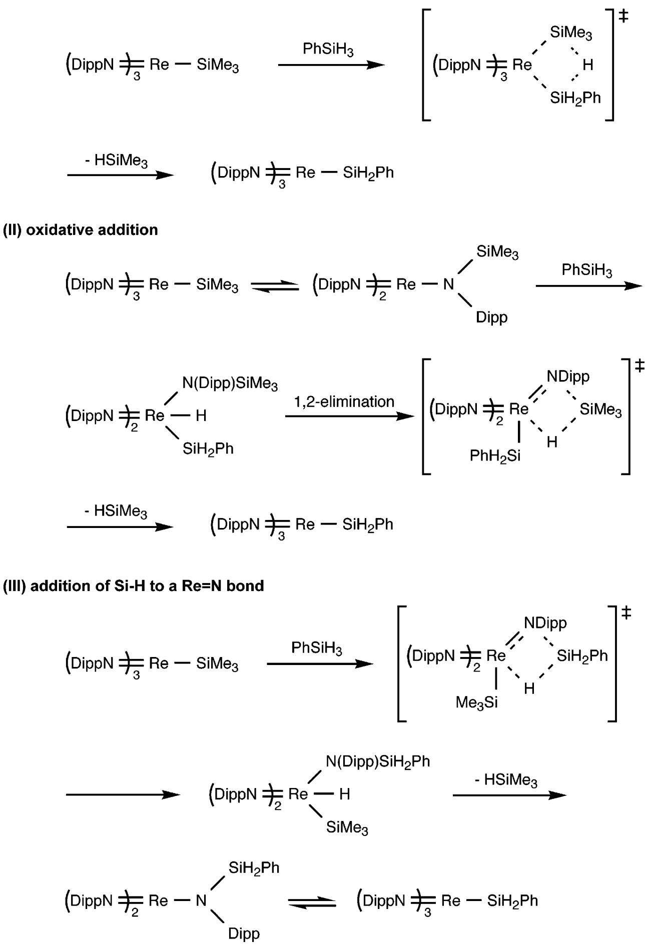
d_{12}, this reaction was observed to produce C_6H_6 (0.14 equiv; in benzene-d_6 the C_6H_6 resonance was obscured by the solvent resonance). After 16 days at room temperature, the reaction had not gone to completion. With excess $PhSiH_3$ (10 equiv), 3.00 equiv of $PhSiH_3$ were consumed after 47 h at room temperature, and $HSiMe_3$ (0.71 equiv), SiH_4 (0.14 equiv in solution), and Ph_2SiH_2 (0.94 equiv) were produced. Under these conditions, **2c** was not found among the mixture of products. After 16 days at room temperature (for the reaction of **2a** with 10 equiv of $PhSiH_3$), 4.71 equiv of $PhSiH_3$ were consumed, and increased yields of $HSiMe_3$ (0.97 equiv), SiH_4 (0.15 equiv in solution), and Ph_2SiH_2 (1.49 equiv) were observed. When cyclohexane-d_{12} was used as the solvent in the reaction of **2a** with $PhSiH_3$ (10 equiv, room temperature, 17 days), 6.17 equiv of $PhSiH_3$ were consumed and $HSiMe_3$ (1.00 equiv), SiH_4 (0.30 equiv in solution), Ph_2SiH_2 (2.26 equiv), and C_6H_6 (0.60 equiv) were formed (eq 4). The greater observed yields of the silane and organic products in cyclohexane-d_{12} (versus benzene-d_6) suggest that the reaction proceeds slightly faster in this solvent, although the apparent higher yields of some products (such as SiH_4) may be attributed to enhanced solubility. The formation of SiH_4, Ph_2SiH_2, and C_6H_6 in the reactions of **2a** with $PhSiH_3$ indicates that some type of Si−C bond activation has occurred. Furthermore, the observation of more than 1 equiv of Ph_2SiH_2 shows that this reaction is catalytic with regard to rhenium. However, none of the Re-containing products could be identified in the reaction mixture (by ^1H NMR spectroscopy). Similar product distributions have been observed in the reactions of $[Cp^*_2Ln(\mu\text{-}H)]_2$ (Ln = Sm, Lu) with $PhSiH_3$.[52−54] In these systems, mechanistic studies indicate that σ-bond metathesis reactions via concerted, four-membered transition states are responsible for the formation of products.[52]



2a



When compound **2b** was treated with $PhSiH_3$ (1 equiv) in benzene-d_6 at room temperature, some of the rhenium complex (0.60 equiv) and most of the $PhSiH_3$ (0.96 equiv) were consumed, and compound **2c** (0.28 equiv) and Ph_2SiH_2 (0.39 equiv) were observed as products by ^1H NMR spectroscopy (after 29 h). After 19 days at room temperature, complex **2c** was completely consumed, a small amount of Ph_2SiH_2 (0.12 equiv) remained, and the amount of **2b** had increased (0.62 equiv present). Thus, the Ph_2SiH_2 that is produced in this reaction is eventually converted back to **2b**. When **2b** was treated with excess $PhSiH_3$ (10 equiv) at room temperature (benzene-d_6), the rhenium complex and 2.57 equiv of $PhSiH_3$ were completely consumed within 10 h. Diphenylsilane (0.80 equiv) and SiH_4 (0.06 equiv in solution) were observed as products in the reaction mixture. Over 19 days at room temperature, a total of 6.34 equiv of $PhSiH_3$ was consumed, while Ph_2SiH_2 (1.60 equiv) and SiH_4 (0.07 equiv in solution) formed. Benzene was also formed during the course of this reaction, but it was not quantified due to the overlap of its ^1H NMR resonance with that of the benzene-d_6 solvent.

The mechanism for the formation of **2c** and $HSiMe_3$ in the reaction of **2a** with $PhSiH_3$ is not apparent, and no intermediate species could be identified by monitoring the reaction progress by ^1H NMR spectroscopy. Possible pathways for this reaction are outlined in Scheme 1. In mechanism I, the Re(VII) isomer of **2a** (**A**) reacts with $PhSiH_3$ through a concerted, four-membered transition state to yield **2c** and $HSiMe_3$. The exchange of silyl groups via this concerted σ-bond metathesis pathway is a well-precedented transformation for high-oxidation state, d^0 metal−silyl complexes[50,55,56] in the presence of imido ligands.[34] Another possibility (mechanism II) involves the oxidative addition of $PhSiH_3$ to the Re(V) isomer $(DippN{=})_2ReN(SiMe_3)Dipp$ (**B**) to give the Re(VII) complex $(DippN{=})_2Re[N(SiMe_3)Dipp](H)(SiH_2Ph)$. This compound could then undergo a 1,2-elimination of $HSiMe_3$ to produce **2c**. The formation of a metal−imido bond by silane elimination from d^0 complexes

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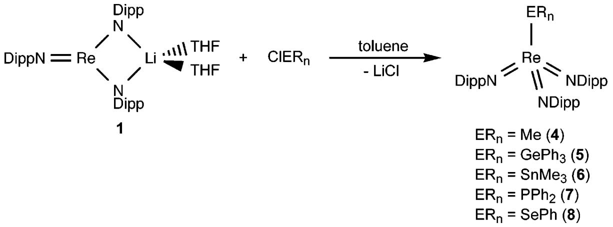
has been previously observed in a tantalum system.[33] A third possibility (mechanism III) involves addition of $PhSiH_3$ across a $Re{=}N$ double bond of the Re(VII) isomer (**A**) to generate the bis(imido) complex $(DippN{=})_2Re[N(SiH_2Ph)Dipp](H)(SiMe_3)$. The addition of silanes across a d^0 metal−imido bond to give a product with silylamido and hydride ligands has been previously observed.[33] This Re(VII) compound could then reductively eliminate $HSiMe_3$ to give $(DippN{=})_2ReN(SiH_2Ph)Dipp$, which is expected to exist in equilibrium with $(DippN{=})_3ReSiH_2Ph$ (**2c**). A related mechanism involving addition of $PhSiH_3$ to a $Re{=}N$ double bond of the Re(V) isomer (**B**), followed by 1,2-elimination of Me_3SiH from the resulting $DippN{=}Re[N(SiMe_3)Dipp][N(SiH_2Ph)Dipp](H)$ complex is also possible.

While the equilibrium between the Re(VII) and Re(V) isomers of **2a** and the lack of identifiable intermediate species in the reaction mixture (by ^1H NMR spectroscopy) cause difficulty in distinguishing among mechanisms I−III, some insight is gained by considering the reactions of **2a**,**b** with H_2. Hydrogen can react with d^0 metal−silyl complexes through a concerted, four-membered transition state (as in mechanism I) and with lower oxidation state compounds by oxidative addition to the metal center (as in mechanism II). However, since neither **2a** nor **2b** reacted with H_2 (vide supra), and since silanes and hydrogen often display similar reactivity patterns toward transition metal complexes, mechanisms I and II seem less likely than mechanism III. While a silane may undergo nucleophilic attack (mechanism III), this type of reaction is very difficult for H_2.

Preparation of Tris(imido) Complexes Containing Rhenium−Main Group Element Bonds. Complex **1** reacted cleanly with a series of main group halides, MeI, Ph_3GeCl, Me_3SnCl, Ph_2PCl, and PhSeCl, to give the corresponding rhenium imido complexes $(DippN{=})_3ReER_n$ (ER_n = Me (**4**, 97%), $GePh_3$ (**5**, 83%), $SnMe_3$ (**6**, 76%), PPh_2 (**7**, 88%), SePh (**8**, 87%); eq 5). To the best of our knowledge, compounds **5** and **6** are the first rhenium imido compounds containing germyl and stannyl ligands. The ^1H NMR spectrum of **4** is consistent with the data previously reported for this compound by Schrock and Williams.[41] No reaction was observed between **4** and $PhSiH_3$ (8.68 equiv) at temperatures as high as 100 °C (benzene-d_6, 17 h). After the reaction mixture was heated to 145 °C for 5 days, 0.77 equiv of $PhSiH_3$ and 0.11 equiv of **4** were consumed, while trace amounts of Ph_2SiH_2 (0.42 equiv) were formed. Thus, the Re−C bond of **4** does not appear to be very reactive in σ-bond metathesis processes.



(5)

X-ray diffraction data were collected for the triphenylgermyl complex $(DippN{=})_3ReGePh_3$ (**5**). Crystals of complex **5** were obtained by cooling a concentrated pentane solution to −35 °C. Although the structure and connectivity (including the rhenium-bound germyl ligand) of complex **5** were confirmed by X-ray crystallography, the refinement of accurate metric parameters was not possible due to severe positional disorder of the phenyl and Dipp groups.

Benzene-d_6 solutions of complex **5** did not react with H_2 (1 atm, 140 °C, 2 days), $PhSiH_3$ (1 equiv, 140 °C, 2 days), CO (1 atm, 140 °C, 2 days), or $(2,6\text{-}Me_2C_6H_3)N{\equiv}C$ (1 equiv, 145 °C, 18 h). Similarly, the trimethylstannyl complex $(DippN{=})_3ReSnMe_3$ (**6**) did not react with H_2 (1 atm, 145 °C, 2 days), $PhSiH_3$ (1 equiv, 140 °C, 2 days), CO (1 atm, 125 °C, 27 h), or $(2,6\text{-}Me_2C_6H_3)N{\equiv}C$ (1 equiv, 135 °C, 2 days). In addition, heating benzene-d_6 solutions of **6** with $^nBu_2SnH_2$ and $MesSnH_3$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) to 125 °C (18 h) and 60 °C (5 days), respectively, resulted in decomposition of the stannanes without any change to complex **6**. Cooling a toluene-d_8 solution of **6** to −92 °C revealed only one set of broadened ligand resonances (by ^1H NMR spectroscopy), which suggests a rhenium-bound stannyl ligand. However, recall that one set of imido ligand resonances was also observed by ^1H NMR spectroscopy at low temperature for compounds **1** and **2a**.

The diphenylphosphido complex $(DippN{=})_3RePPh_2$ (**7**) is related to the rhenium phosphido compounds $(^tBuN{=})_3RePR_2$ (R_2 = Ph_2, $(SiMe_3)_2$, Mes(H)) reported previously by Wilkinson and co-workers.[57] The crystal structure of the $(^tBuN{=})_3RePPh_2$ complex revealed a rhenium-bound phosphido ligand with a pyramidal geometry about phosphorus. Furthermore, the $^{31}P\{^1H\}$ NMR resonance of this compound at −8.78 ppm (R_2 = Ph_2) is indicative of a pyramidal phosphorus and a Re−P single bond. Complex **7** possesses a low-frequency $^{31}P\{^1H\}$ NMR chemical shift at 28.33 ppm, which suggests that this complex also features pyramidal phosphorus and a Re−P single bond.[58,59] No reaction was observed for benzene-d_6 solutions of complex **7** with H_2 (1 atm, 145 °C, 2 days), $PhSiH_3$ (1 equiv, 140 °C, 2 days), CO (1 atm, 125 °C, 27 h), or $(2,6\text{-}Me_2C_6H_3)N{\equiv}C$ (1 equiv, 135 °C, 2 days). In contrast, some early metal (d^0) phosphido complexes have been found to insert unsaturated substrates such as CO and $C_6H_{11}N{\equiv}C$. Bercaw and co-workers reported the reaction of $Cp^*HfCl_2(P^tBu_2)$ with CO to give $Cp^*HfCl_2[\eta^2\text{-}C(O)P^tBu_2]$,[18] and Hey-Hawkins and co-workers described the reaction of $Cp^\circ_2ZrCl(PHC_6H_{11})$ with $C_6H_{11}N{\equiv}C$ to yield $Cp^\circ_2ZrCl[\eta^2\text{-}C(NC_6H_{11})P(H)(C_6H_{11})]$ (Cp° = $\eta^5\text{-}C_5EtMe_4$).[17]

The phenylselenido complex $(DippN{=})_3ReSePh$ (**8**) appears to be the first example of a rhenium compound that contains both terminal imido and terminal selenido ligands. However, Batail and co-workers have previously described rhenium clusters that contain bridging imido and selenido groups.[60] The $^{77}Se\{^1H\}$ NMR spectrum of **8** contains a single

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resonance at 245.8 ppm (relative to $SeMe_2$[61]). Complex **8** did not react with $PhSiH_3$ (1 equiv, 140 °C, 2 days, benzene-*d*$_6$).

Concluding Remarks

In an effort to develop highly reactive reagents and catalysts for new chemical processes, we have explored the synthesis and reactivity of rhenium imido complexes containing rhenium−main group element bonds. These compounds are readily prepared in high yield by the treatment of $(THF)_2Li(\mu,\mu\text{-NDipp})_2Re(=NDipp)$ (**1**) with main group element halides. Spectroscopic and chemical reactivity studies suggest that **2a**−**c** are Re(VII) silyl complexes that are in equilibrium with Re(V) $(DippN=)_2ReN(SiR_3)Dipp$ isomers. The trapping of isomer **B** by CO provides support for the presence of the equilibrium in eq 2. This type of equilibrium also appears to be operative for the rhenium hydride complex $(DippN=)_3ReH$ reported by Schrock and Williams.[41] In the latter system, spectroscopic data support formulation of the complex as either the Re(VII) hydride or Re(V) bis(imido)−amido isomers, and chemical reactivity indicates that an equilibrium involving these two structures exists.

The silyl complexes **2a**,**b** exhibit somewhat unusual reactions with $PhSiH_3$, since these processes involve some type of Si−C bond activation. Related chemistry has been observed for lanthanide complexes of the type $[Cp^*{}_2Ln(\mu\text{-}H)]_2$ (Ln = Sm, Lu).[52−54] Mechanistic studies indicate that these lanthanide complexes react with $PhSiH_3$ through a concerted, four-membered transition state to yield SiH_4, Ph_2SiH_2, and C_6H_6.[52] While a concerted σ-bond metathesis pathway could occur for the reaction of **2a**,**b** with $PhSiH_3$ to form **2c** (Scheme 1, mechanism I), the equilibrium between **A** and **B** raises other mechanistic possibilities. Alternative mechanisms involve oxidative addition of $PhSiH_3$ to the rhenium metal center of structure **B** (mechanism II) or the addition of $PhSiH_3$ across the Re=N double bond of structure **A** (mechanism III). Considering the lack of reactivity of **2a**,**b** with H_2 (which generally reacts with metal complexes via a four-membered transition state or oxidative addition), mechanism III seems more likely than mechanisms I and II for the formation of **2c** and $HSiMe_3$ from **2a** (or **2b**) and $PhSiH_3$.

In summary, the tris(imido)rhenium fragment $(DippN=)_3Re$ is capable of supporting an array of main group element ligands. The bond-activation and redistribution chemistry observed in the reactions of **2a**,**b** with $PhSiH_3$ provides further evidence that new stoichiometric and catalytic processes might be based on reactive silyl complexes containing imido ligands. Current investigations are directed toward developing such reactions and expanding the range of main group element derivatives for this tris(imido) fragment.

Experimental Procedures

General Procedures. All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox unless otherwise noted. Dry, oxygen-free solvents were used unless otherwise indicated. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and saturated $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4 Å molecular sieves, and distilled from potassium benzophenone ketyl under a nitrogen atmosphere. Thiophene impurities were removed from toluene and benzene by treatment with H_2SO_4 and saturated $NaHCO_3$. Toluene and benzene were then dried over $MgSO_4$ and distilled from potassium under a nitrogen atmosphere. Tetrahydrofuran was distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Benezene-*d*$_6$ was purified and dried by vacuum distillation from sodium/potassium alloy.

NMR spectra were recorded at 500.132 (^1H), 194.371 (^7Li), 125.759 (^{13}C), 99.376 (^{29}Si), 202.457 (^{31}P), 95.363 (^{77}Se), or 186.50 (^{119}Sn) MHz using a Bruker DRX-500 spectrometer. ^1H NMR spectra were referenced internally to the residual solvent signal relative to tetramethylsilane. ^7Li NMR spectra were referenced using a 10% aqueous LiCl external standard. $^{13}C\{^1H\}$ NMR spectra were referenced internally by the ^{13}C NMR signal of the NMR solvent relative to tetramethylsilane. ^{29}Si NMR spectra were referenced using a tetramethylsilane external standard. $^{31}P\{^1H\}$ NMR spectra were referenced relative to an 85% aqueous H_3PO_4 external standard. $^{77}Se\{^1H\}$ NMR spectra were referenced relative to $SeMe_2$ via a secondary Se_2Cl_2 external standard.[61] $^{119}Sn\{^1H\}$ NMR spectra were referenced using a tetramethylstannane external standard. In some cases, distortionless enhancement by polarization transfer (DEPT) was used to assign the ^{13}C NMR resonances as CH_3, CH_2, CH, or C groups, and ^1H-coupled and decoupled insensitive nuclei enhanced by polarization transfer (INEPT) were used to identify ^{29}Si resonances and $^1J_{SiH}$ values. Heteronuclear multiple quantum coherence (HMQC) was used to identify some $^1H,^{13}C$ and $^1H,^{29}Si$ couplings, heteronuclear multiple bond correlation (HMBC) was used to identify some $^1H,^{29}Si$ couplings, and total correlation spectroscopy (TOCSY) was used to identify some coupled ^1H NMR systems. All spectra were recorded at room temperature (~22 °C) unless otherwise indicated. Infrared spectra were recorded as KBr pellets using a Mattson FTIR spectrometer at a resolution of 4 cm^{-1}. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

All chemicals were purchased from Aldrich or Fluka and used without further purification. Carbon monoxide was purchased from Scott Specialty Gases. The compounds $(2,6\text{-}^iPr_2C_6H_3N=)_3ReCl$,[41] $(THF)_3LiSi(SiMe_3)_3$,[62] $DippN(SiMe_3)H$,[63] and $[DippN(SiMe_3)Li]_2$[64] were prepared as reported in the literature. Phenylsilane was prepared by the reduction of $PhSiCl_3$ with $LiAlH_4$.

$(THF)_2Li(\mu,\mu\text{-DippN})_2Re(=NDipp)$ (1). Method A. A mixture of $(DippN=)_3ReCl$ (1.47 g, 1.97 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (0.954 g, 2.02 mmol) was dissolved in toluene (100 mL) to give a dark, yellow-orange reaction mixture. After the reaction mixture was stirred at room temperature for 2 h, the solvent was removed in vacuo to produce a red-orange oily solid. The solid was extracted with pentane (4 × 30 mL) and the extracts were filtered to give a red-orange solution. The solution was concentrated to ca. 35 mL and cooled to −35 °C to yield dark, red-orange crystals of **1** (1.26 g, 74%).

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Method B. A solution of ^{t}BuLi in pentane (1.7 M, 1.05 mmol) was added via syringe to a stirred solution of (DippN=)$_3$ReCl (0.388 g, 0.519 mmol) and tetrahydrofuran (0.170 mL, 2.10 mmol) in toluene (20 mL). Upon addition, the reaction mixture appeared dark red-orange. After the reaction mixture was stirred at room temperature for 1 h, the solvent and volatile byproducts were removed in vacuo to leave behind a dark red-orange, oily solid. The solid was extracted with pentane (5 × 10 mL) and the combined extracts were filtered to give a dark red-orange solution. The solution was concentrated to ca. 7 mL and cooled to −35 °C to afford dark red-orange crystals of **1** (0.312 g, 70%). ^{1}H NMR (benzene-d_6): δ 1.11 (m, 8 H, THF), 1.30 (d, 36 H, J = 6 Hz, ^{i}Pr-Me), 3.24 (m, 8 H, THF), 4.10 (septet, 6 H, J = 7 Hz, ^{i}Pr-H), 7.12 (t, 1 H, J = 5 Hz, Ar-H), 7.14 (d, 7 H, J = 4 Hz, Ar-H), 7.16 (d, 1 H, J = 4 Hz, Ar-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.0 (^{i}Pr-Me), 25.6 (THF), 30.0 (^{i}Pr-CH), 69.2 (THF), 122.6 (CH), 136.0, 157.6 (aromatic C's). ^{7}Li NMR (benzene-d_6): δ 4.73. IR (KBr, cm^{-1}): 680 (vw), 753 (m), 796 (w), 879 (w), 918 (w), 933 (w), 975 (m), 1036 (m), 1058 (w), 1098 (w), 1115 (w), 1158 (vw), 1178 (vw), 1221 (w), 1281 (s), 1331 (s), 1357 (m), 1380 (m), 1424 (s), 1460 (m), 1547 (vw), 1585 (w), 1917 (vw), 2869 (m), 2886 (m), 2929 (m), 2960 (s), 3055 (w). Anal. Calcd for $C_{44}H_{67}LiN_3O_2Re$: C, 61.22; H, 7.82; N, 4.87. Found: C, 61.01; H, 7.87; N, 5.19.

(DippN=)$_3$ReSiMe$_3$ (2a). Chlorotrimethylsilane (77 μL, 0.61 mmol) was added via syringe to a stirred solution of compound **1** (0.481 g, 0.557 mmol) in toluene (20 mL) to give a red-purple reaction mixture. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo to leave behind a dark red solid. The solid was extracted with pentane (3 × 15 mL) and the extracts were filtered to give a red-purple solution. The solution was concentrated to ca. 10 mL and cooled to −78 °C to yield three crops of red-purple crystals of **2a** (0.437 g, 99%). ^{1}H NMR (benzene-d_6): δ 0.85 (s, 9 H, SiMe$_3$), 1.20 (d, 36 H, J = 7 Hz, ^{i}Pr-Me), 3.92 (septet, 6 H, J = 7 Hz, ^{i}Pr-H), 7.04 (m, 1 H, Ar-H), 7.05 (s, 1 H, Ar-H), 7.06 (s, 2 H, Ar-H), 7.07 (s, 2 H, Ar-H), 7.08 (d, 1 H, J = 5 Hz, Ar-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 9.2 (SiMe$_3$), 24.2 (^{i}Pr-Me), 28.6 (^{i}Pr-H), 123.3, 127.0 (CH's), 141.8, 154.2 (aromatic C's). ^{29}Si{^{1}H} NMR (benzene-d_6): δ 34.31 (SiMe$_3$). IR (KBr, cm^{-1}): 450 (vw), 541 (vw), 620 (w), 689 (w), 753 (s), 796 (m), 837 (s), 934 (w), 988 (m), 1047 (vw), 1058 (w), 1102 (w), 1113 (w), 1159 (vw), 1178 (vw), 1241 (m), 1290 (s), 1331 (vs), 1360 (m), 1382 (w), 1424 (m), 1459 (m), 1567 (vw), 1928 (vw), 2869 (m), 2888 (m), 2926 (m), 2962 (vs), 3022 (vw), 3056 (w). Anal. Calcd for $C_{39}H_{60}N_3ReSi$: C, 59.66; H, 7.70; N, 5.35. Found: C, 59.68; H, 7.57; N, 5.29.

(DippN=)$_3$ReSiHPh$_2$ (2b). Chlorodiphenylsilane (73 μL, 0.37 mmol) was added via syringe to a stirred solution of compound **1** (0.308 g, 0.357 mmol) in toluene (10 mL) to give a red-purple reaction mixture. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo to leave behind a red-purple oily solid. The solid was extracted with pentane (3 × 10 mL) and the combined extracts were filtered to give a red-purple solution. Evaporation of the solvent gave compound **2b** as a red-purple sticky solid (0.194 g, 61%). ^{1}H NMR (benzene-d_6): δ 1.07 (d, 36 H, J = 7 Hz, ^{i}Pr-Me), 3.78 (septet, 6 H, J = 7 Hz, ^{i}Pr-H), 7.00 (m, 6 H, SiPh$_2$), 7.06 (m, 9 H, Ar-H), 7.62 (s, 1 H, SiH), 7.72 (m, 4 H, SiPh$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.0 (^{i}Pr-Me), 28.9 (^{i}Pr-CH), 123.3, 127.6, 128.7, 130.0, 137.4 (CH's), 137.7, 142.4, 154.4 (aromatic C's). ^{29}Si NMR (benzene-d_6): δ 14.97 (d of pentets, $^1J_{SiH}$ = 199 Hz, $^4J_{SiH}$ = 6 Hz, SiHPh$_2$). IR (KBr, cm^{-1}): 407 (w), 428 (w), 456 (w), 484 (m), 597 (vw), 699 (s), 714 (s), 749 (s), 796 (m), 853 (vw), 933 (w), 987 (m), 1046 (w), 1058 (w), 1101 (m), 1157 (vw), 1178 (w), 1227 (vw), 1250 (m), 1287 (s), 1329 (s), 1360 (m), 1382 (m), 1426 (s), 1459 (s), 1559 (w), 1567 (w), 1585 (w), 1653 (w), 2105 (m, ν_{SiH}), 2868 (s), 2924 (s), 2962 (vs), 3021 (w), 3054 (m). Anal. Calcd for $C_{48}H_{62}N_3ReSi$: C, 64.39; H, 6.98; N, 4.69. Found: C, 64.34; H, 7.04; N, 4.51.

ClSiH$_2$Ph. A solution of PhSiH$_3$ (5.30 g, 49.0 mmol) in benzene (10 mL) was added to solid Ph$_3$CCl (13.6 g, 48.8 mmol). The reaction vessel was sealed and heated to 60 °C for 1 week. After the colorless reaction mixture was cooled to room temperature, large crystals of Ph$_3$CH formed and were isolated by filtration. Benzene was removed by distillation under N$_2$ (1 atm), and ClSiH$_2$Ph was collected as a colorless liquid (3.82 g, 50%) that distilled at ca. 165 °C. The isolated ClSiH$_2$Ph was degassed and stored under nitrogen. The spectroscopic data for this compound agree with those reported previously by Ishikawa and co-workers.[65]

(DippN=)$_3$ReSiH$_2$Ph (2c). Chlorophenylsilane (27 μL, ~0.17 mmol) was added via syringe to a stirred solution of compound **1** (0.146 g, 0.169 mmol) in toluene (10 mL) to give a red reaction mixture. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo to leave behind a red oily solid. This solid was extracted with pentane (3 × 10 mL) and the combined extracts were filtered to give a red solution. The solution was concentrated to ca. 5 mL and cooled to −78 °C for 3 months to yield dark red crystals of compound **2c** (0.081 g, 59%). ^{1}H NMR (benzene-d_6): δ 1.15 (d, 36 H, J = 7 Hz, ^{i}Pr-Me), 3.87 (septet, 6 H, J = 7 Hz, ^{i}Pr−H), 6.59 (s, 2 H, J_{SiH} = 201 Hz, SiH), 6.96 (d, 1 H, J = 2 Hz, SiPh), 6.96 (d, 2 H, J = 2 Hz, SiPh), 7.04 (t, 1 H, J = 5 Hz, Ar-H), 7.06 (d, 6 H, J = 4 Hz, Ar-H), 7.08 (d, 2 H, J = 5 Hz, Ar-H), 7.65 (m, 2 H, SiPh). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.0 (^{i}Pr-Me), 28.9 (^{i}Pr-CH), 123.2, 127.8, 128.6, 130.2 (CH's), 134.9 (aromatic C), 137.0 (CH), 142.5, 154.4 (aromatic C's). ^{29}Si NMR (benzene-d_6): δ −16.52 (tt, $^1J_{SiH}$ = 201 Hz, $^4J_{SiH}$ = 7 Hz, SiH$_2$Ph). IR (KBr, cm^{-1}): 410 (w), 453 (vw), 488 (w), 706 (m), 753 (s), 780 (vs), 914 (m), 932 (m), 988 (m), 1046 (w), 1060 (w), 1102 (m), 1114 (m), 1226 (vw), 1250 (m), 1287 (s), 1328 (vs), 1360 (m), 1382 (m), 1421 (m), 1461 (m), 1549 (vw), 1567 (w), 1585 (w), 2127 (m, ν_{SiH}), 2146 (m, ν_{SiH}), 2869 (m), 2924 (m), 2962 (vs), 3021 (w), 3056 (m). Anal. Calcd for $C_{42}H_{58}N_3ReSi$: C, 61.58; H, 7.14; N, 5.13. Found: C, 61.60; H, 7.06; N, 4.99.

DippN(SiMe$_3$)H. This compound was prepared according to the method described by Wigley and co-workers.[63] ^{29}Si{^{1}H} NMR (benzene-d_6): δ 3.70.

[DippN(SiMe$_3$)Li]$_2$. This compound was prepared according to the method described by Roesky and co-workers.[64] ^{29}Si{^{1}H} NMR (benzene-d_6): δ −11.52.

(DippN=)$_2$Re[N(SiMe$_3$)Dipp](CO) (3). Compound **2a** (0.204 g, 0.260 mmol) was dissolved in toluene (10 mL), and the resulting solution was transferred to a 50 mL reaction vessel. The solution was degassed, CO (1 atm) was admitted, and the reaction solution was stirred at room temperature. After 1.5 h, the solvent was removed in vacuo to leave behind a dark red solid that was extracted into pentane (3 × 10 mL). The combined extracts were concentrated to ca. 5 mL and cooled to −35 °C to afford two crops of red-brown crystals of compound **3** (0.145 g, 69%). ^{1}H NMR (benzene-d_6): δ 0.37 (s, 9 H, SiMe$_3$), 1.04 (broad s, 18 H, ^{i}Pr-Me), 1.09 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.25 (broad d, 6 H, J = 7 Hz, ^{i}Pr-Me), 3.40 (broad s, 4 H, ^{i}Pr-H), 3.76 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 6.97 (d, 4 H, J = 7.5 Hz, Ar-H), 7.07 (m, 5 H, Ar-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 4.5 (broad, SiMe$_3$), 23.5 (^{i}Pr-Me), 24.6 (broad, ^{i}Pr-Me), 25.9 (^{i}Pr-Me), 28.3 (^{i}Pr-H), 28.9 (^{i}Pr-H), 123.6

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(65) Kunai, A.; Kawakami, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1992**, *11*, 2708.

(CH), 125.1 (broad, CH), 125.9 (CH), 127.7 (CH), 142.6 (aromatic C), 145.7 (broad, aromatic C), 156.8 (aromatic C), 260.6 (broad, CO). ^{29}Si{^{1}H} NMR (benzene-d_6): δ 24.36 (SiMe$_3$). IR (KBr, cm^{-1}): 439 (w), 476 (vw), 533 (w), 632 (vw), 679 (vw), 745 (m), 761 (w), 792 (m), 833 (m), 853 (m), 880 (w), 908 (m), 932 (w), 978 (w), 1049 (vw), 1058 (vw), 1101 (w), 1180 (w), 1247 (m), 1274 (w), 1292 (w), 1337 (w), 1360 (w), 1382 (w), 1422 (w), 1430 (w), 1460 (w), 1584 (vw), 1927 (vs, ν_{CO}), 2867 (w), 2926 (w), 2963 (s), 3059 (vw). Anal. Calcd for $C_{40}H_{60}N_3OReSi$: C, 59.08; H, 7.44; N, 5.17. Found: C, 59.33; H, 7.37; N, 5.37.

(DippN=)$_3$ReMe (4). Iodomethane (20 μL, 0.32 mmol) was added via syringe to a stirred solution of compound **1** (0.256 g, 0.297 mmol) in toluene (10 mL) to give a dark red reaction mixture. After the reaction mixture was stirred at room temperature for 2 h, the solvent and excess MeI were removed in vacuo to leave behind a dark red solid. The solid was extracted with pentane (3 × 10 mL) and the combined extracts were filtered to give a dark red solution. The solution was concentrated to ca. 5 mL and cooled to -35 °C to yield two crops of dark red crystals of compound **4** (0.210 g, 97%). The spectroscopic data for this compound agree with those reported previously by Schrock and co-workers.[41]

(DippN=)$_3$ReGePh$_3$ (5). Compound **1** (0.368 g, 0.426 mmol) and Ph$_3$GeCl (0.145 g, 0.427 mmol) were dissolved in toluene (15 mL) to give a red-orange reaction mixture. Over the course of 1 day, the reaction mixture became red-purple in color. After the reaction mixture was stirred at room temperature for 3 days, the solvent was removed in vacuo to leave behind a red-purple oily solid. The solid was extracted with pentane (3 × 10 mL) and the combined extracts were filtered to give a red-purple solution. The solution was concentrated to ca. 8−10 mL and cooled to -35 °C to yield three crops of red crystals of compound **5** (0.361 g, 83%). ^{1}H NMR (benzene-d_6): δ 0.97 (d, 36 H, $J = 7$ Hz, ^{i}Pr-Me), 3.65 (septet, 6 H, $J = 7$ Hz, ^{i}Pr-H), 7.01 (m, 10 H, Ar-H), 7.03 (s, 2 H, Ar-H), 7.04 (s, 4 H, Ar-H), 7.06 (d, 2 H, $J = 2$ Hz, Ar-H), 7.66 (m, 6 H, GePh$_3$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.0 (^{i}Pr-Me), 28.9 (^{i}Pr-CH), 123.3, 127.4, 129.0, 129.3, 136.6 (CH's), 142.2, 142.6, 154.3 (aromatic C's). IR (KBr, cm^{-1}): 457 (m), 468 (m), 541 (vw), 600 (vw), 670 (w), 699 (s), 736 (s), 751 (s), 795 (m), 933 (w), 988 (m), 1024 (vw), 1046 (w), 1058 (w), 1083 (m), 1104 (w), 1114 (w), 1176 (w), 1186 (w), 1227 (w), 1251 (m), 1287 (vs), 1308 (m), 1329 (vs), 1360 (m), 1382 (m), 1428 (s), 1460 (s), 1482 (w), 2803 (w), 2868 (s), 2885 (m), 2925 (s), 2963 (vs), 3023 (w), 3052 (m). Anal. Calcd for $C_{54}H_{66}GeN_3Re$: C, 63.84; H, 6.55; N, 4.14. Found: 63.97; H, 6.37; N, 4.09.

(DippN=)$_3$ReSnMe$_3$ (6). Compound **1** (0.270 g, 0.313 mmol) and Me$_3$SnCl (0.0624 g, 0.313 mmol) were dissolved in toluene (10 mL) to give a red-purple reaction mixture. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo to leave behind a red-purple oily solid. The solid was extracted with pentane (3 × 10 mL) and the combined extracts were filtered to give a red-purple solution. The solution was concentrated to ca. 3 mL and cooled to -35 °C to yield two crops of red crystals of compound **6** (0.207 g, 76%). ^{1}H NMR (benzene-d_6): δ 0.73 (s, 9 H, $J_{SnH} = 50$ Hz, SnMe$_3$), 1.20 (d, 36 H, $J = 7$ Hz, ^{i}Pr-Me), 3.86 (septet, 6 H, $J = 7$ Hz, ^{i}Pr-H), 7.03 (m, 1 H, Ar-H), 7.05 (s, 2 H, Ar-H), 7.06 (s, 4 H, Ar-H), 7.07 (d, 2 H, $J = 5$ Hz, Ar-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ -0.9 (SnMe$_3$), 24.0 (^{i}Pr-Me), 28.8 (^{i}Pr−CH), 123.2, 126.9 (CH's), 141.5, 154.3 (aromatic C's). ^{119}Sn{^{1}H} NMR (benzene-d_6): δ 69.54. IR (KBr, cm^{-1}): 448 (vw), 507 (w), 524 (m), 753 (s), 795 (m), 933 (w), 989 (s), 1046 (w), 1058 (w), 1103 (w), 1112 (w), 1159 (vw), 1178 (w), 1227 (w), 1250 (m), 1291 (s), 1332 (s), 1360 (m), 1382 (m), 1423 (s), 1459 (s), 2706 (w), 2722 (w), 2753 (w), 2803 (w), 2868 (s), 2886 (m), 2924 (s), 2961 (s), 3022 (w), 3056 (w). Anal. Calcd for $C_{39}H_{60}N_3ReSn$: C, 53.48; H, 6.91; N, 4.80. Found: C, 53.43; H, 7.00; N, 5.12.

(DippN=)$_3$RePPh$_2$ (7). Chlorodiphenylphosphine (61 μL, 0.34 mmol) was added via syringe to a stirred solution of compound **1** (0.292 g, 0.339 mmol) in toluene (10 mL) to give a red-purple reaction mixture. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo to leave behind a red-purple solid. The solid was extracted with pentane (3 × 10 mL) and the combined extracts were filtered to give a red-purple solution. The solution was concentrated to ca. 5 mL and cooled to -78 °C to yield red crystals of compound **7** (0.268 g, 88%). ^{1}H NMR (benzene-d_6): δ 1.03 (s, 36 H, $J = 7$ Hz, ^{i}Pr-Me), 3.62 (septet, 6 H, $J = 7$ Hz, ^{i}Pr-H), 6.86 (t, 2 H, $J = 8$ Hz, PPh$_2$), 6.97 (td, 4 H, $J = 8$ Hz, $J = 2$ Hz, PPh$_2$), 7.01 (dd, 3 H, $J = 9$ Hz, $J = 6$ Hz, Ar-H), 7.04 (s, 4 H, Ar−H), 7.06 (d, 2 H, $J = 2$ Hz, Ar-H), 7.70 (td, 4 H, $J = 8$ Hz, $J = 2$ Hz, PPh$_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.2 (^{i}Pr-Me), 28.9 (^{i}Pr-CH), 123.2, 127.4, 128.7 (CH's), 129.1 (d, $^3J_{PC} = 6$ Hz, *m*-PPh$_2$), 136.6 (d, $^2J_{PC} = 18$ Hz, *o*-PPh$_2$), 141.0 (d, $^1J_{PC} = 28$ Hz, aromatic-PPh$_2$), 142.6 (aromatic C), 154.1 (d, $^3J_{PC} = 1$ Hz, aromatic C). ^{31}P{^{1}H} NMR (benzene-d_6): δ 28.33 (s, $J_{PC} = 18$ Hz, PPh$_2$). IR (KBr, cm^{-1}): 504 (w), 696 (m), 739 (m), 753 (s), 796 (w), 934 (w), 1046 (vw), 1058 (w), 1102 (w), 1114 (w), 1179 (vw), 1226 (w), 1250 (m), 1285 (vs), 1307 (m), 1328 (vs), 1359 (m), 1382 (m), 1421 (m), 1432 (m), 1460 (m), 1581 (vw), 2801 (vw), 2867 (m), 2924 (m), 2962 (vs), 3022 (vw), 3055 (m). Anal. Calcd for $C_{48}H_{61}N_3PRe$: C, 64.26; H, 6.85; N, 4.68. Found: C, 64.48; H, 6.98; N, 4.62.

(DippN=)$_3$ReSePh (8). Compound **1** (0.182 g, 0.210 mmol) and PhSeCl (0.041 g, 0.21 mmol) were dissolved in toluene (10 mL) to give a red-brown reaction mixture. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo to leave behind a red-brown solid. The solid was extracted with pentane (3 × 10 mL) and the combined extracts were filtered to give a dark, red-brown solution. The solution was concentrated to ca. 5 mL and cooled to -35 °C to yield two crops of long, blocklike, brown crystals of compound **8** (0.160 g, 87%). ^{1}H NMR (benzene-d_6): δ 1.08 (d, 36 H, $J = 7$ Hz, ^{i}Pr-Me), 3.74 (septet, 6 H, $J = 7$ Hz, ^{i}Pr-H), 6.80 (tt, 1 H, $J = 7$ Hz, $J = 2$ Hz, *p*-SePh), 6.87 (tt, 2 H, $J = 7$ Hz, $J = 2$ Hz, SePh), 6.99 (dd, 3 H, $J = 9$ Hz, $J = 6$ Hz, Ar-H), 7.03 (s, 4 H, Ar-H), 7.05 (d, 2 H, $J = 2$ Hz, Ar-H), 7.87 (dq, 2 H, $J = 8$ Hz, $J = 1$ Hz, SePh). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.0 (^{i}Pr-Me), 29.2 (^{i}Pr-CH), 123.1, 127.0, 127.6, 129.7 (CH's), 131.6 (aromatic C), 135.4 (CH), 142.6, 154.0 (aromatic C's). ^{77}Se{^{1}H} NMR (benzene-d_6): δ 245.8 (SePh). IR (KBr, cm^{-1}): 429 (vw), 445 (vw), 460 (vw), 540 (vw), 597 (vw), 665 (vw), 690 (w), 738 (m), 753 (s), 797 (m), 934 (m), 987 (m), 1021 (w), 1046 (w), 1061 (m), 1102 (m), 1116 (w), 1159 (vw), 1178 (w), 1227 (w), 1251 (m), 1287 (vs), 1328 (vs), 1360 (m), 1382 (m), 1420 (m), 1438 (m), 1460 (m), 1574 (m), 1926 (vw), 1942 (vw), 2711 (vw), 2722 (vw), 2754 (vw), 2801 (vw), 2867 (m), 2924 (m), 2960 (vs), 3023 (vw), 3057 (w). Anal. Calcd for $C_{42}H_{56}N_3ReSe$: C, 58.11; H, 6.50; N, 4.84. Found: C, 58.33; H, 6.69; N, 4.69.

X-ray Structure Determinations. X-ray diffraction measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation. The crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range 4° (or 3.5°) $< 2\theta <$ 45°. The frame data were integrated using the program SAINT.[66] An empirical absorp-

Table 3. Crystallographic Data for Compounds **1** and **3**

param	**1**	**3**
empirical formula	$C_{44}H_{67}N_3O_2LiRe$	$C_{40}H_{60}N_3OReSi$
fw	863.18	813.23
cryst color, habit	red plate	red block
cryst size (mm)	0.22 × 0.20 × 0.12	0.35 × 0.35 × 0.30
cryst system	monoclinic	triclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	17.9687(4)	9.8121(5)
b (Å)	13.1938(4)	11.4850(6)
c (Å)	18.5450(5)	18.3071(9)
α (deg)		96.247(1)
β (deg)	100.643(1)	92.516(1)
γ (deg)		101.806(1)
V (Å^3)	4320.9(2)	2002.8(2)
orientatn reflcns (2θ range (deg))	6169 (3.5−49.3)	7919 (4.487−49.509)
Z value	4	2
D_{calc} (g/cm^3)	1.327	1.348
F_{000}	1784.00	836.00
μ(Mo Kα) (cm^{-1})	28.50	30.97
diffractometer	SMART	SMART
graphite-monochromated radiatn (λ (Å))	Mo Kα (0.710 69)	Mo Kα (0.710 69)
temp (°C)	−124.0	−112
scan type (0.3°/frame)	ω	ω
scan rate (s/frame)	10.0	10.0
2θ_{max} (deg)	49.3	49.5
reflcns measd	tot.: 9610 unique: 3709	tot.: 10 132 unique: 6352
R_{int}	0.042	0.032
transm factors	$T_{max} = 0.71$ $T_{min} = 0.48$	$T_{max} = 0.395$ $T_{min} = 0.338$
struct soln	direct methods (SIR92)	direct methods (SIR92)
no. of observns	3001 ($I > 3.00\sigma(I)$)	5483 ($I > 3.00\sigma(I)$)
no. of variables	233	415
reflcns/param ratio	12.88	13.21
residuals: R; R_w; R_{all}	0.029; 0.033; 0.036	0.033; 0.038; 0.037
goodness of fit	1.13	1.25
max shift/error in final cycle	0.00	0.00
max and min peaks in final diff map (e$^-$/Å^3)	1.22, −1.38	1.60, −2.25

tion correction based on measurements of multiply redundant data was performed using the program SADABS.[67] XPREP[68] clearly indicated the space group. Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. A secondary extinction correction was applied if appropriate. The structures were solved using the teXsan crystallographic software package of the Molecular Structure Corp., using direct methods, and expanded with Fourier techniques. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions but not refined unless otherwise noted. The function minimized in the full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a p-factor to downweight the intense reflections. Crystallographic data are summarized in Table 3.

Compound 1. Crystals suitable for X-ray diffraction were obtained by cooling a concentrated pentane solution of **1** to −35 °C. An orientation matrix gave a *C*-centered, monoclinic cell with dimensions described in Table 3. Data were collected for 10 s frames. The raw data were integrated using SAINT,[66] and an empirical absorption correction was applied using SADABS.[67] In addition, XPREP[68] clearly indicated the space group was $C2/c$ (No. 15). The structure was solved using direct methods (SIR92) and was found to contain one molecule of the rhenium complex/asymmetric unit. The molecule lies on a 2-fold axis at [0, *y*, 0.25], and as such, half of the atoms are related by symmetry. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically in geometrically calculated positions.

Compound 3. Crystals suitable for X-ray diffraction were obtained by cooling a concentrated pentane solution of **3** to −35 °C. An orientation matrix gave a primitive, triclinic cell with dimensions described in Table 3. Data were collected for 10 s frames. The raw data were integrated using SAINT,[66] and an empirical absorption correction was applied using SADABS.[67] In addition, XPREP[68] clearly indicated the space group was $P\bar{1}$ (No. 2). The structure was solved using direct methods (SIR92) and was found to contain one molecule of the rhenium complex/asymmetric unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically in geometrically calculated positions.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for complexes **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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