Cis and Trans Rhenium Hydrido Dinitrogen Complexes from Protonation Reactions of Cp*Re(PMe$_3$)$_2$(N$_2$)

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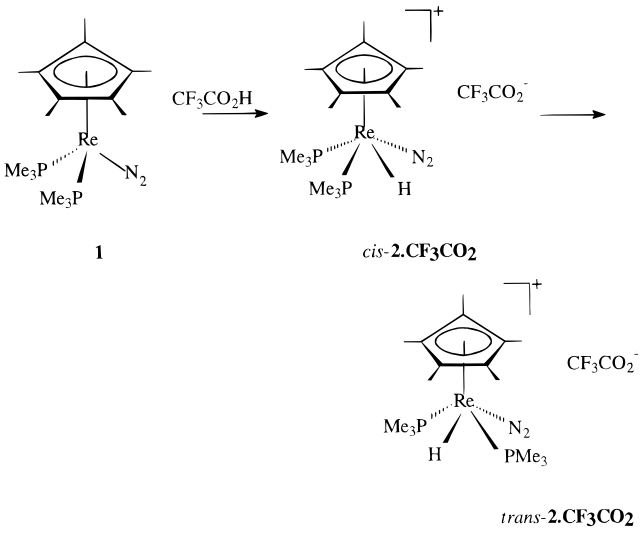
The dinitrogen complex Cp*Re(PMe$_3$)$_2$(N$_2$) (**1**) undergoes protonation at rhenium but not at the rhenium-bound dinitrogen ligand under conditions described here. Protonation by using CF_3CO_2H, HBF_4·OEt_2, or CF_3SO_3H at 213 K afforded the respective rhenium hydrido dinitrogen complexes *cis*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][CF_3CO_2] (*cis*-**2**(CF_3CO_2)), *cis*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][BF_4] (*cis*-**2**(BF_4)), and *cis*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][CF_3SO_3] (*cis*-**2**(CF_3SO_3). These complexes isomerized smoothly to the corresponding trans isomers as the temperature was raised to 273 K. The cis and trans isomers have been fully characterized by using a combination of IR and ^{1}H, ^{31}P, and ^{15}N NMR spectroscopy, with the dinitrogen ligand singly-labeled in either the N_α or N_β positions. The trans isomers are all thermally unstable at room temperature, but *trans*-**2**(CF_3CO_2) is significantly more stable than its analogs, indicating that the counteranion may play a role in stabilizing these cationic rhenium hydrido dinitrogen complexes.

Introduction

In view of its importance and relevance to understanding the mechanism of biological nitrogen fixation, there is continuing interest in the outcome of attempts to protonate the dinitrogen ligand in well-defined transition metal dinitrogen complexes.[1−3]

In a previous paper, we described the synthesis of the title complex Cp*Re(PMe$_3$)$_2$(N$_2$) (**1**) shown in Scheme 1.[4] The relatively electron-donating ligands Cp* and PMe$_3$ and the low oxidation state Re(I) ensure that the rhenium in **1** is relatively electron-rich. As a result, back-bonding from the d_π (d^6) orbitals into the dinitrogen π* orbitals is expected to be significant, in agreement with the observed ν(NN) stretching frequency at 1975 cm^{-1}. We therefore considered that a protonation study of this complex was warranted, to determine the susceptibility of the dinitrogen ligand to protonation. As described in this paper, under the conditions utilized the outcome to date is protonation of rhenium rather than the dinitrogen ligand. However, the dinitrogen ligand remains coordinated to afford cis and trans isomers of a new hydrido dinitrogen complex.

Scheme 1



Results

Preliminary Reactions of Cp*Re(PMe$_3$)$_2$(N$_2$) (1) with HBF_4·OEt_2, CF_3SO_3H, or CF_3CO_2H at Room Temperature. When a 5-fold excess of HBF_4·OEt_2 was added to a pale yellow solution of Cp*Re(PMe$_3$)$_2$(N$_2$) (**1**) in acetone-d_6 at room temperature, the solution immediately turned dark orange. An IR spectrum showed the complete disappearance of the ν(NN) absorption of **1**, but no concomitant growth of new absorptions in the 2400−1400 cm^{-1} region, and the absence of any ν(NH) absorption band suggested that the product did not contain a protonated dinitrogen ligand. The ^{1}H NMR spectrum, acquired *ca.* 1 h after the addition, did not exhibit signals assignable to NH or hydride resonances. Workup of the NMR solution revealed trace amounts of Cp*ReO$_3$[5] and trimethylphosphine oxide. No other rhenium-containing product could be identified. Analogous results were obtained when the protonation of **1** was repeated using trifluoromethanesulfonic acid. Surprisingly, however, this was not the case for trifluoroacetic acid. The solution of **1** turned orange upon addition of a 5-fold excess of CF_3CO_2H, and an IR spectrum recorded immediately showed the complete disappearance of **1** and the presence of a weak, broad absorption at 2080 cm^{-1} possibly assignable to ν(NN) of a new dinitrogen complex, but no absorption that could be assigned to ν(NH), indicating that the dinitrogen ligand had not been protonated. The ^{1}H NMR spectrum, obtained *ca.* 1 h after the addition, exhibited

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a singlet at δ 2.05 assigned to the Cp* group, a virtual doublet at δ 1.75 [$(^2J_{H-P} + {}^4J_{H-P}) = 9.5$ Hz] assigned to the PMe_3 ligands, and a high field triplet ($J = 49.6$ Hz) at δ −10.58, integrating to 1 proton, assigned to a hydride coupled to two symmetry-equivalent PMe_3 ligands. The IR and NMR are consistent with formulation of the product as *trans*-[Cp*ReH(N_2)(PMe_3)$_2$][CF_3CO_2] (*trans*-**2**(CF_3CO_2); see Scheme 1). Interestingly, the same NMR sample 12 h later showed the total disappearance of all resonances for this newly-formed rhenium hydrido dinitrogen complex, and from the workup of the NMR sample only minor amounts of Cp^*ReO_3 and trimethylphosphine oxide were identified, as noted previously for the reactions using $HBF_4{\cdot}OEt_2$ and CF_3SO_3H.

The protonation of **1** in acetone with CF_3CO_2H was repeated at room temperature in an attempt to isolate and further identify *trans*-**2**(CF_3CO_2). After evaporation of the solvent, the product was insoluble in hexane or diethyl ether but was very soluble in acetone. Mass spectra obtained by using electron impact (EI), low voltage electron impact, or chemical ionization (CI) mass spectrometry in all cases showed no parent ion corresponding to *trans*-**2**(CF_3CO_2), or *trans*-**2**$^+$, presumably owing to thermal instability. The mass spectra instead exhibited a parent peak and fragmentation pattern consistent with Cp*ReH(CF_3CO_2)(PMe_3)$_2$, which we propose to result from *trans*-**2**(CF_3CO_2) under the mass spectroscopic conditions. Clearly, assignment of the original sample as this hydride is not consistent with the IR and subsequent ^{15}N NMR results (see below).

Low-Temperature Reactions of Cp*Re(PMe_3)$_2$(N_2) (1), (1-$^{15}N_\alpha$), or (1-$^{15}N_\beta$) with CF_3CO_2H. A 5-fold excess of CF_3CO_2H was added to Cp*Re(PMe_3)$_2$(N_2) (**1**) in acetone-d_6 at 195 K. The ^1H NMR spectrum at 213 K, *ca.* 1 h after the addition, showed the complete disappearance of **1** and the apparent formation of a single rhenium product which exhibited a singlet at δ 2.08 (Cp*), an apparent broad triplet at δ 1.76 integrating to 18 protons with $J = 8.8$ Hz, assigned to the PMe_3 ligands, and a doublet at δ −10.96 integrating to 1 proton with $J = 64.2$ Hz; no signal corresponding to an NH resonance was evident. This result is again indicative of protonation of the metal in **1** to give a rhenium hydrido complex, but the NMR data clearly differ from those at room temperature already assigned to *trans*-**2**(CF_3CO_2).

The $^{31}P\{^1H\}$ NMR spectrum of the same sample at 213 K showed two resonances at δ −42.16 and δ −38.67 in a typical AB quartet pattern with $J_{P-P} = 48.6$ Hz indicating two symmetry-*inequivalent* PMe_3 ligands (Figure 1). This suggests that the apparent PMe_3 triplet observed in the ^1H NMR spectrum is actually two overlapping doublets. Selectively decoupling only the PMe_3 methyl resonance caused the phosphorus resonance at δ −42.16 to appear as a doublet of doublets arising from coupling to the other phosphorus and to the metal hydride ($J_{P-H} = 64.4$ Hz; $J_{P-P} = 48.6$ Hz). Notably, the ^{31}P resonance at δ −38.67 remained a doublet. This result is consistent with the ^1H NMR spectrum which showed that the rhenium hydride resonance was observably coupled to only one PMe_3 ligand. Taken together with subsequent ^{15}N NMR results, these NMR data are congruent with assignment of the low-temperature product as *cis*-[Cp*ReH(N_2)(PMe_3)$_2$][CF_3CO_2] (*cis*-**2**(CF_3CO_2); see Scheme 1).

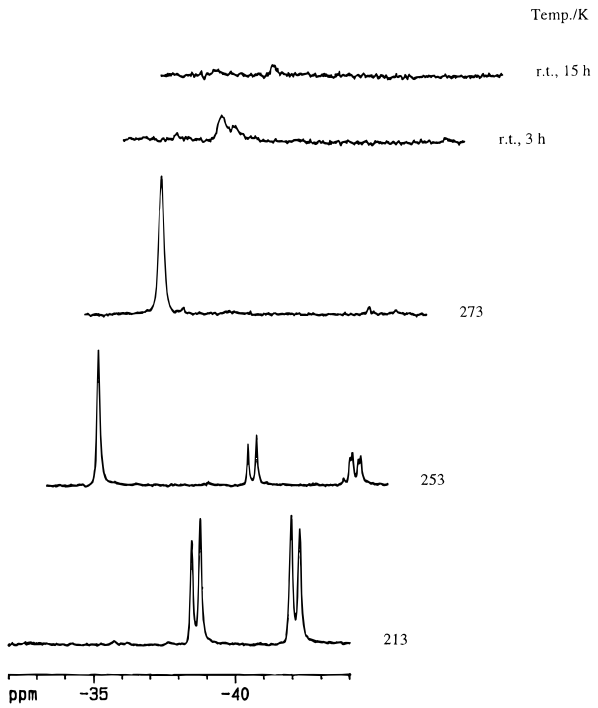

Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (162 MHz) for the reaction of Cp*Re(PMe_3)$_2$(N_2) (**1**) and CF_3CO_2H in acetone-d_6.

A sequence of ^1H and $^{31}P\{^1H\}$ NMR spectra (Figure 1) with increasing temperature demonstrated the decay of this product and the concomitant growth of resonances corresponding to *trans*-**2**(CF_3CO_2), and at 273 K the conversion was complete. The ^1H NMR spectrum at 273 K now exhibited a singlet at δ 2.05 (Cp*), a virtual doublet at δ 1.75 [$(^2J_{H-P} + {}^4J_{H-P}) = 9.8$ Hz] (PMe_3), and a hydride triplet at δ −10.60 ($J = 50.3$ Hz) integrating to 1 proton; no NH resonance was observed. These data are clearly similar to those assigned earlier to *trans*-**2**(CF_3CO_2) in the room-temperature experiment. Furthermore, the $^{31}P\{^1H\}$ NMR spectrum at 273 K (Figure 1) exhibited only a singlet at δ −34.71 in agreement with symmetry-*equivalent* PMe_3 ligands. By selective decoupling of only the PMe_3 methyl resonance, this ^{31}P resonance appeared as a doublet indicating that each equivalent phosphorus is coupled to the hydride ($J_{P-H} = 50.1$ Hz) in agreement with the triplet observed for the hydride ^1H resonance.

The NMR sample was then warmed to room temperature. The ^1H NMR spectrum recorded after 3 h showed a significant loss in intensity and the spectrum recorded 12 h later showed the complete disappearance of all the resonances of this complex. Results consistent with these were obtained from $^{31}P\{^1H\}$ NMR spectra (Figure 1). The elapsed time taken for the variable-temperature NMR experiments just described (from the initial reaction to the point where the products apparently decomposed) was about 19 h. The protonation of **1** with CF_3CO_2H was repeated in acetone-d_6 at 195 K, and the resulting solution was kept at 195 K for *ca.* 32 h. The *room-temperature* ^1H NMR spectrum observed immediately after this time was identical to the variable-temperature ^1H NMR spectrum obtained previously at 273 K and indicated only *trans*-**2**(CF_3CO_2).

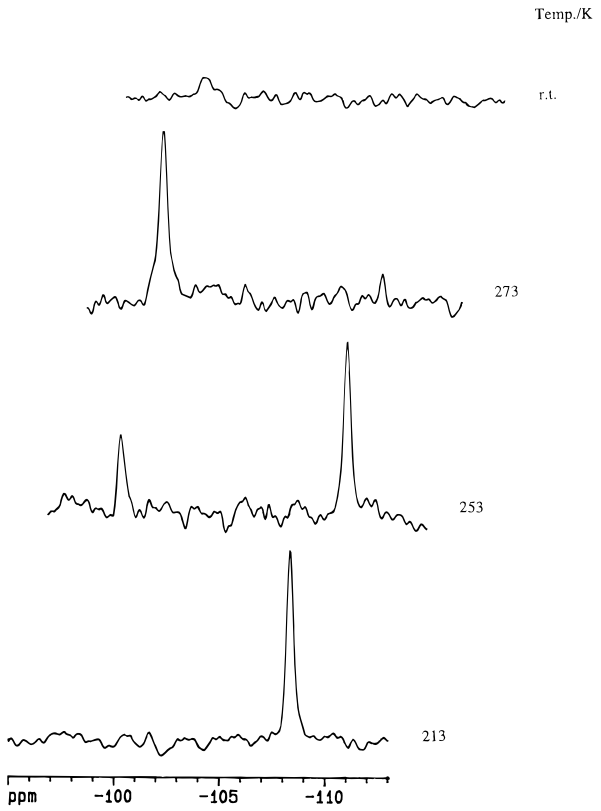

Figure 2. Variable-temperature ^{15}N NMR spectra (40.6 MHz) for the reaction of Cp*Re$(PMe_3)_2(^{15}N^{14}N)$ (**1**-$^{15}N_\alpha$) and CF_3CO_2H in acetone-d_6.

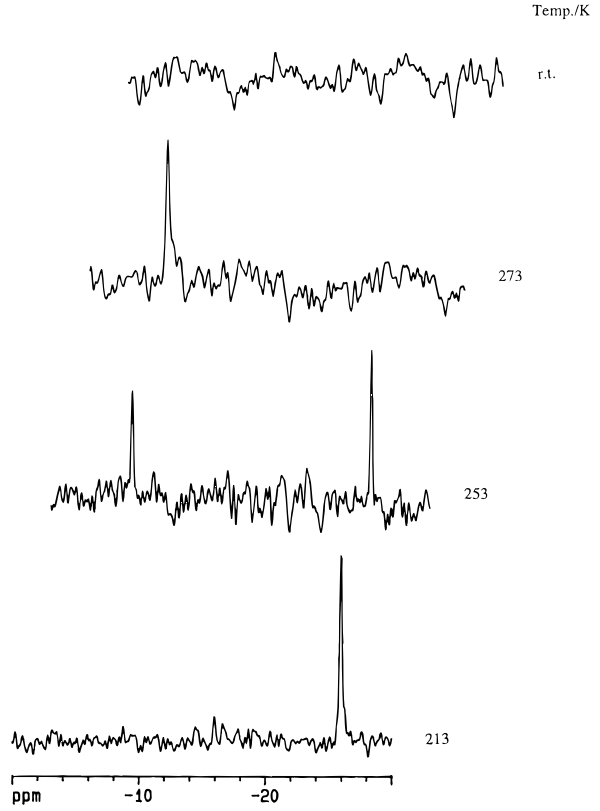

Figure 3. Variable-temperature ^{15}N NMR spectra (40.6 MHz) of the reaction of Cp*Re$(PMe_3)_2(^{14}N^{15}N)$ (**1**-$^{15}N_\beta$) and CF_3CO_2H in acetone-d_6.

In an effort to confirm the retention of the dinitrogen ligand in these protonation products, the reaction of **1** with CF_3CO_2H was followed by ^{15}N NMR spectroscopy using ^{15}N-labeled **1**. A 5-fold excess of CF_3CO_2H was added to a solution of the $^{15}N_\alpha$-labeled complex Cp*Re$(PMe_3)_2(^{15}N^{14}N)$ (**1**-$^{15}N_\alpha$) in acetone-d_6 at 195 K. The ^{15}N NMR spectrum obtained at 213 K, *ca.* 2 h after the addition, showed the total disappearance of **1**-$^{15}N_\alpha$ and the formation of a product which exhibited a singlet at δ −108.3 (Figure 2). This result clearly demonstrates that the coordinated dinitrogen in **1** has not been protonated at N_α, since this would have yielded a doublet for the ^{15}N resonance. The chemical shift is reasonable for a rhenium-bound nitrogen atom in a dinitrogen complex,[6,7] but of course, this single measurement does not unambiguously prove the presence of dinitrogen. The ^{15}N NMR spectrum of free N_2 in the same solvent under the same acidic conditions exhibited a resonance at δ −73.7, showing that free dinitrogen is not responsible. The ^1H NMR spectrum at 213 K of this product formed from **1**-$^{15}N_\alpha$ reproduced the results obtained previously for the reaction using unlabeled **1**; that is to say, no coupling with ^{15}N was evident in the hydride resonance.

A sequence of ^{15}N NMR spectra with increasing temperature (Figure 2) showed the gradual decay of the original ^{15}N resonance and the concomitant growth of a second singlet at δ −98.6 until, at 273 K, only the second resonance was present. As the temperature was raised to room temperature, the new ^{15}N resonance disappeared without the concomitant growth of any new resonances to indicate that protonation or reduction of the dinitrogen had occurred. Presumably dinitrogen is evolved, but it was not detected in the NMR spectra because of its limited solubility.

Similar results were obtained when a solution of the $^{15}N_\beta$ labeled dinitrogen complex Cp*Re$(PMe_3)_2(^{14}N^{15}N)$ (**1**-$^{15}N_\beta$) in acetone-d_6 was reacted with a 5-fold excess of CF_3CO_2H at 195 K. The ^{15}N NMR spectrum of this solution at 213 K, recorded *ca.* 2 h after the addition, showed the complete disappearance of **1**-$^{15}N_\beta$ and the presence of a singlet at δ −26.0 (Figure 3). This singlet indicates that the coordinated dinitrogen had not been protonated at N_β, but the presence of a ^{15}N signal after protonation again shows that a new nitrogen-containing species has been produced, and taken with the result of **1**-$^{15}N_\alpha$ it indicates the retention of *both* nitrogen atoms of the original dinitrogen complex **1** in the product. Though this does not entirely prove the presence of a *dinitrogen* ligand in the product, it is clearly the most reasonable conclusion. The ^1H NMR spectrum of the same solution reproduced the results obtained from unlabeled **1** and for **1**-$^{15}N_\alpha$; the hydride resonance again showed no coupling to ^{15}N. A sequence of ^{15}N NMR spectra acquired with increasing temperature once again showed the gradual decay of the original ^{15}N resonance and now the concomitant growth of a second singlet at δ −6.2 (Figure 3). At 273 K the conversion to the new product was complete. As the temperature was raised to room temperature, the ^{15}N resonance due to the new product again disappeared with no concomitant growth of resonances assignable to any nitrogen-containing derivatives.

In order to substantiate the presence of a dinitrogen ligand in the protonation products, the ^{15}N isotopic shift

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Table 1. IR and ^{15}N NMR Data for Selected Hydrido Dinitrogen and Dinitrogen Complexes

complex	^{15}N NMR[a] $\delta(^{15}N_\alpha)$	$\delta(^{15}N_\beta)$	IR $\nu(^{14}N_2)$[b]	ref
$Cp^*Re(PMe_3)_2(N_2)$ **(1)**	−82.1[c]	−51.7[c]	1975[d]	this work
trans-$W(N_2)_2(dppe)_2$	−60.1[e]	−48.6[e]	1946[f]	6
trans-$Mo(N_2)_2(dppe)_2$	−43.1[e]	−42.8[e]	1976[f]	6
$Fe(N_2)(dmpe)_2$			1975[e]	10
cis-$[Cp^*ReH(N_2)(PMe_3)_2][CF_3CO_2]$ (*cis*-**2**(CF_3CO_2))	−108.3[c]	−26.0[c]		this work
trans-$[Cp^*ReH(N_2)(PMe_3)_2][CF_3CO_2]$ (*trans*-**2**(CF_3CO_2))	−98.6[c]	−6.2[c]	2079[c]	this work
trans-$[WH(N_2)_2(dppe)_2][HCl_2]$	−75.3[e]	−48.6[e]		6
$[FeH(N_2)(dmpe)_2][BPh_4]$			2094[e]	10
trans-$ReH(N_2)(dppe)_2$			2006[g]	17
$[ReH_2(N_2)(dppe)_2][BF_4]$			2118[g]	17
cis-$ReH(N_2)(PMe_2Ph)_4$			2000[h]	19

[a] Referenced to external $MeNO_2$. [b] In cm^{-1}. [c] Acetone (IR) or acetone-d_6 (NMR) solvent. [d] Hexane solvent. [e] THF solvent. [f] In Nujol. [g] In CsI disk. [h] Ether solvent.

on the IR band previously assigned to ν(NN) in the product identified at 273 K (i.e., *trans*-**2**(CF_3CO_2)) was measured. The protonation of the unlabeled dinitrogen complex **1** with CF_3CO_2H in acetone at 273 K gave a broad, moderately intense ν(NN) absorption at 2079 cm^{-1}, and upon repeating the reaction using **1**-$^{15}N_\alpha$ $\nu(^{15}NN)$ occurred at 2047 cm^{-1}. The 32 cm^{-1} isotopic shift in ν(NN) is of the expected magnitude. Taken together the ^1H, ^{31}P, and ^{15}N NMR and the IR results strongly indicate the final protonation product to be *trans*-**2**(CF_3CO_2) and the low-temperature precursor *cis*-**2**(CF_3CO_2).

Low-Temperature Reactions of $Cp^*Re(PMe_3)_2(N_2)$ (1) with HBF_4·OEt_2 or CF_3SO_3H. A 5-fold excess of HBF_4·OEt_2 was added to **1** in acetone-d_6 at 195 K. The ^1H NMR spectrum at 213 K *ca.* 1 h after the addition showed the total disappearance of **1** and the presence of a singlet at δ 2.05 (Cp*), an apparent broad triplet integrating to 18 protons with J = 9.8 Hz at δ 1.73 (PMe_3), and a hydride doublet at δ −10.99 integrating to 1 proton with J = 64.1 Hz; no NH resonance was evident. These results are similar to the foregoing, and by analogy indicate the formation of *cis*-**2**(BF_4). Raising the temperature resulted in decay of the resonances assigned to this hydrido complex and the concomitant growth of resonances corresponding to a new hydrido product, and the conversion was complete at 273 K. The spectrum at 273 K exhibited a singlet at δ 2.03 (Cp*) and a virtual doublet at δ 1.72 assigned to PMe_3 ligands with $(^2J_{H-P} + {}^4J_{H-P}) = 9.7$ Hz. There was also a hydride triplet at δ −10.63 integrating to 1 proton with J = 50.4 Hz; no NH resonance was observed. These data are similarly assigned to the formation of *trans*-**2**(BF_4). At room temperature, the ^1H resonances due to the new product disappeared. Analogous results to these were obtained for the reaction between $Cp^*Re(PMe_3)_2(N_2)$ (**1**) and CF_3SO_3H, resulting in the formation of *cis*-**2**(CF_3SO_3) and *trans*-**2**(CF_3SO_3), respectively.

Discussion

To summarize the results, $Cp^*Re(PMe_3)_2(N_2)$ (**1**) is susceptible to protonation at the metal but not at the coordinated dinitrogen ligand under the conditions used. The cation *cis*-$\mathbf{2}^+$ is formed and isomerizes to *trans*-$\mathbf{2}^+$ upon increasing the temperature. Quite apart from the ^1H, and ^{31}P NMR evidence for a rhenium hydride, the ^{15}N NMR spectra do not support protonation of the dinitrogen ligand. Notably, the $^{15}N_\beta$ resonance of a metal-bound dinitrogen ligand [e.g., *trans*-$W(N_2)_2(dppe)_2$: $\delta(^{15}N_\alpha)$ −60.1, $\delta(^{15}N_\beta)$ −48.6][6] is known to undergo a dramatic change in chemical shift if it is protonated to give a diazenido complex [e.g., *trans*-$WBr(N_2H)(dppe)_2$: $\delta(^{15}N_\alpha)$ −25.9, $\delta(^{15}N_\beta)$ −187.1]; a smaller change in chemical shift is observed for the $^{15}N_\alpha$ resonance.[6] By contrast, the ^{15}N NMR spectra at 213 K for the reaction between $Cp^*Re(PMe_3)_2(^{15}N^{14}N)$ (**1**-$^{15}N_\alpha$) or $Cp^*Re(PMe_3)_2(^{14}N^{15}N)$ (**1**-$^{15}N_\beta$) and CF_3CO_2H, exhibited a singlet in each case (Table 1) in the region expected for a typical metal-bound dinitrogen ligand.[6,7]

Furthermore, the reaction appears to be independent of the acid used since treatment of **1** with CF_3CO_2H, HBF_4·OEt_2, or CF_3SO_3H, formed the same cationic rhenium hydrido dinitrogen complex *cis*-$\mathbf{2}^+$ at 213 K. In all cases, isomerization to *trans*-$\mathbf{2}^+$ was complete at 273 K. Interestingly, while the three salts of *trans*-$\mathbf{2}^+$ were thermally unstable at room temperature, *trans*-**2**(CF_3CO_2) was significantly more stable than the others, inferring that the counteranion may play a role in stabilizing these cationic rhenium hydrido dinitrogen complexes.

As was pointed out in the Introduction, the presence of the two PMe_3 ligands and the Cp* ligand in **1** is expected to make the Re center relatively electron-rich and enhance back-bonding to the dinitrogen ligand. Of the family of related Cp or Cp* half-sandwich rhenium dinitrogen complexes with carbonyl or phosphine ligands, **1** was considered to be the most likely candidate for attempted protonation of the dinitrogen ligand since it has the lowest value of ν(NN).[4] Furthermore, the value of **1** (ν(NN) 1975 cm^{-1}) is similar to values for other dinitrogen complexes that are known to undergo protonation (Table 1). Examples are *trans*-$Mo(N_2)_2(dppe)_2$ (ν(NN) 1976 cm^{-1}), *trans*-$W(N_2)_2(dppe)_2$ (ν(NN) 1946 cm^{-1}), and $Fe(N_2)(dmpe)_2$ (ν(NN) 1975 cm^{-1}).[8−11] However, this optimism must be tempered by noting that the rhenium dinitrogen complex $ReCl(N_2)(PMe_2Ph)_4$ is reported *not* to protonate at nitrogen (but does so at Re) despite having a ν(NN) value as low as 1920 cm^{-1}.[12,13]

In the family of rhenium dinitrogen complexes Cp′Re$(CO)_2(N_2)$ (Cp′ = Cp or Cp*) and $Cp^*ReL(CO)(N_2)$ (L =

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PMe_3, $P(OMe)_3$), the N_α chemical shift (δ) systematically moves to lower field with increasing electron-donating ability of the coligands.[4,14] $CpRe(CO)_2(N_2)$ has the highest field N_α resonance (δ −121), and $Cp^*Re(CO)(PMe_3)(N_2)$ has the lowest (δ −91). The value for **1** is even lower (δ −82). By contrast, the resonance for N_β changes only from *ca* δ −27 to −33 in the sequence of coligands $Cp(CO)_2$ (−27) > $Cp^*(CO)_2$ (−28) > $Cp^*(CO)(PMe_3)$ (−33) = $Cp^*(CO)\{P(OMe)_3\}$ (−33), so varying the electron density on the metal evidently produces smaller changes in $\delta(N_\beta)$ than those observed in $\delta(N_\alpha)$ for these complexes. However, complex **1** is an exception. The N_β chemical shift is moved considerably, to δ −51.7. It appears that the electron-donating ancillary ligands in **1** have a substantial effect on the electronic environment of both N_α and N_β, and it is again notable that $\delta(N_\beta)$ is comparable with the values reported for some of the dinitrogen complexes cited above, such as *trans*-$Mo(N_2)_2(dppe)_2$ ($\delta(N_\beta)$ −42.8) and *trans*-$W(N_2)_2(dppe)_2$ ($\delta(N_\beta)$ −48.6) that undergo protonation of N_β.[6]

A further incentive to try to protonate N_2 in **1** was the observation that if a single proton were delivered to N_β this would produce a cationic rhenium diazenido complex, $[Cp^*Re(PMe_3)_2(N_2H)]^+$. Much previous work in this laboratory has shown that tetrafluoroborate salts of *aryl*diazenido analogs $[Cp^*Re(L)_2(N_2Ar)]^+$ are common, and in the present context $[Cp^*Re(PMe_3)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ specifically is known to be a stable compound.[4,15] While this complex actually has been obtained from reactions of the arenediazonium ion, nevertheless its existence and stability may reasonably be grounds for optimism that the parent diazenido complex could also be observable.

Although protonation of N_2 in **1** did not occur under the conditions used, and protonation of rhenium resulted instead, it is possible that it could occur if the proper conditions can be found. Protonation of N_2 is known to be notoriously solvent, acid, and concentration dependent,[3,9,16] so this system does warrant further investigation. In particular, it is worth noting that *trans*-$W(N_2)_2(dppe)_2$ and $Fe(N_2)(dmpe)_2$, which afford the corresponding hydrido dinitrogen complexes $[WH(N_2)_2(dppe)_2]^+$ and $[FeH(N_2)(dmpe)_2]^+$, respectively, also undergo protonation of nitrogen in competition or under the right conditions.[9,11] Therefore, the results obtained for **1** are encouraging.

While several examples of hydrido dinitrogen complexes are known, very few have, in fact, been the result of protonation of a well-defined dinitrogen complex. Those that we are aware of are $[ReH_2(N_2)(dppe)_2]^+$, $[ReHCl(N_2)(PMe_2Ph)_4]^+$, $[WH(N_2)_2(dppe)_2]^+$, $[MoH(N_2)_2(depe)_2]^+$, and $[FeH(N_2)(dmpe)_2]^+$.[8,9,11,12,16,17] In a related case, protonation of a methyl dinitrogen complex does proceed with retention of the dinitrogen ligand but presumably proton transfer to the ligand occurs, since methane is evolved.[18] Hydrido dinitrogen compounds of rhenium are not common. Other examples are $ReH(N_2)(dppe)_2$ and $ReH(N_2)(PMe_2Ph)_4$.[17,19] To our knowledge, protonation of dinitrogen in rhenium complexes has not yet been accomplished.

The cations *cis*-**2**$^+$ and *trans*-**2**$^+$ have been assigned four-legged piano-stool structures in keeping with the structures of several such $Cp'ReL_4$ species that have been established crystallographically.[20,21] The hydride in the *cis*-**2**$^+$ cation was observed to be coupled to only one of the inequivalent PMe_3 phosphorus atoms. Literature precedent suggests that in four-legged piano-stool type complexes with phosphorus and hydrogen coligands, the magnitude of the cis J_{H-P} coupling is generally large whereas that of the trans J_{H-P} coupling is small and sometimes unobservable. For example, in the cyclometalated complex $Cp^*ReH(CO)(\eta^2\text{-}CH_2PMe_2)$ where P and H (hydride) are cis, the cis J_{H-P} coupling was reported to be 38.2 Hz. However, in the cyclometalated tricyclohexylphosphine derivative $Cp^*ReH(CO)\{\eta^2\text{-}C_6H_{10}P(C_6H_{11})_2\}$ where P is trans to H, the metal hydride ligand was reported to exhibit no observable coupling to the phosphine group.[22,23] Thus, the observed J_{H-P} coupling in the rhenium hydrido dinitrogen cation *cis*-**2**$^+$ is assigned to result from the PMe_3 group cis to the metal hydride ligand.

Conclusion

The bis(trimethylphosphine) dinitrogen complex $Cp^*Re(PMe_3)_2(N_2)$ (**1**) undergoes protonation at rhenium but not at the rhenium-bound dinitrogen ligand under conditions described here. Furthermore, the protonation appears to be independent of the acid used since CF_3CO_2H, $HBF_4{\cdot}OEt_2$, or CF_3SO_3H afforded the respective rhenium hydrido dinitrogen complexes *cis*-$[Cp^*ReH(N_2)(PMe_3)_2][CF_3CO_2]$ (*cis*-**2**(CF_3CO_2)), *cis*-$[Cp^*ReH(N_2)(PMe_3)_2][BF_4]$ (*cis*-**2**(BF_4)), and *cis*-$[Cp^*ReH(N_2)(PMe_3)_2][CF_3SO_3]$ (*cis*-**2**(CF_3SO_3)) at 213 K, and these complexes isomerized to their corresponding trans isomers as the temperature was raised to 273 K. Interestingly, the trans isomers were found to be thermally unstable at room temperature, although *trans*-**2**(CF_3CO_2) was observed to be significantly more stable than its analogs inferring that the counteranion may play a role in stabilizing these cationic rhenium hydrido dinitrogen complexes.

Experimental Section

General Methods and Syntheses. The dinitrogen complex $Cp^*Re(PMe_3)_2(N_2)$ (**1**), and its ^{15}N derivatives **1**-$^{15}N_\alpha$ and **1**-$^{15}N_\beta$, were prepared and purified as described previously.[4] $HBF_4{\cdot}OEt_2$, CF_3SO_3H, and CF_3COOH were purchased from Aldrich and were stored under nitrogen.

IR spectra were measured by using a Bomem Michelson Model 120 FT-IR instrument. The spectra at 273 K were recorded as solutions in acetone by using a variable-temperature Research and Industrial Instruments Model VLT-2 cell modified with attached cannulae and equipped with CaF_2 windows (0.5 mm). The IR spectrum of the ^{15}N-labeled complex was obtained for a 99% ^{15}N isotopically enriched sample. The cell was flushed with argon and dry acetone prior

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to transfer of the solution *via* cannula to the cell. ^{1}H NMR chemical shifts are referenced to tetramethylsilane. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4. ^{14}N and ^{15}N NMR chemical shifts are referenced to external nitromethane ($MeNO_2$). The term "virtual doublet" refers to the non-first-order multiplet for PMe_3 which is seen in some of the ^{1}H NMR spectra; the apparent coupling constant is given by the separation between the two outside peaks.[24−26] The variable-temperature ^{1}H, ^{31}P, and ^{15}N NMR spectra of the products resulting from the protonation of complexes **1**, **1**-$^{15}N_\alpha$, or **1**-$^{15}N_\beta$ were recorded at 400, 162, and 40.6 MHz, respectively, on a Bruker AMX 400 instrument equipped with a B-VT 1000 variable-temperature unit. Acetone-d_6 (Isotec Inc.) was the solvent for the variable-temperature NMR work.

Room-Temperature ^{1}H NMR Experiments: Reaction of Cp*Re(PMe$_3$)$_2$(N$_2$) (1) with HBF$_4$·OEt$_2$, CF$_3$SO$_3$H, or CF$_3$CO$_2$H. A 5-fold excess of HBF_4·OEt_2, CF_3SO_3H, or CF_3CO_2H was added by syringe to a pale yellow solution of **1** (50 mg, 0.10 mmol) in acetone-d_6 at room temperature. In all cases, the solution immediately changed from yellow to orange. The respective solutions were then transferred under argon to a 5 mm NMR tube. Room-temperature ^{1}H NMR spectra, acquired *ca.* 1 h after the addition of HBF_4·OEt_2 or CF_3SO_3H, exhibited in each case a singlet at δ 2.09 and a doublet at δ 1.67 (J_{H-P} = 13.7 Hz) assigned to Cp*ReO_3 and $OPMe_3$, respectively. In both cases, removal of the solvent under vacuum gave a yellow-brown oil. Diethyl ether extractions of the oil gave trace amounts of Cp*ReO_3 and $OPMe_3$. The remaining yellow-brown oil exhibited no ^{1}H NMR resonances and no diagnostic IR absorptions. A room-temperature ^{1}H NMR spectrum, recorded *ca.* 1 h after the addition of CF_3CO_2H, was assigned to the rhenium hydrido dinitrogen complex *trans*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][CF_3CO_2] (*trans*-**2**(CF_3CO_2)). IR (acetone-d_6): ν(NN) 2080 cm^{-1}. ^{1}H NMR (acetone-d_6): δ −10.58 (t, 1H, ReH, J_{H-P} = 49.6 Hz), 1.75 (virtual doublet, 18H, PMe_3, J_{app} = 9.5 Hz), 2.05 (s, 15H, Cp*). A room-temperature ^{1}H NMR spectrum recorded 12 h later showed the complete disappearance of *trans*-**2**(CF_3CO_2) and the presence of resonances due to Cp*ReO_3 and $OPMe_3$. Subsequent removal of the solvent under vacuum gave a yellow-brown oil. Diethyl ether extraction of the oil gave residual amounts of Cp*ReO_3 (4.4 mg, 0.012 mmol) and $OPMe_3$ and the remaining yellow-brown oil exhibited no ^{1}H NMR resonances and no diagnostic IR absorptions.

Variable-Temperature ^{1}H, ^{31}P, and ^{15}N NMR Experiments: Reaction of Cp*Re(PMe$_3$)$_2$(N$_2$) (1), (1-$^{15}N_\alpha$), or (1-$^{15}N_\beta$) with CF$_3$CO$_2$H. A pale yellow solution of **1**, **1**-$^{15}N_\alpha$, or **1**-$^{15}N_\beta$ (50 mg, 0.10 mmol) in acetone-d_6 was transferred to an NMR tube (5 mm tube for ^{1}H and ^{31}P; 10 mm tube for ^{15}N) kept in a Schlenk tube under a positive pressure of argon. The Schlenk tube was then cooled to 195 K. Under a strong purge of argon, the addition of a 5-fold excess of CF_3CO_2H by syringe to the NMR tube resulted in an orange solution. The NMR tube was then quickly removed from the cold bath and placed in the Bruker AMX 400 spectrometer whose cooling unit had been previously set to 213 K. An NMR spectrum was then acquired, *ca.* 60 min after the acid addition. An identical procedure was used for obtaining spectra for all the NMR nuclei. The product formed at 213 K was assigned as the rhenium hydrido dinitrogen complex *cis*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][CF_3CO_2] (*cis*-**2**(CF_3CO_2)), *cis*-**2**(CF_3CO_2)-$^{15}N_\alpha$, or *cis*-**2**(CF_3CO_2)-$^{15}N_\beta$. ^{1}H NMR (acetone-d_6, 213 K): δ −10.96 (broad doublet, 1H, ReH, J_{H-P} = 64.2 Hz), 1.76 (apparent triplet, 18H, PMe_3, J_{H-P} = 8.8 Hz), 2.08 (s, 15H, Cp*). ^{31}P NMR (PMe_3 methyl decoupled, acetone-d_6, 213 K): δ −42.16 (dd, PMe_3, $J_{P-H(hydride)}$ = 64.4 Hz, J_{P-P} = 48.6 Hz), −38.67 (d, PMe_3, J_{P-P} = 48.6 Hz). ^{15}N NMR (acetone-d_6, 213 K): δ −108.3 (s, $^{15}N_\alpha$), −26.0 (s, $^{15}N_\beta$). As the temperature of the solution was raised to 273 K the *cis* complexes isomerized to give *trans*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][CF_3CO_2] (*trans*-**2**(CF_3CO_2)), *trans*-**2**(CF_3CO_2)-$^{15}N_\alpha$, or *trans*-**2**(CF_3CO_2)-$^{15}N_\beta$, respectively. IR (acetone, 273 K): ν(NN) 2079 cm^{-1} (2047 cm^{-1} for ^{15}N-labeled complex). ^{1}H NMR (acetone-d_6, 273 K): δ −10.60 (t, 1H, ReH, J_{H-P} = 50.3 Hz), 1.75 (virtual doublet, 18H, PMe_3, J_{app} = 9.8 Hz), 2.05 (s, 15H, Cp*). ^{31}P NMR (PMe_3 methyl decoupled, acetone-d_6, 273 K): δ −34.71 (d, PMe_3, $J_{P-H(hydride)}$ = 50.1 Hz). ^{15}N NMR (acetone-d_6, 273 K): δ −98.6 (s, $^{15}N_\alpha$), −6.2 (s, $^{15}N_\beta$). The temperature of the NMR sample was then raised to room temperature. The room-temperature ^{1}H, ^{31}P, and ^{15}N NMR spectra recorded 3 h later demonstrated the decay of *trans*-**2**(CF_3CO_2), *trans*-**2**(CF_3CO_2)-$^{15}N_\alpha$ or *trans*-**2**(CF_3CO_2)-$^{15}N_\beta$ respectively; after 15 h the trans rhenium hydrido dinitrogen complexes had completely disappeared. Removal of the solvent under vacuum gave a yellow-brown oil. Diethyl ether extractions of the oil gave residual amounts of Cp*ReO_3 (5.5 mg, 0.015 mmol) and $OPMe_3$. The remaining yellow-brown oil exhibited no ^{1}H NMR resonances and no diagnostic IR absorptions.

Variable-Temperature ^{1}H NMR Experiments: Reaction of Cp*Re(PMe$_3$)$_2$(N$_2$) (1) with HBF$_4$·OEt$_2$ or CF$_3$SO$_3$H. A procedure was used similar to that described above for the low-temperature NMR experiments involving CF_3CO_2H. The product formed at 213 K using HBF_4·OEt_2 was assigned as *cis*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][BF_4] (*cis*-**2**(BF_4)). ^{1}H NMR (acetone-d_6, 213 K): δ −10.99 (broad doublet, 1H, ReH, J_{H-P} = 64.1 Hz), 1.73 (apparent triplet, 18H, PMe_3, J_{H-P} = 9.8 Hz), 2.05 (s, 15H, Cp*). The product formed at 213 K using CF_3SO_3H was assigned as *cis*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][CF_3SO_3] (*cis*-**2**(CF_3SO_3)). ^{1}H NMR (acetone-d_6, 213 K): δ −11.06 (broad doublet, 1H, ReH, J_{H-P} = 64.3 Hz), 1.64 (apparent triplet, 18H, PMe_3, J_{H-P} = 9.9 Hz), 1.97 (s, 15H, Cp*). As the temperature was raised to 273 K the cationic cis complexes isomerized to give respectively *trans*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][BF_4] (*trans*-**2**(BF_4)) (^{1}H NMR (acetone-d_6, 273 K): δ −10.63 (t, 1H, ReH, J_{H-P} = 50.4 Hz), 1.72 (virtual doublet, 18H, PMe_3, J_{app} = 9.7 Hz), 2.03 (s, 15H, Cp*)) and *trans*-[Cp*ReH(N$_2$)(PMe$_3$)$_2$][CF_3SO_3] (*trans*-**2**(CF_3SO_3)) (^{1}H NMR (acetone-d_6, 273 K): δ −10.65 (t, 1H, ReH, J_{H-P} = 50.7 Hz), 1.63 (virtual doublet, 18H, PMe_3, J_{app} = 9.6 Hz), 1.94 (s, 15H, Cp*)). As the temperature was raised to room temperature, the ^{1}H resonances corresponding to *trans*-**2**(BF_4) and *trans*-**2**(CF_3SO_3) slowly disappeared. Removal of the solvent under vacuum gave a yellow-brown oil, and diethyl ether extraction of the oil gave results described in the previous section.

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