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Chemistry of Coordinated Nitroxyl. Reagent-Specific Protonations of *trans*-Re(CO)$_2$(NO)(PR$_3$)$_2$ (R = Ph, Cy) That Give the Neutral Nitroxyl Complexes *cis,trans*-ReCl(CO)$_2$(NH═O)(PR$_3$)$_2$ or the Cationic Hydride Complex [*trans,trans*-ReH(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$]

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The reactions of hydrochloric and triflic acids with the five-coordinate nitrosyl complexes *trans*-Re(CO)$_2$(NO)(PR$_3$)$_2$ (**2a**, R = Ph; **2b**, R = Cy) have been investigated. Reaction of anhydrous HCl with **2** results in a *formal* protonation of the nitrosyl ligand and addition of chloride to the metal, giving the neutral nitroxyl complex *cis,trans*-ReCl(CO)$_2$(NH═O)(PR$_3$)$_2$ (**3a**, R = Ph; **3b**, R = Cy). Reaction of Brønsted bases with **3a** or **3b** results in clean conversion of **3** to **2** when the base is appropriately strong (p$K_b \approx 7$). Addition of HOSO$_2$CF$_3$ to solutions of **2a** results in protonation at the metal and formation of the cationic rhenium hydride [*trans,trans*-ReH(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**4**) in 74% yield; the deuteride [*trans,trans*-Re(^{2}H)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**4-d**) was analogously prepared from ^{2}HOSO$_2$CF$_3$. **4** crystallized from CH$_2$Cl$_2$/Et$_2$O solution in the orthorhombic space group *Pnma*, with $a = 17.2201(2)$ Å, $b = 23.6119(3)$ Å, $c = 9.2380(2)$ Å, and $Z = 4$. The least-squares refinement converged to $R(F) = 0.039$ and $R(wF^2) = 0.063$ for the 4330 unique data with $I > 2\sigma(I)$. The structure of **4** shows that the hydride (Re−H = 1.74 Å) occupies the position *trans* to the linear nitrosyl ligand (Re−N−O = 178.1(4)°) in the pseudooctahedral complex cation. Complex **4** does not react with chloride to give **3a**. DFT calculations carried out on free nitroxyl and its model complexes [Re(CO)$_5$(NH═O)$^+$] (**5**), [*mer,trans*-Re(CO)$_3$(NH═O)(PH$_3$)$_2$$^+$] (**6**), and *cis,trans*-ReCl(CO)$_2$(NH═O)(PH$_3$)$_2$ (**7**) indicate that coordinated nitroxyl acts as both a σ-donor and π-acceptor ligand, consistent with the observed trend for ν(NO) in free HN═O (1563 cm^{-1}), [*mer,trans*-Re(CO)$_3$(NH═O)(PPh$_3$)$_2$$^+$] (**1**, 1391 cm^{-1}), **3a** (1376 cm^{-1}), and **3b** (1335 cm^{-1}).

Introduction

Nitroxyl (HN═O) is a highly reactive, unstable molecule attracting current interest primarily because of its relationship to nitric oxide (NO). Nitric oxide plays numerous physiological roles, mainly functioning as a cell-signaling agent, and much recent work has been devoted to elucidating its biochemistry.[1] The one-electron redox relatives of NO, the nitrosonium cation (NO$^+$), and the nitroside anion (NO$^-$), as well as the conjugate acid of NO$^-$, nitroxyl, have been suggested to be responsible for some of the myriad functions attributed to nitric oxide in mammalian biochemistry.[1a,b] Interest in nitroxyl also stems from its postulated intermediacy in photochemical and free-radical reactions and the role its formation and decomposition may play in mechanisms for the combustion of nitrogen-containing fuels and the oxidation of atmospheric nitrogen.[2,3]

In contrast to its cousins NO and NO$^+$, which are commercially available reagents, a facile synthesis for NO$^-$ (or HN═O) remains elusive.[4] HN═O has been typically prepared by the reaction of hydrogen atoms with nitric oxide in the gas phase and in frozen Ar matrixes,[2] and an interesting recent report describes the trapping of an isolated NO$^-$ ion in a "molecular oxide bowl" along with the structural characterization of the complex salt.[5] Importantly, like the isoelectronic 1,2-diazene,[6−8] nitroxyl represents a classic example of an unstable molecule whose stability can be greatly enhanced by coordination to a transition metal. Roper's discovery that the addition of anhydrous HCl to the nitrosylosmium(0) complex Os(Cl)(CO)(NO)(PPh$_3$)$_2$ affords the nitroxyl complex *cis,trans*-Os(Cl)$_2$(CO)(NH═O)(PPh$_3$)$_2$ marked the first example of the stabilization of nitroxyl by coordination to a transition metal.[9,10] Sellman and co-workers have recently demonstrated that an HN═O

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(1) (a) Butler, A. R.; Flitney, F. W.; Williams, D. L. H. *Trends Pharmacol. Sci.* **1995**, *16* (1), 18, and references therein. (b) Stamler, J. S.; Singel, D. J.; Loscalzo, J. *Science* **1992**, *258*, 1898, and references therein. (c) Culotta, E.; Koshland, D. E., Jr. *Science* **1992**, *258*, 1862.

(2) (a) Dalby, F. W. *Can. J. Phys.* **1958**, *36*, 1336. (b) Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1973**, *48*, 536.

(3) Guadagnini, R.; Schatz, G. C.; Walch, S. P. *J. Chem. Phys.* **1995**, *102*, 774, and references therein.

(4) Smith, P. A. S.; Hein, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 5731.

(5) Kawanami, N.; Ozeki, T.; Yagasaki, A. *J. Am. Chem. Soc.* **2000**, *122*, 1239.

(6) Smith, M. R., III; Cheng, T.-Y.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 8638.

(7) Cheng, T.-Y.; Peters, J. C.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1994**, *116*, 204.

(8) Cheng, T.-Y.; Ponce, A.; Rheingold, A. L.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 657.

(9) Grundy, K. R.; Reed, C. A.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1501.

(10) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336.

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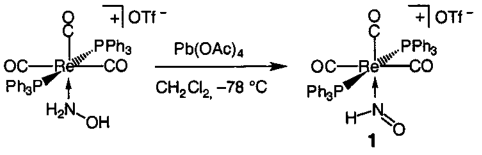
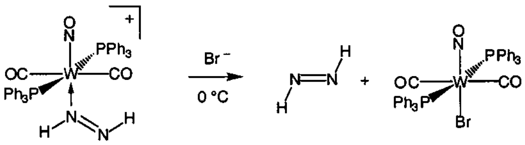
ligand can be prepared by the action of hydride on a coordinated nitrosyl, along with the structural characterization of the resulting complex.[11] In an important study with clear biological relevance, Farmer and co-workers have reported the synthesis, isolation, and characterization of an HN═O adduct of myoglobin.[12] Our group has described the synthesis of a cationic, pseudooctahedral nitroxyl complex of rhenium, [*mer,trans*-Re(CO)$_3$(NH═O)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**1**), produced by the selective oxidation of the hydroxylamine ligand of [*mer,trans*-Re(CO)$_3$(NH$_2$OH)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] using lead tetraacetate (eq 1).[13] By analogy to transition-metal complexes of 1,2-diazene (NH═NH), which react with bromide to provide clean sources of the free NH═NH molecule (eq 2),[6] it is hoped that these nitroxyl complexes can ultimately serve as HN═O synthons.



(1)



(2)

To better understand the factors that give rise to stable nitroxyl complexes and to compare the properties of charge-neutral derivatives with cationic derivatives such as **1**, the reactions of the five-coordinate rhenium nitrosyl complexes *trans*-Re(CO)$_2$(NO)(PR$_3$)$_2$ (**2a**, R = Ph; **2b**, R = Cy) with the Brønsted acids HCl and HOSO$_2$CF$_3$ have been investigated. In 1974, LaMonica et al. reported that **2a** and HCl react in alcohol or ether to give a mixture of products, one component of which exhibits a low-energy ν(NO) suggestive of ligated HN═O.[14] We have found the products of these reactions to be reagent specific, depending on the nature of the counterion, and these results are described herein.

Experimental Section

General Considerations. Reactions were carried out using standard high-vacuum and Schlenk techniques using dry, air-free solvents. Elemental analyses were performed by Desert Analytics (Tucson, AZ). NMR spectra were recorded using a Bruker DRX400 spectrometer. ^{1}H NMR spectra were obtained at 400 MHz and were referenced to residual proton peaks of the solvent (CD$_2$Cl$_2$, δ 5.32). ^{31}P{^{1}H} NMR spectra were recorded at 162.0 MHz and referenced to external 85% phosphoric acid (δ 0). Infrared spectra were recorded on a Nicolet 20SXB spectrometer in a Fluorolube-S30 mull with CaF$_2$ plates. Re(CO)$_2$(NO)(PPh$_3$)$_2$ (**2a**) was prepared according to the literature procedure.[14]

Re(CO)$_2$(NO)(PCy$_3$)$_2$ (2b). This preparation is a modification of a literature procedure for Re(CO)$_2$(NO)(PMe$_3$)$_2$.[15] A 500 mL Schlenk flask was evacuated on a vacuum line. Under argon, 10 mL of mercury were added to the flask, followed by 1.0 g of sodium metal in small portions (the reaction between mercury and sodium is very exothermic) with stirring, to produce the sodium amalgam for reaction. Under an argon counterflow, Re(Cl)$_2$(CO)(NO)(PCy$_3$)$_2$[15] (1.078 g, 1.23 mmol) was added to the flask, whose contents were at room temperature. The flask was then evacuated at −78 °C. At room temperature, 60 mL of diethyl ether was transferred to the flask via a cannula under a CO atmosphere. The contents of the flask were stirred under a CO atmosphere for 3 days, after which the flask was attached to a preevacuated swivel-frit assembly with a Schlenk collection flask under argon. The solution was filtered through Celite, and the Schlenk flask containing the brown-red filtrate was fitted with a septum under argon. The contents of the flask were evaporated to dryness, and the brown-red residue was treated with 30 mL of N$_2$-purged absolute ethanol. The flask was attached to another preevacuated swivel-frit assembly under argon, and the insoluble brown-red solid was filtered, washed with N$_2$-purged absolute ethanol, and dried under vacuum to afford 0.197 g (19.2% yield) of air-sensitive **2b**. Anal. Calcd for C$_{38}$H$_{66}$O$_3$NP$_2$Re: C, 54.79; H, 7.98; N, 1.68. Found: C, 54.84; H, 8.14; N, 1.43. IR: ν(CO) 1916 (m), 1827 (s) cm^{-1}; ν(NO) 1582 (s) cm^{-1}. ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$, 20 °C): δ 23.5 (s).

***cis,trans*-Re(Cl)(CO)$_2$(NH═O)(PPh$_3$)$_2$ (3a).** This procedure is a modification of the literature procedure.[14] A two-necked round-bottomed flask attached to a swivel-frit assembly and containing a septum was placed on a vacuum line, 20 mL of diethyl ether was vacuum transferred into the flask at −78 °C, and the flask was filled with argon. The apparatus was removed from the line and purged with anhydrous HCl in a hood for 1 min, then was again placed on a vacuum line in a hood. Under an argon counterflow, 0.101 g (0.127 mmol) of **2a** and 0.050 g (0.191 mmol) of PPh$_3$ were added, and the solution was stirred at room temperature for 20 min. The dark red-brown solid was insoluble in diethyl ether and turned green in color during the reaction. This green solid was filtered, washed with diethyl ether, and dried under vacuum to yield 0.084 g (79.2% yield) of **3a** (85% of product mixture); IR and ^{31}P{^{1}H} NMR spectroscopies also show the presence of *mer,-trans*-Re(Cl)(CO)$_3$(PPh$_3$)$_2$ (8%) and *cis,trans*-Re(Cl)$_2$(CO)(NO)(PPh$_3$)$_2$ (7%).[14,16] Anal. Calcd for C$_{38.01}$H$_{30.85}$O$_{2.93}$N$_{0.92}$Cl$_{1.07}$P$_2$Re: C, 54.77; H, 3.73; N, 1.55. Found: C, 55.57; H, 3.55; N, 1.58. **3a**: IR: ν(NH) 3057 (w) cm^{-1}; ν(CO) 1975 (vs), 1878 (vs) cm^{-1}; ν(NO) 1376 (s) cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 20 °C): δ 20.66 (s, 1 H, N*H*═O, $|^1J_{NH}|$ = 66.2 Hz), 7.75−7.55 (m, 12 H, *Ph*), 7.50−7.35 (m, 18 H, *Ph*). ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$, 20 °C): δ 15.4 (s).

***cis,trans*-Re(Cl)(CO)$_2$(NH═O)(PCy$_3$)$_2$ (3b).** A 0.189 g (0.227 mmol) sample of **2b** was added to a two-necked round-bottomed flask equipped with a septum and attached to a swivel-frit assembly, and the apparatus was evacuated on a vacuum line. At room temperature under argon, 10 mL (20 mmol) of a 2.0 M solution of hydrogen chloride in diethyl ether (Aldrich) was added to the flask via syringe. The red-brown solid, which is insoluble in Et$_2$O, immediately turned blue-green in color. This heterogeneous solution was stirred at room temperature for 30 min and was then filtered. The blue-green solid was recrystallized from benzene/diethyl ether to yield 0.057 g (29% yield) of deep green **3b**·1/2C$_6$H$_6$ as a benzene solvate. The solid shows at least short-term (∼12 h) air stability. Anal. Calcd for C$_{41}$H$_{70}$O$_3$NClP$_2$Re: C, 54.20; H, 7.77; N, 1.54. Found: C, 54.48; H, 8.37; N, 1.52. IR: ν(CO) 1968 (vs), 1872 (vs) cm^{-1}; ν(NO) 1335 (s) cm^{-1}. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 20 °C): δ 21.35 (s, 1 H, N*H*═O), 7.35 (s, 1 H, 1/2 C$_6$*H*$_6$), 2.33 (br m, 7 H, *Cy*), 1.95 (d, 6 H, *Cy*, *J* = 12.0 Hz), 1.83 (m, 19 H, *Cy*), 1.68 (br s, 5 H, *Cy*), 1.45 (m, 10 H, *Cy*), 1.25 (m, 19 H, *Cy*). ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$, 20 °C): δ 16.4 (s).

Reaction of 3 with Brønsted Bases. In a typical reaction, 1.2−1.7 equiv of the base was added to a solution of **3** in CH$_2$Cl$_2$ (preparatory-scale reactions) or CD$_2$Cl$_2$ (NMR-scale reactions). Preparatory-scale reactions were run under argon by warming from −78 °C to room temperature and monitored by IR. NMR-scale reactions were run at room temperature, and the potential disappearance of the reactant nitroxyl complex (δ 15.4 (**3a**), δ 16.4 (**3b**)) and the formation of the product nitrosyl complex (δ 19.8 (**2a**), δ 23.5 (**2b**)) was monitored by ^{31}P{^{1}H} NMR (162.0 MHz). DBU, piperidine, triethylamine, ammonia, 4-(*N,N*-dimethylamino)pyridine, 2-aminomethylpyridine, 2,4,6-collidine, imidazole, *N,N*-diethylaniline, and pyridine were used as bases. Results of these reactions appear in Table 3.

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(11) Sellmann, D.; Gottschalk-Gaudig, T.; Häussinger, D.; Heinemann, F. W.; Hess, B. A. *Chem. Eur. J.* **2001**, *7*, 2099.

(12) Lin, R.; Farmer, P. J. *J. Am. Chem. Soc.* **2000**, *122*, 2393.

(13) Southern, J. S.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 12406.

(14) LaMonica, G.; Freni, M.; Cenini, S. *J. Organomet. Chem.* **1974**, *71*, 57.

(15) Hund, H.-U.; Ruppli, U.; Berke, H. *Helv. Chim. Acta* **1993**, *76*, 963.

(16) Cameron, T. S.; Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1982**, *21*, 4149.

Table 1. Spectroscopic Data for HN=O Ligands of **3a** and **3b**

compound	ν(NO)[a]	ν(NH)[a]	δ(N*H*=O), $\lvert ^1J_{NH}\rvert$[b]
$Re(Cl)(CO)_2(NH{=}O)(PPh_3)_2$ (**3a**)	1376	3059	20.66, 66.2
$Re(Cl)(CO)_2(NH{=}O)(PCy_3)_2$ (**3b**)	1335	*c*	21.35, *c*

[a] Fluorolube-S30 mull; cm^{-1}. [b] ^{1}H NMR (CD_2Cl_2, 400 MHz); *J* in Hz. [c] Not observed or determined.

Table 2. Relevant Bond Distances (Å) and Bond Angles (deg) for **4**

Re−H	1.74	Re−N	1.829(5)
N−O(3)	1.185(6)	Re−C(19)	2.036(6)
C(19)−O(1)	1.129(7)	Re−C(20)	2.039(6)
C(20)−O(2)	1.129(7)	Re−P	2.4685(11)
Re−N−O(3)	178.1(4)	Re−C(19)−O(1)	175.9(5)
Re−C(20)−O(2)	172.6(5)	P′−Re−P	161.46(4)
C(19)−Re−C(20)	163.8(2)	N−Re−C(19)	97.6(2)
N−Re−C(20)	98.5(2)	N−Re−P′	99.26(2)

Table 3. Results of Reaction of **3a**,**b** with Bases at Room Temperature

base	pK_b[a]	**3a** → **2a**	**3b** → **2b**
DBU[b]	2.5[c]	yes	yes
piperidine	2.8		yes
triethylamine	3.2	yes	yes
(*N*,*N*-dimethylamino)pyridine	4.3	yes	
ammonia	4.8	yes	
2-aminomethylpyridine	5.4	yes	
2,4,6-collidine	6.5	yes	
imidazole	6.9	yes	yes
N,*N*-diethylaniline	7.4	no	no
pyridine	8.8	no	no

[a] Measured in H_2O; from Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965 (except where noted). [b] 1,8-Diaza[5.4.0]bicycloundec-7-ene. [c] Yamanaka, H.; Yokoyama, M.; Sakamoto, T.; Shiraishi, T.; Sagi, M.; Mizugaki, M. *Heterocycles* **1983**, *20*, 1541.

[*trans,trans*-Re(H)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (4). A 0.287 g (0.361 mmol) sample of **2a** was placed in a two-necked round-bottomed flask attached to a swivel-frit assembly and containing a septum. The apparatus was placed on a vacuum line, 20 mL of diethyl ether was vacuum transferred into the flask at −78 °C (solid is insoluble in diethyl ether), and the flask was filled with argon. At room temperature, triflic acid (0.11 mL, 1.24 mmol) was added via syringe. The solution was allowed to stir for 60 min, during which time the insoluble solid changed from a dark red-brown to a pale yellow color. This yellow solid was filtered, washed with diethyl ether, and dried under vacuum to afford 0.252 g (73.9% yield) of **4**. Anal. Calcd for $C_{39}H_{31}O_6NSF_3P_2Re$: C, 49.47; H, 3.30; N, 1.48. Found: C, 49.56; H, 3.18; N, 1.46. IR: ν(CO) 2103 (w), 2039 (s) cm^{-1}; ν(NO) 1766 (s) cm^{-1} [coupled to ν(ReH) (not observed)]. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ 7.70−7.55 (m, 18 H, *Ph*), 7.50−7.40 (m, 12 H, *Ph*), −0.68 (t, 1 H, Re-*H*, $^2J_{PH}$ = 21.9 Hz). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 20 °C): δ 9.4 (s).

[*trans,trans*-Re(^{2}H)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (4-d) was produced in an analogous manner by reaction with triflic acid-*d* ($^2HOSO_2CF_3$, Aldrich Chemical Co., 98 atom % D). IR: ν(CO) 2103 (w), 2039 (s) cm^{-1}; ν(NO) 1781 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 20 °C): δ 9.4 (s).

Crystal Structure Determination of 4. Crystal data: $C_{39}H_{31}O_6NSF_3P_2Re$, *M* = 946.85, orthorhombic, space group *Pnma*, *a* = 17.2201(2) Å, *b* = 23.6119(3) Å, *c* = 9.2380(2) Å, *V* = 3756.16(9) Å^3, *Z* = 4, D_x = 1.674 g·cm^{-3}, *F*(000) = 1872, μ = 34.39 cm^{-1}, λ = 0.71073 Å, *R*(*F*) = 0.039 *R*(*wF*^{2}) = 0.063 for the 4330 unique data with $I > 2\sigma(I)$.

Crystals of excellent quality of **4** were obtained by vapor diffusion of diethyl ether into a solution of the complex in CH_2Cl_2 at 0 °C. A suitable crystal was selected and mounted in a thin-walled glass capillary under an inert atmosphere. The systematic absences in the diffraction data were consistent for space groups *Pna*2$_1$ and *Pnma*. *E*-statistics suggested the centrosymmetric space group *Pnma*, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. The least-squares refinement converged to *R(F)* = 0.039 and *R*(*wF*^{2}) = 0.063 for the 4330 unique data with $I > 2\sigma(I)$. The cation is located on a mirror plane and atoms S, F(3), and O(4) of the triflate anion are disordered over a mirror plane. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom on the rhenium atom was located from the difference map, and its displacement parameter was allowed to refine. All other hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (version 5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI). Table 2 contains a listing of relevant bond distances and bond angles. A perspective view of the complex, along with the atom-numbering scheme, is shown in Figure 2.

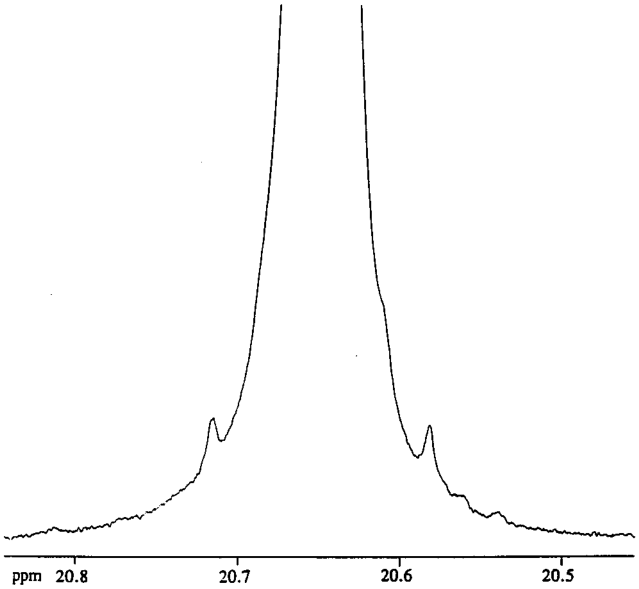


Figure 1. Amplification of the nitroxyl proton in the ^{1}H NMR spectrum of **3a** (CD_2Cl_2, 400 MHz, 20 °C). The central resonance is due to ^{14}N*H*=O (δ 20.66) and the satellites ($\lvert ^1J_{NH}\rvert$ = 66.2 Hz) are due to natural-abundance^{15}N*H*=O (shifted 9 ppb upfield).

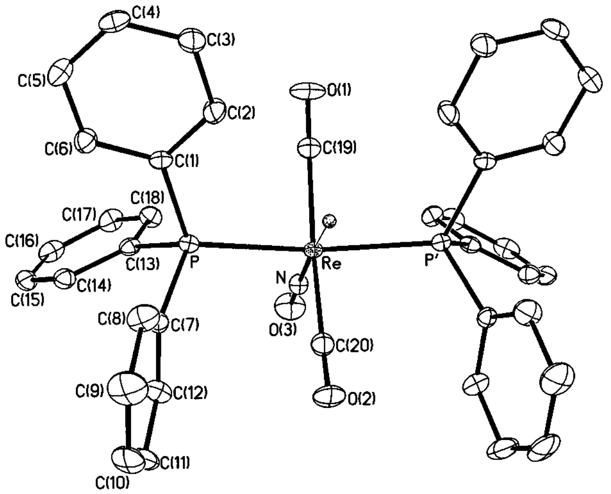
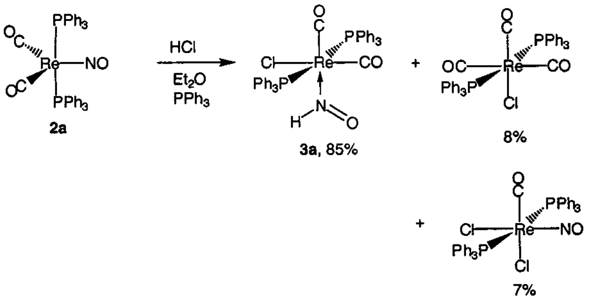


Figure 2. Perspective view of the complex cation of **4** showing the atom-numbering scheme. The triflate anion and the phenyl hydrogen atoms are omitted for clarity.

Results and Discussion

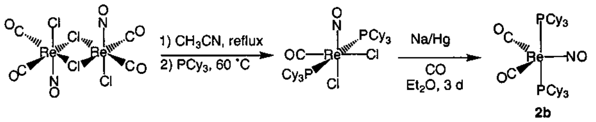
Reaction of *trans*-Re(CO)$_2$(NO)(PR$_3$)$_2$ with HCl. The addition of solid *trans*-Re(CO)$_2$(NO)(PPh$_3$)$_2$ (**2a**) to a diethyl ether solution saturated with anhydrous HCl results in an immediate color change of the ether-insoluble solid from red-brown to deep green. Formal protonation of the nitrosyl ligand and addition of chloride to the metal result, yielding the charge-neutral nitroxyl complex *cis,trans*-Re(Cl)(CO)$_2$(NH=O)(PPh$_3$)$_2$ (**3a**) as the major metal-containing product in excellent yield (eq 3). Additionally, two side products, *mer,trans*-Re(Cl)(CO)$_3$(PPh$_3$)$_2$ and *cis,trans*-Re(Cl)$_2$(CO)(NO)(PPh$_3$)$_2$,[14] are formed in the reaction. The addition of 1.5 equiv of triphenylphosphine to the reaction mixture before addition of the nitrosyl complex allowed for the minimization of these side products (**3a**, 85% of the product mixture; Re(Cl)(CO)$_3$(PPh$_3$)$_2$, 8%; Re(Cl)$_2$(CO)(NO)(PPh$_3$)$_2$, 7%), but we were unable to separate these three compounds, as they were produced under all reaction conditions we investigated and cocrystallized regardless of the solvent combinations we used for recrystallization. For example, beautiful crystals with well-formed faces of the green solid were grown from toluene/Et$_2$O, but they were not suitable for X-ray analysis because of side-product contamination in the individual crystals. (Note that these products are the same as reported by LaMonica[14] but optimized for **3a**.)



(3)

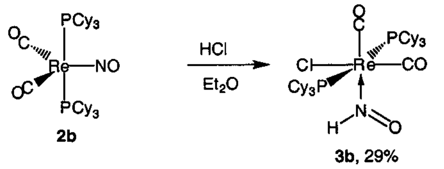
Complex **3a** has been characterized by spectroscopic methods (IR, ^{1}H and ^{31}P{^{1}H} NMR) and by its reaction chemistry. The spectroscopic data for **3a** are summarized in Table 1 and are similar to those observed for **1** as well as for other reported nitroxyl complexes.[9−14] A diagnostic singlet is observed at δ 20.66 for the Re(N*H*=O) proton in the ^{1}H NMR spectrum (CD$_2$Cl$_2$, 20 °C) of **3a**. Upon amplification of this resonance, ^{15}N (0.37% natural abundance) satellites are observable (Figure 1). The observed $|^1J_{NH}|$ of 66.2 Hz is a typical value for an *N*-bound nitroxyl ligand.[10−13] As in the cationic complex **1**, there is an isotopic perturbation of the chemical shift in **3a**, with the doublet resonance for Re(^{15}N*H*=O) shifting 9 ppb upfield of the Re(^{14}N*H*=O) singlet resonance. The infrared spectrum of **3a** shows ν(NO) (1376 (m) cm^{-1}) and ν(NH) (3059 (w) cm^{-1}) vibrations for the nitroxyl ligand. The *cis*-(CO)$_2$ geometry is confirmed by two intense vibrations for ν(CO) at 1975 and 1878 cm^{-1}. The chemically equivalent triphenylphosphine groups resonate as a singlet at δ 15.4 in the ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 20 °C).

The tricyclohexylphosphine analogue of **2a**, *trans*-Re(CO)$_2$(NO)(PCy$_3$)$_2$ (**2b**), was prepared in order to study the effect of varying the phosphine ligands on the HCl-addition reaction. Complex **2b** was prepared by the route Berke and co-workers have reported for the preparation of Re(CO)$_2$(NO)(PMe$_3$)$_2$ that utilizes the reduction of dichlororhenium(I) complexes.[15] Reduction of Re(Cl)$_2$(CO)(NO)(PCy$_3$)$_2$[15] with sodium amalgam under a CO atmosphere (Et$_2$O solution, 3 days) yields the desired nitrosyl complex **2b** in low (19%) yield (eq 4). Complex **2b** was isolated as an air-sensitive, analytically pure red-brown solid and characterized by standard spectroscopic methods (IR, ^{1}H and ^{31}P{^{1}H} NMR) and by elemental analysis. The infrared spectrum of **2b** shows ν(CO) (1916 (m), 1827 (s) cm^{-1}) and ν(NO) (1582 (s) cm^{-1}) vibrations. As expected, the ν(CO) and ν(NO) vibrations occur at lower energy for **2b** relative to **2a**[14] due to the increased donating ability of PCy$_3$ relative to PPh$_3$.



(4)

When excess anhydrous HCl is added to a suspension of **2b** in diethyl ether, the insoluble compound changes from red-brown to blue-green in color. Recrystallization of the solid product from benzene/Et$_2$O affords the charge-neutral nitroxyl complex *cis,trans*-Re(Cl)(CO)$_2$(NH=O)(PCy$_3$)$_2$ (**3b**·1/2 C$_6$H$_6$) as a deep green benzene solvate in modest yield, uncontaminated by byproducts (eq 5). No additional tricyclohexylphosphine was added to the reaction mixture. Complex **3b** has been characterized by spectroscopic methods (IR, ^{1}H and ^{31}P{^{1}H} NMR), by elemental analysis, and by its reaction chemistry. Both **3a** and **3b** show short-term air stability and are moderately stable in CD$_2$Cl$_2$ solution. The presence of a pure compound and the good stability of **3b** in solution allowed for the growth of single crystals of **3b** from CH$_2$Cl$_2$/Et$_2$O solution. Unfortunately, the resultant X-ray structure exhibited unresolvable site disorder of the Cl, CO, and HN=O ligands in the equatorial plane.



(5)

The spectroscopic data for **3b** are summarized in Table 1 and are very typical for a metal−nitroxyl complex.[9−14] The ^{1}H NMR spectrum (CD$_2$Cl$_2$, 20 °C) of **3b** shows a low-field singlet at δ 21.35 for the nitroxyl proton. The infrared spectrum of **3b** shows a low-energy ν(NO) of medium intensity at 1335 cm^{-1}, but the ν(NH) vibration was not identifiable. Two strong vibrations at 1968 and 1872 cm^{-1} indicate a *cis*-orientation of the CO ligands. The tricyclohexylphosphine groups resonate as a singlet at δ 16.4 in the ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 20 °C).

Reaction of *trans*-Re(CO)$_2$(NO)(PPh$_3$)$_2$ with HOSO$_2$CF$_3$. The reaction of trifluoromethanesulfonic acid with **2a** proceeds differently from that of hydrochloric acid. Addition of HOSO$_2$CF$_3$ to a suspension of **2a** in diethyl ether causes the insoluble red-brown solid to turn yellow in color. In contrast to the reaction of **2a** with HCl (eq 3), which results in formal protonation of the nitrosyl ligand and production of a nitroxyl complex, the addition of triflic acid results in protonation at the metal center, affording the cationic hydride complex [*trans,trans*-Re(H)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**4**) as a pale yellow, analytically pure compound in 74% isolated yield (eq 6). Reagent-specific protonations of this type have been observed for other low-valent metal−nitrosyl complexes. For example, the reaction of Ir(NO)(PPh$_3$)$_3$ with excess HCl results in multiple protonations of the nitrosyl ligand, affording IrCl$_3$(NH$_2$OH)(PPh$_3$)$_2$,[9] while reaction with HClO$_4$ results in protonation at the metal center, yielding [Ir(H)(NO)(PPh$_3$)$_3$$^+$][ClO$_4$$^-$].[17]

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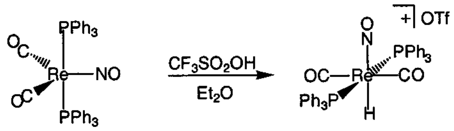
(17) (a) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1969**, 155. (b) Mingos, D. M. P.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 1479.



2a

4, 74%

(6)

Complex **4** has been characterized by standard spectroscopic methods (IR, ^{1}H and ^{31}P{^{1}H} NMR), elemental analysis, and a single-crystal X-ray diffraction study. The ^{1}H NMR spectrum (CD_2Cl_2, 20 °C) of **4** exhibits a high-field 1:2:1 triplet at δ −0.68 indicative of a rhenium−hydride moiety coupled to two magnetically equivalent phosphine ligands ($^2J_{PH} = 21.9$ Hz). The IR spectrum of **4** shows ν(CO) vibrations (2103 (w), 2039 (s) cm^{-1}) typical of trans-disposed carbonyl ligands, and ν(NO) at 1766 (s) cm^{-1}. The ν(ReH) vibration is not easily identifiable in the expected 1700−2200 cm^{-1} range, even when compared to the spectrum of the deuteride, [*trans,trans*-Re(^{2}H)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**4-d**). Complex **4-d** is prepared in a manner analogous to **4** by reacting **2a** with triflic acid-*d* (98 atom % ^{2}H). The ν(NO) of **4-d** (1781 cm^{-1}) shifts significantly relative to that of protio **4** (1766 cm^{-1}, $\Delta = 15$ cm^{-1}), indicative of a resonance interaction between the trans ν(NO) and (unobserved) ν(ReH) modes in **4**.[18,19] The trans relationship between these two ligands has been confirmed in the X-ray diffraction analysis.

Figure 2 shows the geometry of the complex cation of **4**. Relevant bond distances and bond angles appear in Table 2. Complete lists of bond distances and angles and crystal and structural refinement data appear in the Supporting Information. The metal-bound hydrogen atom was located from the difference map, and its displacement parameter was allowed to refine. The complex cation is approximately pseudooctahedral in geometry with trans carbonyl ligands, trans triphenylphosphine ligands, and a linear nitrosyl ligand (∠Re−N−O(3) = 178.1(4)°) trans to the hydride ligand. The atoms Re, C(19), O(1), C(20), O(2), N, O(3), and H lie in a crystallographic mirror plane. The Re−H bond distance (1.74 Å) compares favorably with those of neutral rhenium−hydride complexes of the type $Re(H)(CO)_{3-x}(PR_3)_{2+x}$ ($x = 0$, R = O^{i}Pr; $x = 1$, 2, R = Me) calculated by Berke and co-workers (1.69−1.77 Å) from ^{1}H NMR T_1 relaxation measurements.[20] There is substantial bending of the triphenylphosphine and carbonyl ligands toward the hydride site in **4** (∠P′−Re−P = 161.46(4)°, ∠C(19)−Re−C(20) = 163.8(2)°). Similar octahedral distortions are observed in the related neutral group 6 hydrides *trans,trans*-W(H)(CO)$_2$(NO)(PPh$_3$)$_2$ (∠P−W−P = 170.9(1)°, ∠C−W−C = 159.7(2)°)[21] and *trans,trans*-Cr(H)(CO)$_2$(NO)(PPh$_3$)$_2$ (∠P−Cr−P = 165.5(1)°, ∠C−Cr−C = 153.7(2)°).[22] While these distortions are expected on steric grounds, electronic factors also favor the bending of the carbonyl and triphenylphosphine ligands toward the purely σ-donating hydride ligand and away from the nitrosyl ligand, a strong π-acceptor.[17b,21−23]

The stereochemistry of **4** is that expected for the protonation of **2a** at Re under both thermodynamic and kinetic conditions. The trans triphenylphosphine ligands of **2a** remain trans in the product, minimizing steric interactions. Due to the instability of metal complexes containing *trans*-disposed nitrosyl and carbonyl ligands,[24] a trans arrangement of the carbonyl ligands is preferred. Additionally, the trans relationship between the nitrosyl ligand, the most proficient π-acceptor ligand in the complex, and the strong σ-donor hydride ligand also contributes to the thermodynamic stability of **4**. Kinetically, the orbital most available for protonation in **2a** is mainly metal d_{z^2} in character, facilitating protonation trans to the nitrosyl ligand.[25]

Mechanism of HCl Addition to *trans*-Re(CO)$_2$(NO)(PPh$_3$)$_2$. The mechanism of HCl addition to **2** deserves comment, since the linear, formally electrophilic nitrosyl ligand (NO$^+$) of **2** might not be expected to be susceptible to protonation at nitrogen. Furthermore, the independent observation that the strong acid $HOSO_2CF_3$ protonates at the metal and not at nitrogen leads one to conclude that either (i) an event occurs prior to protonation (at N) to render the nitrosyl ligand nucleophilic, presumably by bending, or (ii) the transformation of the Re−NO ligand to the Re(NH═O) ligand does not involve classical "protonation" of a nitrogen lone-pair.

Enemark and Feltham have reported that addition of Br$^-$ to dicationic, trigonal bipyramidal Co(diars)$_2$(NO)$^{2+}$ (∠Co−N−O = 178(2)°) results in bending of the NO ligand in the six-coordinate product Co(diars)$_2$(Br)(NO)$^+$ (∠Co−N−O = 132(1)° in the analogous NCS$^-$ complex).[26,27] In light of the differing reactivities of hydrochloric and triflic acids toward **2** and considering that the anions Cl$^-$ and SO$_3$CF$_3$$^-$ have significantly different coordinating characteristics (triflate being relatively more weakly coordinating),[28] we have looked for evidence of interactions between nucleophiles and **2a** that might lead to coordination and concomitant nitrosyl bending. No spectroscopic change (monitored by IR and ^{31}P{^{1}H} NMR) is observed upon the addition of 20 equiv of [*n*-Bu$_4$N$^+$][Cl$^-$] to a CD_2Cl_2 solution of the neutral complex **2a**, and while negative evidence of this type is by its nature inconclusive, we see no evidence of even a small equilibrium concentration of a bent-nitrosyl species (e.g., Re(Cl)(CO)$_2$(NO)(PPh$_3$)$_2$$^-$) in this system.

A second mechanistic possibility for the production of **3** from **2** involves initial (kinetic) protonation at the metal followed by H-migration from rhenium to nitrogen with chloride ligation. This mechanistic postulate is testable since we have prepared the putative hydride intermediate independently. We have shown that the cationic hydride complex **4** does not react with added chloride to yield **3a**; hence it is probably not an intermediate in the formation of **3a** from **2a**. The observation that **4** is the kinetic product of protonation of **2** also argues against initial protonation at the nitrosyl oxygen followed by H-migration, although it

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[18] No ν(Re^{2}H) is observed for **4-d**, indicating that this band has very low intrinsic intensity. Analogous results were obtained for the charge-neutral group 6 analogues *trans,trans*-M(H)(CO)$_2$(NO)(PPh$_3$)$_2$ (M = Mo, W), which show strong resonance coupling of the *trans*-disposed nitrosyl and hydride ligands (for M = Mo[19a] and W[19b]).

[19] (a) Smith, M. R., III; Cheng, T.-Y.; Hillhouse, G. L. *Inorg. Chem.* **1992**, *31*, 1535. (b) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876.

[20] Gusev, D. G.; Nietlispach, D.; Vymenits, A. B.; Bakhmutov, V. I.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3270.

[21] van der Zeijden, A. A. H.; Sontag, C.; Bosch, H. W.; Shklover, V.; Berke, H.; Nanz, D.; von Philipsborn, W. *Helv. Chim. Acta* **1991**, *74*, 1194, and references therein.

[22] Peters, J. C.; Hillhouse, G. L.; Rheingold, A. L. *Polyhedron* **1994**, *13*, 1741.

[23] Elian, M.; Hoffman, R. *Inorg. Chem.* **1975**, *14*, 1058.

[24] Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *Inorg. Chem.* **1984**, *23*, 957, and references therein.

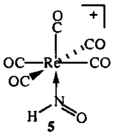
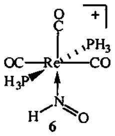
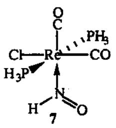
[25] Enemark, J. H.; Feltham, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 3534.

[26] (a) Enemark, J. H.; Feltham, R. D.; Riker-Nappier, J.; Bizot, K. F. *Inorg. Chem.* **1975**, *14*, 624. (b) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339, and references therein.

[27] A significant decrease in ν(NO) is reported for the transformation of Co(diars)$_2$(NO)$^{2+}$ (1852 cm^{-1}) to Co(diars)$_2$(Br)(NO)$^+$ (1565, 1550 cm^{-1}).[26] The authors report that the bent nitrosyl ligand of Co(diars)$_2$(Br)(NO)$^+$ is protonated upon reaction with HClO$_4$, forming Co(diars)$_2$(Br)(NH═O)$^{2+}$, but the reported spectroscopic values of the product are inconsistent with those of ligated nitroxyl.[9−14]

[28] Lupinetti, A. J.; Strauss, S. H. *Chemtracts-Inorg. Chem.* **1972**, *11*, 565.

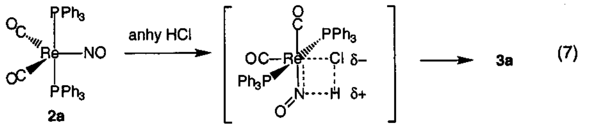
Table 4. Calculated Bond Distances and Observed Vibrational Frequencies

	free HN=O	5	6	7
d(Re–N) (Å)	——	2.125	2.068	2.047
d(N–O) (Å)	1.199	1.201	1.215	1.220
ν(NO) (cm^{-1})	1563^{a}	——	1391^{b}	1376,^{c} 1335^{d}
d(N–H) (Å)	1.065	1.043	1.042	1.045
ν(NH) (cm^{-1})	2717^{a}	——	3056^{b}	3059^{c}
		 5	 6	 7

[a] Vibration contains significant HNO bending character (ref 2a). [b] Experimental infrared values for **1** (ref 13). [c] Experimental infrared values for **3a**. [d] Experimental infrared values for **3b**.

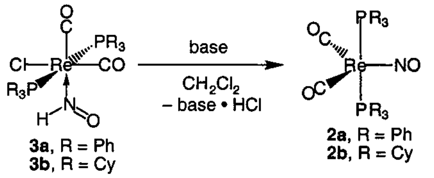
should be noted that the metastable NOH isomer has been spectroscopically characterized in an Ar matrix.[29]

An alternative scenario that merits discussion is one involving direct 1,2-addition of HCl across the Re−N multiple bond of the nitrosyl, as depicted in eq 7. The ν(NO) exhibited by **2a** (1622 cm^{-1}) is a low value for a linearly coordinated nitrosyl ligand. This value is indicative of strong dπ(Re)→p*(NO) back-bonding and a relatively large amount of electron density at nitrogen. A similar mechanism has been proposed for the intermolecular exchange of nitrosyl and chloride ligands in other transition metal systems[30] and is consistent with the observed stereochemistry for **3a** having Cl cis to the HN=O ligand. This same orientation is found in the structure of Os(Cl)$_2$(CO)(NH=O)(PPh$_3$)$_2$.[10]



(7)

Reaction of Re(Cl)(CO)$_2$(NH=O)(PR$_3$)$_2$ with Brønsted Bases. The reactions of **3a** and **3b** with proton-accepting nitrogen bases have been investigated. In a typical reaction for **3a**, 1.5 equiv of the nitrogen base was added to a CH$_2$Cl$_2$ or CD$_2$Cl$_2$ solution of the complex, and the reaction was monitored by solution IR and/or ^{31}P{^{1}H} NMR spectroscopy. The ^{31}P{^{1}H} NMR spectra show clean conversion of **3a** (δ 15.4) to **2a** (δ 19.8) (eq 8) when an appropriately strong base is used (summarized in Table 3). Importantly, both **3a** and **3b** are stable in solution with respect to HCl loss in the absence of added base.



(8)

The successful reactions for **3a** shown in Table 3 are rapid, with complete conversion requiring ca. 5 min. An exception is the reaction of **3a** with 2,4,6-collidine, which requires >30 min for complete conversion to **2a**, probably due to the steric properties of the base. The reaction shown in eq 8 is irreversible; no reaction is observed between **2a** and Et$_3$N·HCl or pyridine·HCl (∼3 equiv). In an analogous manner, **3b** eliminates HCl in the presence of sufficiently strong Brønsted bases. By monitoring the reactions by ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C), a clean conversion of **3b** (δ 16.4) to **2b** (δ 23.5) is observed when an appropriately strong base is used (Table 3). For both **3a**,**b**, imidazole (pK_b = 6.9) is strong enough to effect dehydrochlorination to give **2a**,**b**, but the nitroxyl compounds fail to react with *N*,*N*-diethylaniline (pK_b = 7.4) or weaker bases. In comparison to **3a**, a qualitatively slower rate is observed for the reactions of **3b** with the bases, with complete conversion by suitably strong bases requiring >30 min in all cases, possibly a consequence of greater steric hindrance by the bulkier PCy$_3$ ligands.

For purposes of reference, the pK_a of free HN=O in water has been measured as 4.7 in pulse radiolysis experiments,[31] although in our experiments we are not directly measuring the pK_a of bound nitroxyl since we are both removing a proton from nitrogen and breaking a Re−Cl bond. Nonetheless, these data show that it is qualitatively more difficult to remove a proton from bound HN=O in **3a**,**b** than from the free molecule, a point addressed in the following section.

DFT Calculations on Nitroxyl and Model Nitroxyl Complexes. To obtain a better understanding of the stability that metal coordination confers to the nitroxyl molecule, DFT calculations were used to examine the bonding in nitroxyl and the model nitroxyl complexes Re(CO)$_5$(NH=O)$^+$ (**5**), *mer*,*trans*-Re(CO)$_3$(NH=O)(PH$_3$)$_2$$^+$ (**6**), and *cis*,*trans*-Re(Cl)(CO)$_2$(NH=O)(PH$_3$)$_2$ (**7**), the structures of which are shown in Table 4. Complexes **6** and **7** were chosen as models for the known nitroxyl complexes **1**,[13] and **3a**,**b**, respectively. The substitution of PH$_3$ in the model complexes for the PR$_3$ (R = Ph, Cy) ligands in **1** and **3a**,**b** simplifies the calculations by reducing the number of atoms present in the complexes (electronic consequences in making this simplification are addressed below). Calculations were performed on complex **5** in order to probe the electronic effect of increasing the number of strong π-acceptor ligands in this system. The B3LYP functional (GAUSSIAN94),[32] which has been shown to yield reliable results for many transition-

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(29) Maier, G.; Reisenauer, H. P.; De Marco, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 108.

(30) Unbermann, C. B.; Caulton, K. G. *J. Am. Chem. Soc.* **1976**, *98*, 3862.

(31) Grätzel, M.; Taniguchi, S.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1003.

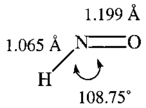

Figure 3. Calculated structural parameters for HN=O.

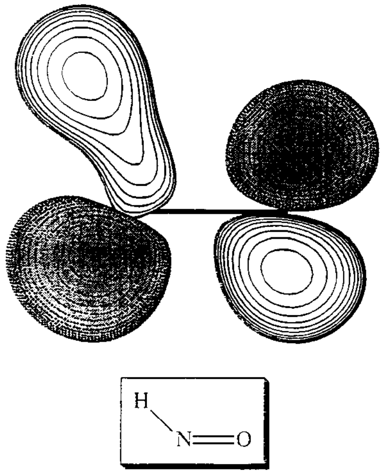

Figure 4. Pictorial representation of the calculated HOMO of HN=O, consisting of N−H σ-bonding and N−O π-antibonding (in the HNO plane) interactions.

metal systems, was used to examine these compounds. The species examined were optimized using the 6-311G(d) basis on all atoms except Re, which was described using the LANL2DZ basis set and effective core potentials.[33]

Calculations on free nitroxyl yielded the following structural parameters: an N−O bond length of 1.199 Å, an N−H bond length of 1.065 Å, and an H−N−O bond angle of 108.75° (see Figure 3 and Table 4). These values are in good agreement with those determined by Dalby from analysis of the electronic absorption spectrum of HN=O (d(N−O) 1.211(6) Å, d(N−H) 1.062(8) Å, ∠H−N−O 108.5(8)°)[2a] and recent theoretical treatments.[34] A view of the HOMO of HN=O, which consists of N−O π-antibonding (in the plane of the hydrogen) and N−H σ-bonding interactions, is pictured in Figure 4. The LUMO of HN=O consists of an N−O π-antibonding interaction in the plane perpendicular to the molecular plane.

Nitroxyl interacts with a metal center in a σ-donor, π-acceptor fashion through its HOMO and LUMO orbitals. For a d^6 metal system, the nitroxyl HOMO interacts in a σ-fashion with an empty metal d_{z^2} orbital, and the filled metal d_{xz} or d_{yz} orbital donates electron density into the HN=O π-system via its overlap with the nitroxyl LUMO. Our calculations on complexes **5**−**7** show that, relative to free nitroxyl, the metal-coordinated species display a lengthened N−O bond. These calculations are consistent with experimentally determined infrared data. For nitroxyl complexes **1**, **3a**, and **3b**, ν(NO) decreases relative to the value for free HN=O (Table 4), indicating that nitroxyl acts as a π-acceptor ligand. It is well appreciated that NO^+ is a strong π-acceptor ligand[35] and HN=O functions in a similar fashion. A significant difference between these two ligands is that NO^+, the stronger π-acceptor, contains two perpendicular π* orbitals for accepting back-donation from the metal (the nitrogen is sp-hybridized), while HN=O contains only one (the nitrogen is sp^2-hybridized).

Further illustrating the π-acceptor nature of nitroxyl, the HN=O ligand in each of the model complexes is oriented in the plane containing the largest number of competing π-acceptor ligands. This allows HN=O to minimize the competition with other ligands for π-donation from the metal center and to maximize its own π-interactions. This phenomenon is also observed structurally. In the X-ray crystal structures of *cis*,*trans*-$Os(Cl)_2(CO)(NH{=}O)(PPh_3)_2$[10] and [*cis*,*trans*-$Os(Br)(CO)_2(NH{=}NH)(PPh_3)_2{}^+$][$SO_3CF_3{}^-$],[8] the HN=X ligand is oriented in the plane containing the greatest number of competing π-acceptor ligands. While this orientational preference could be interpreted as a minimization of steric effects, it is notable that in the structure of the related nitrosoalkane complex $W(CO)_5(N({}^tBu){=}O)$ the ${}^tBuN{=}O$ ligand is aligned in a plane containing three CO ligands, even though more sterically favorable orientations are possible.[36] That nitroxyl is a π-acceptor is clearly illustrated in the results shown in Table 4: the calculated N−O bond length increases (with a concomitant decrease in the Re−N bond length) in complexes **5**−**7** as the number of competing π-acceptor ligands decreases. Further experimental evidence for the π-accepting nature of HN=O is provided by inspection of the carbonyl stretching frequencies of **1** (ν(CO) = 2082(w), 2007(s), 1977(s) cm^{-1}) and its hydroxylamine precursor [*mer*,*trans*-$Re(CO)_3(NH_2OH)(PPh_3)_2{}^+$][$SO_3CF_3{}^-$] ($\nu$(CO) = 2061(w), 1966(s), 1926(s) cm^{-1}; see eq 1).[13] The large increase ($\Delta \approx 21-51$ cm^{-1}) in the values of ν(CO) when the purely σ-donating NH_2OH ligand is converted into the HN=O ligand in an otherwise identical coordination environment reflects decreased back-bonding to the CO ligands of **1** relative to [$Re(CO)_3(NH_2OH)(PPh_3)_2{}^+$][$SO_3CF_3{}^-$] due to competition for metal π-electron density from the nitroxyl ligand. This is apparently also manifested in the excited state. The electronic spectrum (CH_2Cl_2) of **3a** shows an intense band in the visible region at $\lambda_{max} = 418$ nm ($\epsilon \approx 3 \times 10^3$ M^{-1} cm^{-1}), assigned as a metal-to-ligand (M(dπ)→HN=O(π*)) charge-transfer (MLCT) transition. MLCT bands of similar energy and intensity have been observed in related nitrosoarene and nitrosoalkane complexes, which like **1**, **3a**, and **3b** are also are intensely colored.[36,37]

It is appreciated that these calculations using PH_3 (instead of PPh_3 or PCy_3) introduce perturbation in the electronic environment at the metal. However, it should be noted that the lone pair of PH_3 resides in an orbital that is almost purely s in character,[38] making PH_3 a poor σ-donor. The calculations on complexes **5**−**7**, which incorporate PH_3 ligands, thus underestimate the lengthening of the nitroxyl N−O bond and the shortening of the Re−N bond that would occur in **1** and **3a**, which contain the better σ-donor ligand PPh_3, and especially in **3b**, which contains the relatively strong σ-donor ligand PCy_3.

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(32) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Latham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(33) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(34) (a) Mordaunt, D. H.; Flöthmann, H.; Stumpf, M.; Keller, H.-M.; Beck, C.; Schinke, R.; Yamashita, K. *J. Chem. Phys.* **1997**, *107*, 6603. (b) Tschumper, G. D.; Schaeffer, H. F., III. *J. Chem. Phys.* **1997**, *107*, 2529.

(35) Clarkson, S. G.; Basolo, F. *Inorg. Chem.* **1973**, *12*, 1528.

(36) Pilato, R. S.; McGettigan, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1990**, *9*, 312.

(37) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 5605.

(38) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993; p 226.

Table 5. Calculated N−H Bond Dissociation Energies

complex	N−H bond dissociation energy (kcal/mol)
HN═O	48.5[a]
mer,trans-Re(CO)$_3$(NH═O)(PH$_3$)$_2$$^+$ (**6**)	62.1[b]
cis,trans-Re(Cl)(CO)$_2$(NH═O)(PH$_3$)$_2$ (**7**)	64.8[b]

[a] Eq 9. [b] Eq 10.

Our calculations show that the N−H bond of nitroxyl, in contrast, is shortened upon ligation and is not strongly affected by varying ancillary ligands. This result is also consistent with experimentally determined infrared data, which show an increase in ν(NH) for nitroxyl complexes **1** and **3a** relative to the value for free HN═O (Table 4, ν(NH) was not observed for **3b**). Energies of the N−H bonds (Table 5) were calculated using eq 9 and eq 10 for HN═O and its model complexes, respectively. The N−H bond energy for nitroxyl was calculated as the difference in energy between HN═O and the sum of the energies of its separate H and NO components (eq 9). Similarly, the nitroxyl N−H bond energy in model complexes **6** and **7** was calculated as the difference in energy between the complex (L$_n$Re(NH═O)) and the sum of the energies of the H atom and the optimized structure of L$_n$Re(NO) (eq 10). The bond dissociation energy of the weak N−H bond in free HN═O was calculated to be 48.5 kcal/mol, which is in good agreement with the 50.1 kcal/mol value reported using high-level CASSCF/ICCI calculations and other reported values obtained by ab initio methods.[3,34a] As can be seen in Table 5, metal coordination strengthens this bond by 13.6 kcal/mol in cationic **6** and by 16.3 kcal/mol in charge-neutral **7**.

$$E[\text{N–H bond}] = E(\text{HN=O}) - [E(\text{H}) + E(\text{NO})] \tag{9}$$

$$E[\text{N–H bond}] = E[\text{L}_n\text{Re(NH=O)}] - \{E(\text{H}) + E[\text{L}_n\text{Re(NO)}]\} \tag{10}$$

The driving force for strengthening of the N−H bond upon coordination in the d^6 pseudooctahedral metal systems employed here can be seen in the molecular orbital diagram presented in Figure 5. One of the π^* orbitals of NO interacts with a metal t$_{2g}$ orbital in a π-fashion, while the other π^* orbital is positioned for a σ-interaction with the d$_{z^2}$ orbital of the metal e$_g$ set. This σ-interaction stabilizes the π^* level of the coordinated NO unit and places it in closer (relative to the free NO molecule) energetic proximity to the 1s orbital of hydrogen. Since the strength of interaction between two orbitals depends inversely upon their energetic difference, this results in a stronger N−H bond for the metal-coordinated nitroxyl species.

Conclusions

The reaction of trigonal bipyramidal metal−nitrosyl complexes with hydrogen chloride has proved to be a fruitful method for the synthesis of charge-neutral, d^6 pseudooctahedral metal−nitroxyl complexes. The nitroxyl complexes *cis,trans*-Re(Cl)(CO)$_2$(NH═O)(PPh$_3$)$_2$ (**3a**) and *cis,trans*-Re(Cl)(CO)$_2$(NH═O)(PCy$_3$)$_2$ (**3b**) are produced by the addition of anhydrous HCl to diethyl ether suspensions of Re(CO)$_2$(NO)(PPh$_3$)$_2$ (**2a**) and Re(CO)$_2$(NO)(PCy$_3$)$_2$ (**2b**), respectively. Complex **3b** is produced cleanly, after recrystallization, while **3a** is contaminated by small amounts of two side products. Complexes **3a**,**b** exhibit spectroscopic properties typical of nitroxyl complexes, with diagnostic ^{1}H NMR resonances (δ 20.66 for **3a**, δ 21.35 for **3b**) and IR stretches (ν(NO) = 1376 cm^{-1} for **3a**, 1335 cm^{-1} for **3b**) for the HN═O ligand. While further studies are necessary in order to more fully understand the mechanism of the nitrosyl ligand “protonations” in these and related complexes, the evidence currently in hand favors direct 1,2-addition of HCl across the Re−N multiple bond of the nitrosyl, and not simple protonation at nitrogen or the metal. Both **3a**,**b** cleanly eliminate HCl in the presence of sufficiently strong Brønsted bases to re-form the parent nitrosyl complexes.

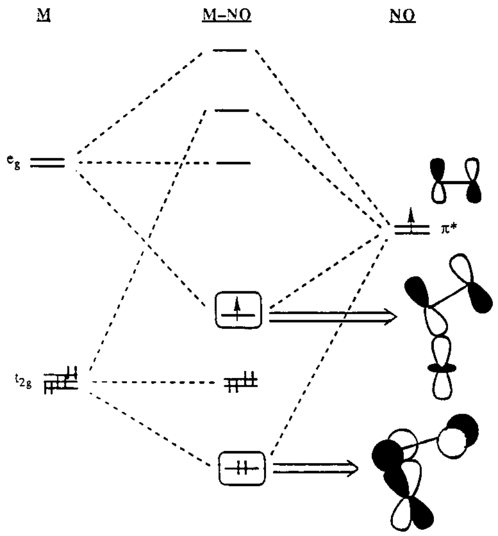

Figure 5. MO diagram of the metal−NO interaction. The NO π^* orbital available for bonding with hydrogen is lowered in energy due to σ-interaction with the metal d$_{z^2}$ orbital.

The protonation reactions are acid-dependent. Reaction of **2a** with triflic acid (HOSO$_2$CF$_3$) results in metal protonation, yielding the cationic hydridorhenium(I) complex [*trans,trans*-Re(H)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**4**), which has been characterized by X-ray crystallography.

Finally, we have carried out DFT calculations on free HN═O and several of its model complexes. The calculations show nitroxyl interacting with these d^6 pseudooctahedral metal centers in a σ-donor, π-acceptor fashion through its HOMO and LUMO orbitals. Moreover, metal coordination strengthens the N−H bond in HN═O bond by ca. 14−16 kcal/mol relative to the weak N−H bond (48.5 kcal/mol) in the free molecule.

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Supporting Information Available: Listings of crystallographic details, atomic coordinates, bond angles and distances, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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