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High-Oxidation-State Rhenium Cp* Complexes Containing Hydrazine, Hydrazido, Ammonia, and Amido Ligands

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Paramagnetic Cp^*ReMe_4 reacts with triflic acid to give $Cp^*ReMe_3(OTf)$ (1) in 90% yield. Hydrazine reacts with 1 to give diamagnetic $[Cp^*ReMe_3(NH_2NH_2)][OTf]$ (**2a**), which is deprotonated to give $Cp^*ReMe_3(NHNH_2)$ (**3a**) in good yield, or with ammonia to give $[Cp^*ReMe_3(NH_3)_2][OTf]$ (**4**). **4** reacts with 1 to give $[Cp^*ReMe_3(NH_3)][OTf]$ (**5**) and is deprotonated to give ammonia and $Cp^*ReMe_3(NH_2)$ (**6a**). Methyl-substituted analogs of **2a** have also been prepared by methods similar to those used to prepare the parent compounds. Reduction of **2a** in the presence of 2,6-lutidine hydrochloride in THF yields 1.20 equiv of ammonia using zinc amalgam and 1.46 equiv of ammonia using 0.5% sodium amalgam. In the absence of protons **2a** is reduced by zinc amalgam to give 1.00 equiv of ammonia. $Cp^*ReMe_3(OTf)$ (1) and $[Cp^*ReMe_3(NH_3)][OTf]$ (**5**) show temperature-dependent proton NMR spectra that are proposed to be the consequence of an equilibrium between a diamagnetic square-pyramidal ground state and a paramagnetic trigonal-bipyramidal excited state.

Introduction

Over the last few years we have been exploring the chemistry of molybdenum and tungsten that is relevant to activation and reduction of dinitrogen, in particular the chemistry of N_2H_x ligands in mono-Cp* tungsten and molybdenum complexes in which the metal is in a relatively high oxidation state (4+, 5+, or 6+). For example, $[Cp^*WMe_3]_2(\mu\text{-}N_2)$ can be prepared in high yield by reducing $Cp^*WMe_3(OTf)$ ($Cp^* = \eta^5\text{-}C_5Me_5$, $OTf = OSO_2CF_3$) in the presence of dinitrogen,[1] good evidence that a metal in a relatively high oxidation state (probably d^2 in this case) can bind dinitrogen. Many monomeric N_2H_x species (x = 2–4) that contain the Cp^*WMe_3 core also are now known, examples being $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]^+$ [2] and $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]^+$,[3,4] as well as complexes containing NH_y ligands that are possible intermediates in a reduction cycle, e.g., $Cp^*WMe_3(NH)$, $Cp^*WMe_3(NH_2)$, and $[Cp^*WMe_3(NH_3)_x]^+$ (x = 1, 2).[5] We have found that ammonia is produced in high yield when monomeric Cp^*WMe_3 species in which the N–N bond is still present are reduced in the presence of protons and that hydrazine can be reduced catalytically to ammonia under similar conditions.[3,4] Analogous Mo complexes have been prepared and employed to reduce hydrazine catalytically in yields comparable to the analogous W complexes,[6] but in general the chemistry of molybdenum has been more difficult to control and elucidate.

One of the most important goals in this area has been to determine how the N–N bond is cleaved. All evidence at this stage suggests that the N–N bond is cleaved in an unobservable d^2 complex, e.g., $Cp^*WMe_3(\eta^x\text{-}N_2H_4)$ (x = 1, 2).[4] The two d electrons in this species are used to cleave the N–N bond to give ammonia and $Cp^*WMe_3(NH)$, a stable species. Several possible mechanisms have been proposed, among them two in which the metal is oxidized from W(IV) to W(VI).[4] Since the proposed, and, in part, observed mechanism of sequential reduction of dinitrogen involves addition of a proton to a given neutral species followed by addition of one electron to the resulting cationic species, approximately half of the intermediates are paramagnetic (d^1) species. An example is $[Cp^*WMe_3(\eta^2\text{-}N_2H_4)]^+$, a stable d^1 species that upon reduction by one electron yields ammonia and $Cp^*WMe_3(NH)$.[3,4]

In this paper we report the chemistry of $[Cp^*ReMe_3(N_2H_x)]^{n+}$ and $[Cp^*ReMe_3(NH_x)_y]^{n+}$ (n = 0, 1) complexes. We were especially interested in whether such species could be prepared, and if so, whether they could be involved in a series of reactions in which dinitrogen is reduced to ammonia. An important secondary reason for exploring rhenium chemistry is that the d^2 Re(V) analogs of paramagnetic d^1 Mo(V) or W(V) intermediates could be diamagnetic. Some of this work has been reported in a preliminary fashion.[7]

Results

Synthesis and Reactivity of $Cp^*ReMe_3(OTf)$ (1). The starting point for Cp^*WMe_3 chemistry has been Cp^*WMe_4, which is prepared in high yield from the readily available Cp^*WCl_4.[8,9] One methyl group is removed from Cp^*WMe_4 upon addition of triflic acid to give $Cp^*WMe_3(OTf)$.[1] The reaction between Cp^*ReMe_4[10] and triflic acid proceeds similarly to produce $Cp^*ReMe_3(OTf)$ (1) as a light yellow solid in 85% yield (eq 1). A proton NMR spectrum of 1 in CD_2Cl_2 is highly temperature dependent

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$$\mathrm{Cp^{*}ReMe_4} \xrightarrow[\mathrm{-CH_4}]{\mathrm{HOTf}} \underset{\mathbf{1}}{\mathrm{Cp^{*}ReMe_3(OTf)}} \qquad (1)$$

in the range −95 to +25 °C (Figures 1 and 2). At −95 °C the Cp* resonance and two methyl resonances (in a ratio of 1:2 at 3.10 and 2.70 ppm, respectively) can be observed in the expected region of the spectrum. The methyl resonances (and to a much smaller degree the Cp* resonance) shift downfield at higher temperatures. At 298 K the predicted chemical shifts of the Me(cis) resonance, on the basis of the best binomial curve fit to the points shown in Figure 2, is 7.76 ppm; the predicted chemical shift of the Me(trans) resonance is 8.18 ppm. The observed resonance is found at a weighted average of those two chemical shifts (7.90 ppm), consistent with interconversion of Me(cis) and Me(trans) on the NMR time scale with a $\Delta G^{\ddagger}$ value of ca. 13–15 kcal mol^{-1} at room temperature for that process. One possible explanation for the observed NMR behavior of **1** is that triflate is being lost from the metal to give [Cp*ReMe$_3$][OTf], in which the three methyl groups are equivalent. That process would not explain the dramatic downfield shift of the methyl resonances (especially) at 25 °C, unless the small amount of [Cp*ReMe$_3$]$^+$ that is present is paramagnetic. However, addition of Li[OTf] to a solution of **1** does not alter the NMR behavior. Therefore, we favor an explanation in which the ground-state structure of **1** consists of a diamagnetic species, most likely a square pyramid, which is in rapid equilibrium with a paramagnetic species, most likely a pseudo trigonal bipyramid containing an axial triflate ligand. The temperature-dependent behavior is discussed in more detail in a later section, since another complex reported later behaves similarly.

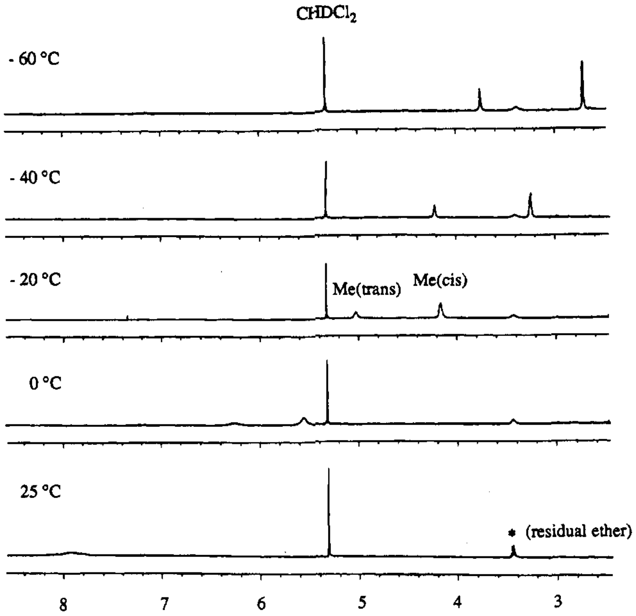


Figure 1. Variable-temperature proton NMR spectra of Cp*ReMe$_3$(OTf) (**1**) in CD$_2$Cl$_2$.

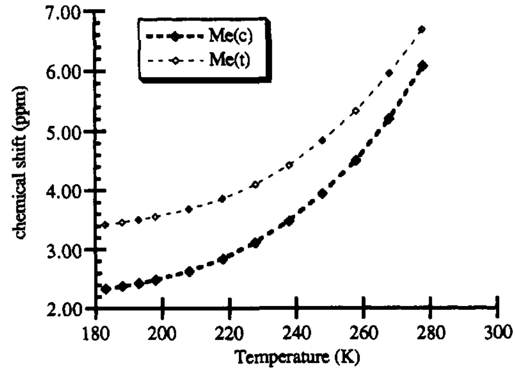


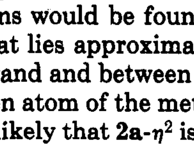
Figure 2. Chemical shift of the Me(cis) and Me(trans) methyl ligands in Cp*ReMe$_3$(OTf) (**1**) versus temperature.

The general characteristics of Cp*ReMe$_3$(OTf) are more similar to those of Cp*MoMe$_3$(OTf)[6] than to those of the relatively stable Cp*WMe$_3$(OTf). Cp*ReMe$_3$(OTf) is not stable in solution (dichloromethane, toluene, ether, etc.) at room temperature for more than a few hours at 25 °C. It decomposes by losing methane; the paramagnetic species that is (are) formed has (have) not been characterized. It also decomposes slowly in the solid state, even at −40 °C. Cyclic voltammetric studies of **1** (in dichloromethane at 25 °C, 0.1 M [NBu$_4$][BF$_4$]) reveal an irreversible reduction wave at −1.06 V and an irreversible oxidation wave at 1.10 V versus FeCp$_2$$^{0/+}$.

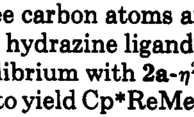
Synthesis and Reactivity of Re(V) Hydrazine Complexes. Addition of hydrazine to **1** in diethyl ether at 25 °C yields pale orange [Cp*ReMe$_3$(N$_2$H$_4$)][OTf] (**2a**; eq 2). IR spectra of **2a** are virtually identical with those

$$\mathrm{Cp^{*}ReMe_3(OTf)} \xrightarrow[\text{ether, 25 °C}]{\mathrm{N_2H_4}} \underset{\mathbf{2a}}{\mathrm{[Cp^{*}ReMe_3(N_2H_4)][OTf]}} \qquad (2)$$

of [Cp*WMe$_3$(η^2-N$_2$H$_4$)][OTf], including absorptions characteristic of ionic triflate.[4] The proton NMR spectrum of **2a** reveals two broad resonances at 5.70 and 6.40 ppm corresponding to two pairs of hydrazine protons. The Cp* resonance is observed at 1.70 ppm, while the Re methyl resonances are found in a 1:2 ratio at 0.45 and 0.05 ppm, respectively. The NMR spectra of **2a** do not vary significantly with temperature. The ^{15}N NMR spectrum of ^{15}N-labeled **2a** revealed two resonances at 44.5 and 12.8 ppm (J_{NH} = 84 Hz, J_{NN} = 8 Hz). These data and difference NOE experiments are consistent with either structure **2a**-η^1 or **2a**-η^2. We favor structure **2a**-η^2 since it is an 18-electron species with a structure analogous to that observed for [Cp*WMe$_3$(η^2-N$_2$H$_4$)][OTf].[4] In **2a**-η^2 the two d electrons would be found in the orbital (approximately d$_{xy}$) that lies approximately parallel to the plane of the Cp* ligand and between the three carbon atoms and one nitrogen atom of the methyl and hydrazine ligands.[4,11] It seems likely that **2a**-η^2 is in equilibrium with **2a**-η^2, since **2a** reacts readily with triflic acid to yield Cp*ReMe$_3$(OTf) (**1**) and [N$_2$H$_5$][OTf] and since both [Cp*ReMe$_3$(NH$_3$)$_2$][OTf] and [Cp*ReMe$_3$(NH$_3$)][OTf] (see below) can be prepared. There is evidence for an analogous equilibrium between [Cp*WMe$_3$(η^2-N$_2$H$_4$)][OTf] and [Cp*WMe$_3$(η^1-N$_2$H$_4$)][OTf].[4]



2a-η^1



2a-η^2

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[11] Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

$[Cp^*ReMe_3(N_2H_4)][OTf]$ (**2a**) is only moderately stable in solution. Over a period of several hours at 25 °C a solution of **2a** decomposes to yield a species whose properties are consistent with it being $Cp^*ReMe_3(\eta^2\text{-}NHNH_2)$ (**3a**). Hydrazinium triflate and **1**, plausible coproducts of decomposition of **2a** via an intermolecular proton transfer, are not observed. (The synthesis and properties of **3a** are reported later.) This behavior is analogous to that reported for $[Cp^*WMe_3(\eta^2\text{-}N_2H_4)][OTf]$, which is believed to decompose by intermolecular proton transfer, except $Cp^*WMe_3(NHNH_2)$ is not observed; it disproportionates (it is proposed) to $Cp^*WMe_3(NNH_2)$ and $Cp^*WMe_3(NH_2NH_2)$. An important point is that **2a** does not decompose to yield ammonia, as does $Cp^*WMe_3(NH_2NH_2)$, an unobserved isoelectronic W(IV) d^2 complex. We will discuss this point in more detail later.

Cyclic voltammetry studies of **2a** (in a 0.1 M solution of $[NBu_4][BF_4]$ in CH_2Cl_2 versus Ag/Ag^+) show that it possesses an irreversible reduction wave at −0.70 V, a second pseudoreversible reduction wave at −0.85 V, and an irreversible oxidation wave at 0.74 V. (Analogous studies of $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]^+$ reveal a reduction wave at −0.65 V,[4] consistent with the greater ease of reducing W(IV) compared to reducing Re(V).) $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]^+$ can be reduced by zinc amalgam in THF in the presence of 2,6-lutidinium chloride to yield 1.86 equiv of ammonia. Reduction of **2a** in the presence of 2,6-lutidinium chloride in THF with sodium amalgam as the reductant yielded 1.50 equiv of ammonia, and with zinc amalgam, 1.20 equiv of ammonia. In the absence of protons **2a** is reduced by zinc amalgam in THF to give 1.00 equiv of ammonia.

Other cationic Re(V) hydrazine adducts can be prepared readily. $Cp^*ReMe_3(OTf)$ (**1**) reacts with methylhydrazine to yield $[Cp^*ReMe_3(N_2H_3Me)][OTf]$ (**2b**), with 1,1-dimethylhydrazine to yield $[Cp^*ReMe_3(NH_2NMe_2)][OTf]$ (**2c**), and with 1,2-dimethylhydrazine to yield $[Cp^*ReMe_3(NHMeNHMe)][OTf]$ (**2d**). The proton NMR spectrum of **2b** shows resonances for three inequivalent Re–methyl resonances at 0.45, 0.20, and 0.05 ppm in CD_2Cl_2, consistent with a structure containing either an η^2-hydrazine ligand or an η^1-hydrazine ligand in which the substituted nitrogen atom is the one bound to the metal. The proton NMR spectrum of **2d** also reveals resonances for inequivalent Re–Me groups. We prefer η^2 descriptions for hydrazine binding in **2b–d** for reasons analogous to those stated for **2a** but suggest that the tautomer that contains the η^1-hydrazine ligand is readily accessible on the chemical time scale.

Synthesis and Reactivity of Re(V) Hydrazido(1−) Complexes. Deprotonation of $[Cp^*ReMe_3(N_2H_4)][OTf]$ (**2a**) with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) at −40 °C in ether yields a flaky off-white solid whose properties are consistent with it being $Cp^*ReMe_3(NHNH_2)$ (**3a**; eq 3). Addition of 1 equiv of triflic acid to **3a** in ether at −40

$$\underset{\mathbf{2a}}{[Cp^*ReMe_3(N_2H_4)]OTf} \xrightarrow[\text{ether, }-40\ ^\circ\text{C}]{\text{DBU}} \underset{\mathbf{3a}}{Cp^*ReMe_3(NHNH_2)} \quad (3)$$

°C produces $[Cp^*ReMe_3(N_2H_4)][OTf]$ (**2a**) quantitatively. The proton NMR spectrum of **3a** shows a set of singlet resonances in a 5:2:1 ratio corresponding to a Cp* ligand, two Re–Me(cis) ligands, and a Re–Me(trans) ligand. A single broad resonance at approximately 3.00 ppm whose integral equals three protons is assigned to the three hydrazido(1−) protons in **3a**. Apparently the three hydrazido protons are interconverting in a process that could not be slowed sufficiently even at −85 °C to allow separate hydrazido protons to be observed; the hydrazido resonance simply broadens into the base line and shifts downfield. A ^{15}N NMR spectrum of **3a**-^{15}N at −60 °C revealed two resonances at 71.2 and 68.8 ppm (J_{NN} = 11 Hz), but the J_{NH} coupling constant for neither nitrogen atom could be observed at −60 °C.

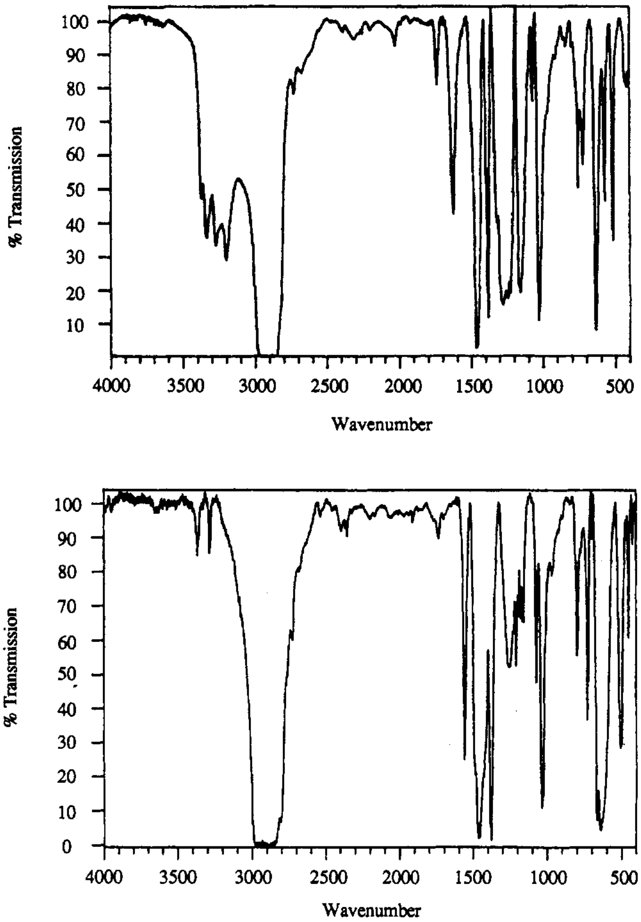
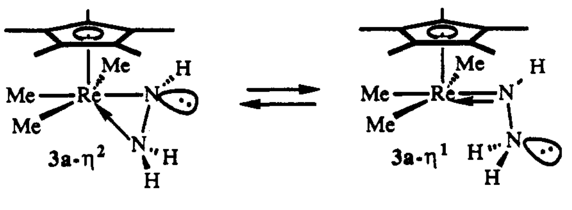


Figure 3. IR spectra of $[Cp^*ReMe_3(NH_3)_2][OTf]$ (top) and $Cp^*ReMe_3(NH_2)$ (bottom).

Two structures for **3a** seem plausible (eq 4). One (**3a**-η^2) is one of two versions in which the hydrazido(1−) ligand is bound in an η^2 fashion. In an η^2-hydrazido structure



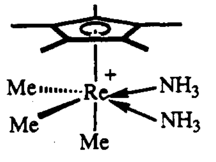
(4)

the two d electrons could be either in the $\pi_\parallel$ orbital (ca. 65% d_{xy} in the analogous Cp^*WMe_3 core[4]), as in **3a**-η^2, or in the $\pi_\perp$ orbital (ca. 50% d_{z^2} in the analogous Cp^*WMe_3 core[4]) if the N–N bond is approximately parallel to the plane of the Cp* ligand. In the η^1-hydrazido structure (**3a**-η^1) the total metal electron count is the same as in **3a**-η^2 (18), but the lone pair on N_α is donated to the metal and the two d electrons are in the $\pi_\perp$ orbital. There is no good reason for opting for one or the other, especially since recent results in the analogous Cp*WMe$_3$ system suggest that the $\pi_\perp$ orbital and $\pi_\parallel$ orbitals are approximately equally available and effective in bonding N_2H_x fragments.[4,12] **3a** decomposes over a period of several hours in solution at 25 °C to as yet undetermined products, but it is relatively stable in the solid state at −40 °C.

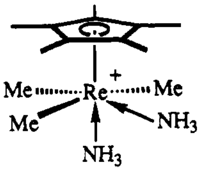
Deprotonation of [Cp*ReMe$_3$(NH$_2$NHMe)][OTf] (**2b**) by DBU in ether produces a mixture of Cp*ReMe$_3$(NHNMeH) (**3b**) and Cp*ReMe$_3$(NMeNH$_2$) (**3b′**). Initially the mixture contains predominantly **3b′**, which can be identified on the basis of the broad resonance at 3.90 ppm, corresponding to the NH$_2$ protons, and the slightly broadened singlet resonance at 2.00 ppm, corresponding to the methyl group on N_α. However, within approximately 1 h at 25 °C **3b′** isomerized entirely to **3b**, which is stable in solution for hours at 25 °C. The proton NMR spectrum of **3b** shows broadened resonances at 12.10 and 6.20 ppm corresponding to $N_\alpha H$ and $N_\beta H$, respectively. A doublet resonance ($^1J_{HH}$ = 6.1 Hz) is observed at 2.30 ppm that can be assigned to $N_\beta Me$. The three Re methyl groups are inequivalent (resonances at 0.95, 0.78, and 0.62 ppm). Evidently the process that leads to proton equilibration in **3a** at 25 °C is relatively slow in **3b**. None of these data help us to decide whether a version analogous to **2a**-η^2 or a version analogous to **2a**-η^1 is the more likely structure for **3b**.

Synthesis and Reactivity of Re(V) Ammonia Complexes. The reaction between Cp*ReMe$_3$(OTf) (1) and excess ammonia yielded a dark yellow precipitate of [Cp*ReMe$_3$(NH$_3$)$_2$][OTf] (4; eq 5) in good yield. IR spectra of 4 (Figure 3) are virtually identical with the spectra of d^1 [Cp*WMe$_3$(NH$_3$)$_2$][OTf].[5] Proton NMR spectra reveal a broad resonance of area 6 for the ammonia ligands at 2.80 ppm that remains unchanged at −80 °C. The ^{15}N NMR spectrum of [Cp*ReMe$_3$(^{15}NH$_3$)$_2$][OTf] −80 °C consists of a quartet at 276.4 ppm (J_{NH} = 75 Hz). A difference NOE experiment shows that only the resonance for the two equivalent methyl groups on the Re is enhanced by approximately 5%. All NMR data are consistent with a pseudooctahedral structure for 4 in which a methyl group occupies the axial site trans to the Cp* ligand (4-A).

$$\underset{\mathbf{1}}{\mathrm{Cp^*ReMe_3(OTf)}} \xrightarrow[\text{ether, }-40\text{ °C}]{\text{excess NH}_3} \underset{\mathbf{4}}{[\mathrm{Cp^*ReMe_3(NH_3)_2}][\mathrm{OTf}]} \tag{5}$$



4–A



4–B

The reaction between 4 and Cp*ReMe$_3$(OTf) yields [Cp*ReMe$_3$(NH$_3$)][OTf] (5; eq 6), while that between 4 and 2 equiv of triflic acid yields Cp*ReMe$_3$(OTf) (1) and 2 equiv of [NH$_4$][OTf]. The reaction between 5 and triflic acid also yields 1 and [NH$_4$][OTf]. [Cp*ReMe$_3$(NH$_3$)][OTf] decomposes readily by losing methane within minutes at 25 °C in solution and hours in the solid state at 25 °C, but it can be stored for short periods of time in the solid state at −40 °C.

$$\mathrm{Cp^*ReMe_3(OTf)} + \mathbf{4} \xrightarrow{\text{THF, }-40\text{ °C}} \underset{\mathbf{5}}{2[\mathrm{Cp^*ReMe_3(NH_3)}][\mathrm{OTf}]} \tag{6}$$

Proton NMR spectra of 5 are dramatically temperature dependent (Figure 4), analogous to NMR spectra of Cp*ReMe$_3$(OTf) (Figure 1). At 20 °C in CD$_2$Cl$_2$ resonances are observed at 16.00 and 14.60 ppm in a 1:2 ratio, respectively, that can be assigned to methyl groups on rhenium; a broadened resonance for the ammonia ligand appears at 10.30 ppm, and the Cp* resonance is observed at 2.10 ppm. At −80 °C the ammonia resonance is found at 5.00 ppm and the methyl resonances are observed in a 1:2 ratio at 4.30 and 2.90 ppm, respectively. The ^{15}N NMR spectrum of 5 at −40 °C reveals a single quartet resonance at 375.2 ppm (J_{NH} = 72 Hz). The explanation is analogous to that proposed for 1; i.e., the ground-state structure of 5 is a diamagnetic square pyramid, but a paramagnetic trigonal bipyramid is thermally accessible. This temperature-dependent chemical shift phenomenon also is discussed in more detail later.

Synthesis and Reactivity of a Re(V) Amido Complex. Addition of an excess of triethylamine to a solution of [Cp*ReMe$_3$(NH$_3$)$_2$][OTf] (4) in THF yields Cp*ReMe$_3$(NH$_2$) (**6a**) as a dark green solid (eq 7). Addition of 1 equiv of triflic acid to a cold THF solution of **6a** at −30 °C produces **5** quantitatively. The IR spectrum of **6a** (Figure 3) shows two absorptions attributable to NH stretching modes at 3200 and 3150 cm^{-1} as well as an absorption corresponding to an NH bending mode at 1575 cm^{-1}. The proton NMR spectrum of **6a** in CD$_2$Cl$_2$ reveals a broad resonance at 10.45 ppm for the two amido protons, while the ^{15}N spectrum of Cp*ReMe$_3$(^{15}NH$_2$) consists of a triplet at 219.8 ppm (J_{NH} = 75 Hz). No dramatic temperature dependence of the NMR spectra is observed, in contrast to the spectra of **1** and **5**.

$$\underset{\mathbf{4}}{[\mathrm{Cp^*ReMe_3(NH_3)_2}][\mathrm{OTf}]} \xrightarrow[+\mathrm{NEt_3},\ -[\mathrm{Et_3NH}][\mathrm{OTf}],\ -\mathrm{NH_3}]{\text{THF, }-40\text{ °C}} \underset{\mathbf{6a}}{\mathrm{Cp^*ReMe_3(NH_2)}} \tag{7}$$

The amido ligand in **6a** can form a dative π bond to the metal using either the $\pi_\perp$ orbital or the $\pi_\parallel$ orbital on Re; the two d electrons on the Re will occupy the π orbital that is not used to form the π bond. A π bond that is formed using the $\pi_\parallel$ orbital would result in inequivalent amido protons (if the two amido protons do not interconvert readily). Formation of a π bond using the $\pi_\perp$ orbital would result in equivalent amido protons. Since we would not expect rotation about the Re–N π bond to be rapid enough in a low-temperature NMR spectrum to equilibrate the amido protons, and since the Re–methyl groups are all inequivalent in the analogous Re=NHMe complex, we

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[12] Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 1985.

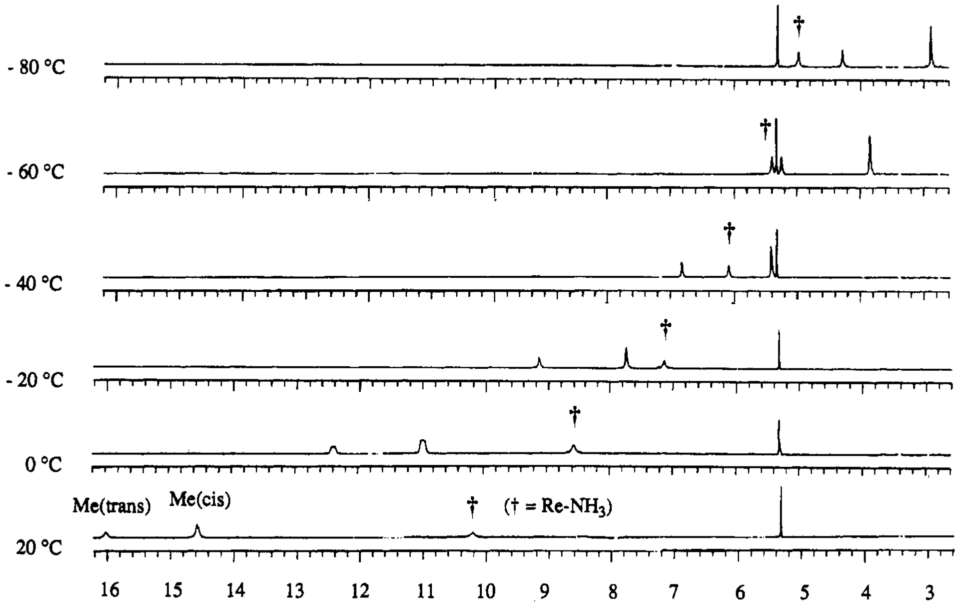
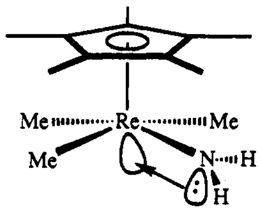


Figure 4. Variable-temperature proton NMR spectra of $[Cp^*ReMe_3(NH_3)][OTf]$ (**5**).

presume that the π bond between Re and N in **6a** is formed using the $\pi_\perp$ orbital:



Therefore, the two d electrons occupy the $\pi_\parallel$ orbital in **6a**.

$Cp^*ReMe_3(NMeH)$ (**6b**), a light green solid, is formed upon adding an excess of methylamine to a solution of **1** (eq 8). The reaction presumably yields an amine complex

$$\underset{\mathbf{1}}{Cp^*ReMe_3(OTf)} \xrightarrow[\text{ether, -40 °C}]{\text{excess } NH_2Me} \underset{\mathbf{6b}}{Cp^*ReMe_3(NMeH)} \quad (8)$$

initially, most likely $[Cp^*ReMe_3(NH_2Me)_x][OTf]$ (probably $x = 1$ for steric reasons), which is then deprotonated by the second equivalent of methylamine to form **6b**. This behavior is analogous to that observed when substitueted amines are added to $Cp^*WMe_3(OTf)$.[5] In contrast, $[Cp^*ReMe_3(NH_3)_2][OTf]$ (**4**) and $[Cp^*WMe_3(NH_3)_2][OTf]$ are formed even in the presence of excess ammonia. All three methyl groups on the Re center are inequivalent in the proton NMR spectrum of **6b**, consistent with a structure in which the $\pi_\perp$ orbital is used to form the π bond between Re and N. Heating a solution of **6b** in C_6D_6 to 70 °C results in only slight broadening of the resonances corresponding to the cis Re methyl groups; therefore, the methylamido ligand must not rotate about the Re–N bond rapidly on the NMR time scale.

Addition of at least 2 equiv of dimethylamine to a solution of **1** yields $Cp^*ReMe_3(NMe_2)$ (**6c**; eq 9), a pentane-soluble yellow crystalline solid. We presume that

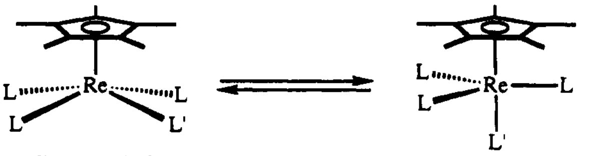
$$\underset{\mathbf{1}}{Cp^*ReMe_3(OTf)} \xrightarrow[\text{ether, -40 °C}]{\text{excess } NMe_2H} \underset{\mathbf{6c}}{Cp^*ReMe_3(NMe_2)} \quad (9)$$

$[Cp^*ReMe_3(NMe_2H)][OTf]$ is formed and deprotonated by the second equivalent of dimethylamine. The proton NMR spectrum of **6c** shows two equivalent amido methyl groups at 3.20 ppm and two different Re–Me groups, consistent with a structure in which the $\pi_\perp$ orbital is used to form the π component of the Re–amido bond.

Cyclic voltammetry of **6a** (in 0.1 M $[NBu_4]BF_4$ in CH_2Cl_2 versus Ag/Ag^+) revealed an irreversible oxidation wave at +0.20 V. Perhaps for that reason, an attempt to prepare $Cp^*ReMe_3(NH)$ by oxidizing **6b** in the presence of excess NEt_3 or DBU resulted in decomposition to as yet undetermined products. It should be noted that $Cp^*ReMe_3(NH)$ would be a 17-electron Re(VI) complex in the absence of a dative π bond from the nitrogen atom to the metal and a 19-electron complex in the presence of a dative π bond.

Behavior of Pseudo-Five-Coordinate Re(V) Complexes. The vast majority of monocyclopentadienyl "piano stool" complexes containing four identical ligands are square pyramids.[11] One notable exception is $[Cp^*WMe_4]^+$, a d^0 species. $[Cp^*WMe_4]^+$ was found to be a trigonal bipyramid in the solid state and in solution, with $\Delta G^\ddagger_{296} = 15.0$ kcal mol^{-1} for equatorial methyl groups interchanging with the axial methyl group, presumably via a square-pyramidal intermediate. On the other hand, a relative of Cp^*WMe_4 was found to be a square pyramid in the solid state.[8] The reversible electrochemistry of Cp^*WMe_4 was consistent with the proposal that Cp^*WMe_4 and $[Cp^*WMe_4]^+$ have different structures.

Pseudo-six-coordinate d^2 Re(V) complexes $[Cp^*ReMe_3(N_2H_4)][OTf]$ (**2a**), $Cp^*ReMe_3(NHNH_2)$ (**3a**), and $[Cp^*ReMe_3(NH_3)_2][OTf]$ (**4**) all have a diamagnetic singlet ground state, as one would expect on the basis of the relatively low symmetry of these species. On the other hand, the structures of $Cp^*ReMe_3(OTf)$ (**1**) and $[Cp^*ReMe_3(NH_3)][OTf]$ (**5**) in theory could be either square pyramidal or trigonal bipyramidal. A simple crystal field analysis would predict that a d^2 square-pyramidal Cp^*ReL_3L' complex should have a diamagnetic ground state and a trigonal-bipyramidal Cp^*ReL_3L' complex in which L′ is in the pseudoaxial position should have a paramagnetic ground state. (In a trigonal-bipyramidal Cp^*ReL_3L' complex in which L is in the pseudoaxial position, the d_{xz}/d_{yz} degeneracy (in crystal field terms) should be lifted sufficiently to yield a diamagnetic species.) Therefore, the variable-temperature ^{1}H NMR behavior of Cp*ReMe$_3$(OTf) (**1**) and [Cp*ReMe$_3$(NH$_3$)][OTf] (**5**) could be ascribed to a fluxional process in which the ground-state diamagnetic square-pyramidal form is in rapid equilibrium with the paramagnetic trigonal-bipyramidal form (eq 10). As the temperature is lowered, the equilibrium should shift toward the lower energy SP form and the NMR resonances should approach the position they would occupy in a sample that consists of solely the SP form. This is one variation of several related phenomena that have been observed in several classes of transition-metal complexes,[13] in some cases studied in considerable depth. Some of the best-known examples of transition-metal species that behave in a related fashion are nickel complexes that interconvert between diamagnetic square-planar and paramagnetic tetrahedral forms.[14] The free energy difference between the two forms is often small (ca. 1 kcal) and the shift in some ligand proton resonances often large (ca. 10^4 Hz). A significant change in structure need not be part of the process. For example, the spin state of manganocene complexes depends upon the type of substituents on the Cp ligands.[15-17] In studies of this nature it is possible to determine the difference in free energy of the two states involved if the observed temperature dependence can be assigned to a specific mechanism or combination of mechanisms.[13]



diamagnetic SP paramagnetic TBP (10)

Shifts of 1000–3000 Hz in the methyl resonances of **1** and the methyl and ammonia resonances of **5** over a temperature range of ca. 100 °C would suggest that the energy difference between the diamagnetic and paramagnetic species is greater than commonly found for (e.g.) the tetrahedral/square-planar equilibrium in the nickel system. However, a potential complication in the case of **1** or **5** is that the barrier between the TBP and SP forms is ca. 15 kcal mol^{-1} (in **1**) or greater (in **5**), which suggests that their interconversion perhaps will not be rapid at the lowest temperatures at which the spectra were recorded. Therefore, in addition to determining the mechanism of the observed shifts, one is faced with the potential problem of a low rate of interconversion of TBP and SP forms at lower temperatures. It should be noted that the Cp* resonance for Cp*ReMe$_4$[10] also was found to be a broad resonance at 12.70 ppm, and the methyl resonances could not be observed. (In contrast, the Cp* resonance in spectra of **1** and **5** is relatively sharp and moves only slightly downfield as the temperature increases.) Variable-temperature proton NMR studies for Cp*ReMe$_4$ showed that the Cp* resonance shifts dramatically *downfield* as the temperature is decreased, more consistent with a circumstance in which the paramagnetic form is the lower energy state. The fact that strongly temperature dependent chemical shifts are observed also for Cp*ReMe$_4$ is some indication that a paramagnetic/diamagnetic equilibrium is responsible for the large chemical shifts in this circumstance also. Exactly what is the explanation (or are the explanations) of the observed temperature-dependent chemical shifts must be left for a future detailed study.

Not all pseudo-five-coordinate Re(V) complexes show evidence of an equilibrium between paramagnetic and diamagnetic forms. For example, Cp*ReMe$_3$(NH$_2$) (**6a**), Cp*ReMe$_3$(NMeH) (**6b**), and Cp*ReMe$_3$(NMe$_2$) (**6c**) do not exhibit any unusual proton NMR behavior. However, such species must be diamagnetic, since the formation of a metal–amido π-bond leaves only one nonbonding orbital in which to pair up the two d electrons. Cp*ReMe$_2$(OTf)$_2$[18] and Cp*ReMe$_2$Cl$_2$[19] are examples of five-coordinate d^2 Re(V) complexes that do not contain π-bonding ligands but that still do not shown unusual proton NMR behavior. Either the d$_{xz}$/d$_{yz}$ degeneracy is lifted sufficiently in the TBP form of these lower symmetry Cp*ReL$_2$L'$_2$ species or virtually no paramagnetic TBP form is present.

Discussion

The results described here establish that the Cp*ReMe$_3$ core, like the Cp*WMe$_3$ core and, to a lesser extent, the Cp*MoMe$_3$ core, also is quite versatile in binding N$_2$H$_x$ and NH$_y$ ligands. The stability of some of these species, e.g., complexes of type **2**, is also surprising in view of the relatively complex chemistry usually observed upon adding hydrazines to transition-metal complexes. But what is perhaps most surprising and informative is the finding that the d^2 complexes [Cp*ReMe$_3$(NH$_2$NH$_2$)]$^+$ and Cp*ReMe$_3$(NHNH$_2$) are relatively stable, whereas the d^2 complex Cp*WMe$_3$(NH$_2$NH$_2$) and the d^1 complex Cp*WMe$_3$(NHNH$_2$) could never be observed before they decomposed.[4] Cp*WMe$_3$(NH$_2$NH$_2$) is proposed to decompose to Cp*WMe$_3$(NH) and ammonia by a process that could involve oxidation of W(IV) to W(VI) (in the absence of acid).[4] The fact that [Cp*ReMe$_3$(NH$_2$NH$_2$)]$^+$ is relatively stable could be taken as evidence that oxidation of the metal may be required for efficient cleavage of the N–N bond in a d^2 complex of this general (Cp*MMe$_3$) type, since oxidation of Re(V) to Re(VII) is not as likely as oxidation of W(IV) to W(VI). Cp*WMe$_3$(NHNH$_2$), which could be viewed as a free radical, is proposed to disproportionate to a mixture of stable Cp*WMe$_3$(η^1-NNH$_2$) and unstable Cp*WMe$_3$(NH$_2$NH$_2$) by intramolecular transfer of a hydrogen atom. Cp*ReMe$_3$(NHNH$_2$) is an *even*-electron species. If it contains an η^1-bound hydrazido(1–) ligand whose lone electron pair on N$_\alpha$ is donated to the metal, then it is an 18-electron species. Its disproportionation would lead to Re(IV) and Re(VI) species, and everything we have seen here suggests that Re(VI) complexes that contain the Cp*ReMe$_3$ core, as well as Re(VII) complexes, are not stable. The difficulty of oxidizing even Re(V) to Re(VI) in complexes of this type may be a factor that contributes significantly to the stability of Cp*ReMe$_3$(NHNH$_2$).

We believe that the failure of the N–N bond to be cleaved in this Re system to give ammonia in high yield is a further indication that d^0, d^1, and d^2 oxidation states of W in

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complexes containing the Cp*WMe$_3$ core may indeed have some special properties that allow the N–N bond to be cleaved in a controlled and stepwise manner. One is that the 4+, 5+, and 6+ oxidation states are all accessible. A second potentially important property may be the ability of d^0 tungsten to form a strong π bond at one end of an N$_2$H$_x$ ligand and thereby to assist in N–N cleavage to give a W═NH complex. Consequently, we do not plan to continue to look for relevant N$_2$H$_x$ chemistry for rhenium complexes in which the metal is in a relatively high oxidation state but will return to studies involving high-oxidation-state tungsten or molybdenum chemistry.

Experimental Section

General Information. Solvents were dried and degassed prior to use and distilled from molten sodium (toluene), sodium/benzophenone (diethyl ether, tetrahydrofuran, pentane), CaH$_2$ (dichloromethane), or P$_2$O$_5$ (acetonitrile). Pentane was washed with 5% HNO$_3$/H$_2$SO$_4$ and dried using tetraglyme to solvate the sodium. All preparations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox, under argon in Schlenkware, or on a high-vacuum line (<10^{-4} Torr). Triflic acid was purchased from Aldrich and used directly from the sealed ampule. NMR operating frequencies and reference standards are as follows: ^{1}H (300.1 MHz, SiMe$_4$ 0 ppm; 75.0 MHz, SiMe$_4$ 0 ppm), ^{6}Li (44.1 MHz, 1.0 M LiCl/D$_2$O 0 ppm), ^{7}Li (116.6 MHz, 1.0 M LiCl/D$_2$O 0 ppm), ^{15}N (30.4 MHz, NH$_2$Ph 56.5 ppm), ^{19}F (282.2 MHz, CFCl$_3$ 0 ppm). Proton and carbon NMR data were referenced using resonances for the partially deuterated NMR solvent. Other nuclei were referenced externally in the same solvent unless otherwise noted. Chemical shifts (δ) are in ppm, and coupling constants and line widths are in hertz. All spectra were acquired at 22 °C unless otherwise noted. Deuterated solvents were dried by passage through alumina and storage over 4-Å molecular sieves. Infrared spectra were acquired on a Mattson Cygnus 100 FT-IR spectrometer as Nujol mulls between KBr plates unless otherwise indicated. Microanalyses (C, H, and N) were performed in our laboratory using a Perkin-Elmer PE2400 microanalyzer. Anhydrous ammonia (Matheson) was used as purchased, and NH$_2$Me (Matheson) and NHMe$_2$ (Matheson) were dried as liquids under pressure over sodium and distilled. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aldrich. Cp*ReMe$_4$ was synthesized by the method reported in the literature.[10] ^{15}N-labeled compounds were prepared by methods analogous to those used to prepare ^{14}N compounds.

Cp*ReMe$_3$(OTf) (1). Cp*ReMe$_4$ (0.830 g, 2.18 mmol) was dissolved in 50 mL of ether at –40 °C in the dark. Triflic acid (0.193 mL, 2.18 mmol) was added directly to the stirred solution. Gas evolution was evident. After 30 min the dark orange-yellow solution was filtered and cooled to –40 °C for several hours and the yellow microcrystalline solid collected and washed with cold ether. The mother liquor was concentrated and cooled to –40 °C to give additional crops. Yellow Cp*ReMe$_3$(OTf) was dried in vacuo and collected (1.030 g, 1.99 mmol, 91%): ^{1}H NMR (C$_6$D$_6$) δ 7.65 (s, 9, ReMe), 1.26 (s, 15, Cp*); ^{13}C NMR (C$_6$D$_6$) δ 107.9 (s, Me$_5$*C*), 101.9 (q, ReMe), 9.95 (q, *Me*$_5$C); IR (Nujol; cm^{-1}) 1370 (s), 1313 (s), 1233 (s), 1176 (s, [OTf]), 1011 (s), 727 (m), 631 (s). Anal. Calcd for ReC$_{14}$H$_{24}$SO$_3$F$_3$: C, 32.61; H, 4.67. Found: C, 32.85; H, 4.77.

[Cp*ReMe$_3$(NH$_2$NH$_2$)][OTf] (2a). Cp*ReMe$_3$(OTf) (0.300 g, 0.572 mmol) was dissolved in 20 mL of ether at room temperature. Hydrazine (0.018 mL, 0.570 mmol) was added directly to the stirred dark orange solution. A light orange precipitate formed within 30 s. After 5 min the pale orange product was isolated from the reaction mixture by filtration, washed with ether, and dried in vacuo: yield 0.235 g (0.429 mmol, 75%); ^{1}H NMR (CD$_2$Cl$_2$) δ 6.37 (br s, 2, NH$_2$), 5.65 (br s, 2, NH$_2$), 1.63 (s, 15, Cp*), 0.44 (s, 3, ReMe$_t$), 0.05 (s, 6, ReMe$_c$); ^{13}C NMR (CD$_2$Cl$_2$, –40 °C) δ 105.8 (s, Me$_5$*C*), 38.6 (q, ReMe$_t$), 14.1 (q, ReMe$_c$), 9.6 (q, *Me*$_5$C); ^{15}N NMR (CD$_2$Cl$_2$, –60 °C) δ 44.5 (t, J_{NH} = 74 Hz), 12.8 (td, J_{NH} = 74 Hz, J_{NN} = 8 Hz); IR (Nujol; cm^{-1}) 3297 (s, NH), 3219 (s, NH), 3183 (s, NH), 3110 (s, NH), 1598 (m, NH$_2$ bend), 1575 (s, NH$_2$ bend), 1280 (s, OTf), 1021 (s), 623 (m). Anal. Calcd for ReC$_{14}$H$_{28}$N$_2$SO$_3$F$_3$: C, 30.71; H, 5.15; N, 5.12. Found: C, 31.08; H, 5.20; N, 4.38.

[Cp*ReMe$_3$(NH$_2$NHMe)][OTf] (2b). Cp*ReMe$_3$(OTf) (0.200 g, 0.388 mmol) was dissolved in 20 mL of ether at –40 °C to form a dark orange solution. Methylhydrazine (0.021 mL, 0.388 mmol) was added directly to the stirred solution. A light purple precipitate formed within 30 s. After 5 min [Cp*ReMe$_3$(NH$_2$NHMe)][OTf] was filtered off, washed with ether, and dried in vacuo: yield 0.175 g (0.312 mmol, 80%); ^{1}H NMR (CD$_2$Cl$_2$) δ 7.00 (br s, 2, NH$_2$), 6.40 (br s, 1, NMe*H*), 2.95 (d, 3, N*Me*H), 1.70 (s, 15, Cp*), 0.48 (s, 3, ReMe), 0.21 (s, 3, ReMe), 0.09 (s, 3 H, ReMe); ^{13}C NMR (CD$_2$Cl$_2$) δ 95.8 (s, Me$_5$*C*), 35.9 (q, NMeH), 13.3 (q, ReMe), 11.4 (q, ReMe), 6.1 (q, ReMe), 9.7 (q, *Me*$_5$C$_5$); IR (Nujol; cm^{-1}) 3278 (s, NH), 3188 (s, NH), 1606 (m, NH$_2$ bend), 1262 (s, OTf), 1027 (s), 722 (m), 636 (m). Anal. Calcd for ReC$_{14}$H$_{28}$N$_2$SO$_3$F$_3$: C, 32.08; H, 5.38; N, 4.99. Found: C, 32.49; H, 4.98; N, 4.74.

[Cp*ReMe$_3$(NH$_2$NMe$_2$)][OTf] (2c). Cp*ReMe$_3$(OTf) (0.200 g, 0.388 mmol) was dissolved in 20 mL of ether at –40 °C. 1,1-Dimethylhydrazine (0.029 mL, 0.388 mmol) was added directly to the dark orange solution. After 5 min the pale purple precipitated product was filtered off, washed with ether, and dried in vacuo: yield 0.170 g (0.295 mmol, 76%); ^{1}H NMR (CD$_2$Cl$_2$) δ 6.95 (br s, 2, NH$_2$), 3.10 (s, 6, NMe$_2$), 1.69 (s, 15, Cp*), 0.50 (s, 3, ReMe$_t$), 0.30 (s, 6, ReMe$_c$); ^{13}C NMR (CD$_2$Cl$_2$) δ 108.4 (s, Me$_5$*C*), 35.8 (q, NMe$_2$), 28.1 (q, ReMe$_t$), 13.7 (q, ReMe$_c$), 10.8 (q, *Me*$_5$C$_5$); IR (Nujol; cm^{-1}) 3207 (m, NH), 3096 (s, NH), 1606 (m, NH$_2$ bend), 1267 (m, OTf), 1020 (s), 687 (m), 630 (s).

[Cp*ReMe$_3$(NHMeNHMe)][OTf] (2d). Cp*ReMe$_3$(OTf) (0.250 g, 0.485 mmol) was dissolved in 20 mL of ether at room temperature. A 1.25 M solution of 1,2-dimethylhydrazine in ether (0.388 mL, 0.485 mmol) was added directly to the stirred solution. After 3 min the pale purple solid was filtered off, washed with ether, and dried in vacuo: yield 0.215 g (0.373 mmol, 77%); ^{1}H NMR (CD$_2$Cl$_2$) δ 6.65 (br s, 1, NMe*H*), 6.05 (br s, 1, NMe*H*), 2.93 (d, 3, N*Me*H), 2.82 (d, 3, N*Me*H), 1.75 (s, 15, Cp*), 0.55 (s, 3, ReMe), 0.39 (s, 3, ReMe), 0.30 (s, 3, ReMe); ^{13}C NMR (CD$_2$Cl$_2$, –20 °C) δ 96.1 (s, Me$_5$*C*), 33.9 (q, NMeH), 30.2 (q, NMeH), 14.4 (q, ReMe), 11.9 (q, ReMe), 9.6 (q, *Me*$_5$C), 8.9 (q, ReMe); IR (Nujol; cm^{-1}) 3231 (s, NH), 3155 (s, NH), 1245 (s, OTf), 1025 (s), 727 (m), 623 (m). Anal. Calcd for ReC$_{14}$H$_{28}$N$_2$SO$_3$F$_3$: C, 33.38; H, 5.60; N, 4.87. Found: C, 33.51; H, 5.47; N, 4.61.

Cp*ReMe$_3$(NHNH$_2$) (3a). [Cp*ReMe$_3$(N$_2$H$_4$)][OTf] (0.300 g, 0.548 mmol) was suspended in 20 mL of cold ether, and DBU (0.078 mL, 0.522 mmol) was added to the stirred suspension. The reaction mixture immediately turned dark yellow-orange. After 15 min the reaction mixture was filtered and the solvent was removed in vacuo from the dark orange filtrate to yield a tan-orange solid. The solid was washed with cold pentane and dried in vacuo: yield 0.170 g (0.428 mmol, 82%); ^{1}H NMR (CD$_2$Cl$_2$) δ 3.05 (br, 3, NHNH$_2$), 1.81 (s, 15, Cp*), 1.38 (s, 6, ReMe$_c$), 0.16 (s, 3, ReMe$_t$); ^{13}C NMR (C$_6$D$_6$) δ 109.4 (s, Me$_5$*C*), 13.6 (q, ReMe), 10.9 (q, *Me*$_5$C), 2.6 (q, ReMe); ^{15}N NMR (THF-d_8, –80 °C) δ 71.2 (d, J_{NN} = 11 Hz), 68.8 (d, J_{NN} = 11 Hz); IR (Nujol; cm^{-1}) 3375 (w, NH), 3326 (w, NH), 3176 (w, NH), 1635 (m, NH$_2$ bend), 1570 (m, NH$_2$ bend). Anal. Calcd for ReC$_{13}$H$_{27}$N$_2$: C, 39.27; H, 6.84; N, 7.05. Found: C, 39.69; H, 6.44; N, 4.35.

Cp*ReMe$_3$(NHNMeH) (3b). [Cp*ReMe$_3$(N$_2$H$_3$Me)][OTf] (0.166 g, 0.296 mmol) was suspended in 20 mL of cold ether. DBU (0.042 mL, 0.281 mol) was added to the stirred suspension. The reaction mixture immediately turned dark orange. After 5 min the reaction mixture was filtered and the solvent was removed in vacuo from the dark orange filtrate to yield a greenish solid. The solid was dissolved in cold pentane, and the pentane was removed in vacuo to give Cp*ReMe$_3$(NHNMeH): yield 0.074 g (0.180 mmol, 61%); ^{1}H NMR (C$_6$D$_6$) δ 12.10 (br, 1, N$_\alpha$H), 6.20 (br, 1 N$_\beta$Me*H*), 2.30 (d, 3, N$_\beta$*Me*H), 1.42 (s, 15, Cp*), 0.95 (s, 3, ReMe), 0.78 (s, 3, ReMe), 0.62 (s, 3, ReMe); ^{13}C NMR (C$_6$D$_6$) δ 91.7 (s, Me$_5$*C*), 38.8 (q, N$_\beta$MeH), 25.2 (q, ReMe), 16.4 (q, ReMe), 12.6 (q, ReMe), 9.5 (q, *Me*$_5$C); IR (Nujol; cm^{-1}) 3375 (w, NH), 3326 (w, NH), 3176 (w, NH), 1635 (m, NH$_2$ bend), 1570 (m, NH$_2$ bend).

[Cp*ReMe$_3$(NH$_3$)$_2$][OTf] (4). Cp*ReMe$_3$(OTf) (0.600 g, 1.17 mmol) was dissolved in 50 mL of ether. The solution was subjected to three freeze–pump–thaw cycles on a high-vacuum line and then frozen in liquid nitrogen. Ammonia (4.66 mmol) was condensed into the reaction flask, which was then warmed to room temperature while the solution was stirred vigorously. A yellow precipitate appeared within 30 s. After 5 min the solvent was removed in vacuo to give a yellow solid. The reaction flask was brought into the drybox, where the product was isolated by filtration, washed with ether, and dried in vacuo: yield 0.516 g (0.938 mmol, 81%); ^{1}H NMR (CD$_2$Cl$_2$) δ 2.77 (br s, 6, NH$_3$), 1.57 (s, 15, Cp*), 0.92 (s, 3, ReMe$_t$), 0.41 (s, 6, ReMe$_c$); ^{13}C NMR (CD$_2$Cl$_2$) δ 97.5 (s, Me$_5$*C*), 58.7 (q, ReMe$_c$), 9.1 (q, *Me*$_5$C), 6.9 (q, ReMe$_t$); ^{15}N NMR (CD$_2$Cl$_2$, −80 °C) δ 276.4 (q, J_{NH} = 75 Hz); IR (Nujol; cm^{-1}) 3371 (m, NH) 3334 (s, NH), 3272 (s, NH), 3198 (s, NH), 1734 (m, NH$_2$ bend), 1626 (s, NH$_2$ bend), 1281 (s, OTf), 1014 (s), 618 (m). Anal. Calcd for ReC$_{14}$H$_{30}$N$_2$SO$_3$F$_3$: C, 30.59; H, 5.50; N, 5.01. Found: C, 30.47; H, 5.27; N, 4.81.

[Cp*ReMe$_3$(NH$_3$)][OTf] (5). Cp*ReMe$_3$(NH$_2$) (0.150 g, 0.392 mmol) was dissolved in 10 mL of ether at −40 °C. Triflic acid (0.035 mL, 0.392 mmol) was added directly to the stirred dark green solution. A yellow precipitate formed immediately and after 10 min was filtered off, washed with ether, and dried in vacuo: yield 0.125 g (0.230 mmol, 60%); ^{1}H NMR (CD$_2$Cl$_2$, 20 °C) δ 16.02 (s, 3, ReMe$_t$), 14.60 (s, 6, ReMe$_c$), 10.20 (br s, 3, NH$_3$), 2.15 (s, 15, Cp*); ^{1}H NMR (CD$_2$Cl$_2$, −80 °C) δ 5.00 (s, 3, NH$_3$), 4.30 (s, 3, ReMe$_t$), 2.90 (s, 6, ReMe$_c$), 1.70 (s, 15, Cp*); ^{15}N NMR (CD$_2$Cl$_2$, −80 °C) δ 375.2 (q, J_{NH} = 74 Hz); ^{13}C NMR (CD$_2$Cl$_2$, −20 °C) δ 118.4 (q, ReMe$_t$), 99.6 (q, *C*$_5$Me$_5$), 92.6 (s, ReMe$_c$), 10.7 (q, C$_5$*Me*$_5$); IR (Nujol; cm^{-1}) 3254 (m, NH stretch), 3178 (m, NH$_2$ stretch), 1628 (m, NH$_2$ bend), 1249 (s, OTf), 1166 (s), 1029 (s), 637 (s), 518 (m). Anal. Calcd for ReC$_{14}$H$_{27}$NSO$_3$F$_3$: C, 31.57; H, 5.11; N, 2.63. Found: C, 31.85; H, 4.99; N, 2.64.

Cp*ReMe$_3$(NH$_2$) (6a). [Cp*ReMe$_3$(NH$_3$)$_2$][OTf] (0.415 g, 0.903 mmol) was dissolved in 30 mL of THF at −40 °C, and triethylamine (0.503 mL, 3.611 mmol) was added. The reaction mixture was stirred for 30 min and became dark green-brown. The solvent was removed in vacuo to produce a green-brown film. The residue was extracted with pentane to yield a green solution. Solvent was removed from the green extract in vacuo to yield green Cp*ReMe$_3$(NH$_2$): yield 0.211 g (0.640 mmol, 71%); ^{1}H NMR (CD$_2$Cl$_2$) δ 10.45 (br s, 2, NH$_2$), 1.63 (s, 15, Cp*), 0.75 (s, 6, ReMe$_c$), 0.26 (s, 3, ReMe$_t$); ^{13}C NMR (CD$_2$Cl$_2$) δ 92.5 (s, Me$_5$*C*), 23.4 (q, ReMe$_c$), 13.4 (q, ReMe$_t$), 10.5 (q, *Me*$_5$C); ^{15}N NMR (CD$_2$Cl$_2$) δ 219.8 (t, J_{NH} = 75 Hz); IR (Nujol; cm^{-1}) 3365 (m, NH), 3282 (m, NH), 1558 (m, NH$_2$ bend). Anal. Calcd for ReC$_{13}$H$_{26}$N: C, 40.82; H, 6.85; N, 3.66. Found: C, 41.22; H, 7.04; N, 3.34.

Cp*ReMe$_3$(NMeH) (6b). Cp*ReMe$_3$(OTf) (0.415 g, 0.903 mmol) was dissolved in 50 mL of ether. The sample was cooled to −196 °C, and methylamine (2.709 mmol) was condensed into the reaction vessel. The reaction mixture was warmed to room temperature and was stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with pentane. Solvent was removed from the green extract in vacuo to give Cp*ReMe$_3$(NMeH) as a green powder: yield 0.283 g (0.741 mmol, 82%); ^{1}H NMR (CD$_2$Cl$_2$) δ 12.20 (br s, 1, NMe*H*), 3.15 (d, 3, N*Me*H), 1.60 (s, 15, Cp*), 0.80 (s, 3, ReMe), 0.50 (s, 3, ReMe), 0.09 (s, 3, ReMe); ^{13}C NMR (CD$_2$Cl$_2$) δ 91.8 (s, Me$_4$*C*), 45.4 (q, NH*Me*), 33.0 (q, ReMe), 25.5 (q, ReMe), 16.3 (q, ReMe), 10.0 (q, *Me*$_5$C). Anal. Calcd for ReC$_{14}$H$_{28}$N: C, 42.40; H, 7.12; N, 3.53. Found: C, 42.40; H, 7.37; N, 3.20.

Cp*ReMe$_3$(NMe$_2$) (6c). Cp*ReMe$_3$(OTf) (0.200 g, 0.388 mmol) was dissolved in 20 mL of ether and cooled to −196 °C. Dimethylamine (1.164 mmol) was condensed into the reaction vessel. The reaction mixture was warmed to room temperature and was stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with pentane. Pentane was removed from the orange filtrate in vacuo to give Cp*ReMe$_3$(NMe$_2$) as an orange cystalline solid: yield 0.133 g (0.324 mmol, 84%); ^{1}H NMR (C$_6$D$_6$) δ 3.20 (s, 6, NMe$_2$), 1.33 (s, 15, Cp*), 1.28 (s, 6, ReMe$_c$), 0.72 (s, 3, ReMe$_t$); ^{13}C NMR (C$_6$D$_6$) δ 91.4 (s, Me$_5$*C*), 59.9 (q, NMe$_2$), 33.5 (q, ReMe$_c$), 27.4 (q, ReMe$_t$), 9.2 (q, *Me*$_5$C). Anal. Calcd for ReC$_{15}$H$_{30}$N: C, 43.88; H, 7.36; N, 3.41. Found: C, 43.73; H, 7.17; N, 3.38.

Reduction of 2a To Yield Ammonia. Under an atmosphere of dinitrogen, 30 mg of [Cp*ReMe$_3$(N$_2$H$_4$)][OTf] was placed in a 50-mL Schlenk flask. Reductant (sodium or zinc amalgam; 4 equiv and 2,6-lutidinium chloride (as a proton source; 8 equiv) were added to the flask, which was then capped with a septum and wired shut. Ten milliliters of cold (−40 °C) THF was added to the flask via syringe, and the reaction mixture was stirred vigorously. After 20 h at 25 °C, 100 μL of concentrated HCl was added to the reaction mixture. The solvent was then removed in vacuo, and the residue was treated with 15 mL of a 4.0 M NaOH solution in a closed system under argon. The mixture was distilled gently into 15 mL of 0.5 N H$_2$SO$_4$ until ∼10–15 mL of the distillate had been collected. The volume of the acid solution was then brought up to 30 mL with distilled water, and ammonia was measured quantitatively by the indophenol method.[20]

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