Classical and Nonclassical Nitrosyl Hydride Complexes of Rhenium in Various Oxidation States[†]

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The paramagnetic rhenium complex $[NEt_4]_2[Re(Br)_5(NO)]$ (**1**) has been used to prepare a series of novel mononitrosyl hydride and dihydrogen rhenium complexes: $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(PR_3)_2]$ (R = ^{i}Pr, **2a**; Cy, **2b**) and $[Re(H)(BH_4)(NO)(PR_3)_2]$ (R = ^{i}Pr, **3a**; Cy, **3b**). The coordinated BH_3 of the derivatives **3** can be replaced by the H_2 or the NO ligand, thus leading to the tetrahydride and dinitrosyl species $[Re(H)_4(NO)L_2]$ (R = ^{i}Pr, **4a**; Cy, **4b**) or $[Re(H)(NO)_2(PR_3)_2]$ (R = ^{i}Pr, **5a**; Cy, **5b**). While $[Re(H)_4(NO)(PPh_3)_2]$ does not seem to be stable, $[Re(H)(NO)_2(PPh_3)_2]$ (**5c**) has been obtained in a fashion similar to the preparation of **3a,b** from the reaction of $[Re(H)(BH_4)(NO)(PPh_3)_2]$ and $NOBF_4$. Detailed investigations of the reactions of **3a,b** with $NOBF_4$ have revealed that the compounds initially formed are the isolable BF_3 adducts $[Re(H)(NO)(NOBF_3)(PR_3)_2]$ (R = ^{i}Pr, **6a**; Cy, **6b**). The source of BF_3 is the nitrosonium salt. Dissociation of BF_3 from **6a,b** takes place in donor solvents such as THF, affording the BF_3-free compounds **5a,b**, whereas in noncoordinating solvents such as toluene, benzene, or CH_2Cl_2 only the species **6a,b** are observable. Apparently due to an unfavorable position of the dissociation equilibrium, the existence of the complex $[Re(H)(NO)(NOBF_3)(PPh_3)_2]$ could only be made plausible from dynamic NMR spectroscopic observations. Attempts to isolate it failed even from nonpolar solvents. X-ray diffraction studies have been carried out on the complexes $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(P^iPr_3)_2]$ (**2a**), $[Re(H)(BH_4)(NO)(PR_3)_2]$ (R = ^{i}Pr, **3a**; Ph, **3c**), $[Re(H)(NO)_2(P^iPr_3)_2]$ (**5a**), and $[Re(H)(NO)(NOBF_3)(P^iPr_3)_2]$ (**6a**). The hydrogen atoms of the $\eta^2\text{-}H_2$ moiety of **2a** could not be located in the X-ray diffraction study, but their most probable position in the molecule has been traced by an extensive search based on DFT calculations.

Introduction

In recent years our group has studied the chemistry of nitrosyl-substituted transition metal hydrides. It has been demonstrated that the nitrosyl ligand[1] can activate the metal−hydrogen bond and induce a quite strong hydridic polarization.[2,3] This effect can be further tuned when the nitrosyl ligand(s) is(are) combined with phosphorus donor substituents of varying electron-donating capability.[4] In addition to this it is a well-known fact that the NO ligand can contribute to the stabilization of quite different oxidation states of a metal center.[1] Both of these NO-based effects tempted us to explore the chemistry of rhenium nitrosyl hydrides in an extended range of oxidation states in order to trace the dependence of their chemistry on this parameter.

Earlier our group has investigated the chemistry of a series of mononitrosyl hydrido complexes containing various phosphorus donor ligands as well as chromium,[5] tungsten,[4,6] and rhenium[7] centers. Our efforts have now been directed toward the synthesis of dinitrosyl hydride derivatives, expecting an enhancement of the described nitrosyl effects.[2,3] In a previous paper we explored the chemistry of a series of manganese complexes of the general formula $[Mn(H)(NO)_2(PR_3)_2]$, which seemed to provide support for this hypothesis. Facile insertions of polar unsaturated molecules were observed in contrast to the related more inert manganese tricarbonyl derivatives $[Mn(H)(CO)_3(PR_3)_2]$.[8]

It was therefore a major focus of our preparative efforts to enable access to related $[Re(H)(NO)_2(PR_3)_2]$

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[†] Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.

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Table 1. Selected NMR Data[a]

		δ^1H NMR	
compd	δ^{31}P{^{1}H} NMR	P*R*$_3$	Re*H*, B*H*
2a	16.32 (s, br)	1.13 (dvt, 18 H, P(CH*Me*$_2$)$_3$, $^3J_{(H-H)} = 7.2$ Hz), 1.32 (dvt, 18 H, P(CH*Me*$_2$)$_3$, $^3J_{(H-H)} = 7.2$ Hz), 2.90 (m, 6 H, P(C*HMe*$_2$)$_3$)	2.07 (t, 2H, $^2J_{(H-P)} = 18.5$ Hz)
2b	7.10 (s, br)	1.0−2.87 (m, 66H, P(C$_6$*H*$_{12}$)$_3$)	2.44 (t, 2H, $^2J_{(H-P)} = 19.1$ Hz)
3a	42.54 (s)	1.20 (dvt, 18H, P(CH*Me*$_2$)$_3$, $^3J_{(H-H)} = 7.1$ Hz), 1.25 (dvt, 18H, P(CH*Me*$_2$)$_3$, $^3J_{(H-H)} = 7.1$ Hz), 2.40 (m, 6H, P(C*H*Me$_2$)$_3$	−6.12 (br, s, 1H, Re-*H*-B, $\Delta = 93$ Hz), −5.09 (td, 1H, Re*H*, $^2J(_{H-P)} = 16.5$ Hz, $^2J_{(H-H)} = 6.2$ Hz), −3.91 (br, s, 1H, Re-*H*-B, $\Delta = 100$ Hz), 6.62 (br, s, 2H, B*H*$_2$)
3b	32.48 (s)	1.10−2.41 (m, 66H, P(C$_6$*H*$_{12}$)$_3$)	−6.39 (br s, 1H, Re-*H*-B, $\Delta = 42$ Hz), −5.44 (td, 1H, Re*H*, $^2J_{(H-P)} = 16.0$ Hz, $^2J_{(H-H)} = 5.0$ Hz), −3.59 (br s, 1H, Re-*H*-B, $\Delta = 40$ Hz), 6.60 (br, s, 2H, B*H*$_2$, $\Delta = 117$ Hz)
3c	33.1 (s)	6.8−8.0 (m, 32H, P(C$_6$*H*$_5$)$_3$ and B*H*$_2$)	−4.53 (br s, 1H, Re-*H*-B, $\Delta = 36$ Hz), −3.29 (td, 1H, Re*H*, $^2J_{(H-P)} = 17.3$ Hz, $^2J_{(H-H)} = 5.6$ Hz), −2.92 (br s, 1H, Re-*H*-B, $\Delta = 42$ Hz)
4a	56.21 (quint, $^2J_{(P-HRe)} = 18$ Hz)[b,c]	1.26 (d, 36 H, P(CH*Me*$_2$)$_3$), 2.31 (sept, 6H, P(C*H*(Me$_2$)$_3$, $^3J_{(H-H)} = 7.1$ Hz)[c]	−7.44 (br s, $\Delta = 80$ Hz, 1H, Re*H*), −1.90 (br s, 3H, Re*H*, $\Delta = 27$ Hz)[c,d] −7.30 (vtdt, 1H, Re*H*, $^2J_{(H-P)} = 23.3$ Hz, $^2J_{(H-H)} = 7.11$ Hz, $^2J_{(H-H)} = 9.0$ Hz), −1.85 (tdt, 1H, Re*H*, $^2J_{(H-P)} = 32.8$ Hz, $^2J_{(H-H)} = 7.11$ Hz, $^2J_{(H-H)} = 5.4$ Hz), −1.57 (m, 2H, Re*H*)[e]
4b	42.9 (s)		−7.16 (tdt, 1H, Re*H*, $^2J_{(H-P)} = 22.4$ Hz, $^2J_{(H-H)} =$ ca. 7 Hz, $^2J_{(H-H)} =$ ca. 7 Hz), −1.80 (m, 3H, Re*H*)[f]
5a	49.2 (s)	1.13 (m, 36H, P(CH*Me*$_2$)$_3$), 2.12 (m, 6H, P(C*H*Me$_2$)$_3$)	4.12 (t, 1H, Re-*H*, $^2J_{(H-P)} = 34.8$ Hz)
5b	39.3 (s)	1.11−2.15 (m, 66H, P(C$_6$*H*$_{11}$)$_3$)	4.38 (t, 1H, Re-*H*, $^2J_{(H-P)} = 35.7$ Hz)
5c[g]	26.2 (s)	7.41−7.58 (m, 30H, P(C$_6$*H*$_5$)$_3$)	6.32 (t, 1H, Re-*H*, $^2J_{(H-P)} = 37.2$ Hz)
6a	52.8 (br, s)	1.01 (m, 36H, P(CH*Me*$_2$)$_3$), 2.09 (m, 6H, P(C*H*Me$_2$)$_3$)	5.91 (br, t, 1H, Re-*H*, $^2J_{(H-P)} = 35.4$ Hz)
6b	42.0 (br, s)	1.03−2.21 (m, 66H, P(C$_6$*H*$_{11}$)$_3$)	5.92 (br, t, 1H, Re-*H*, $^2J_{(H-P)} = 36.3$ Hz)

[a] In C_6D_6 unless otherwise specified. [b] Decoupled from the phosphine protons. [c] In acetone-d_6. [d] Decoupled from phosphorous. [e] In Methylcyclohexane-d_{14} at −40 °C. [f] In THF-d_8 at −40 °C. [g] In CD_2Cl_2.

complexes. In the course of the synthetic developments, by stepwise introduction of NO ligands, we were able to obtain several classical and nonclassical mono- and dinitrosyl hydride rhenium complexes with unusual chemical properties. The starting material for all this chemistry was the paramagnetic salt $[NEt_4]_2[Re(Br)_5(NO)]$ (**1**).[9a]

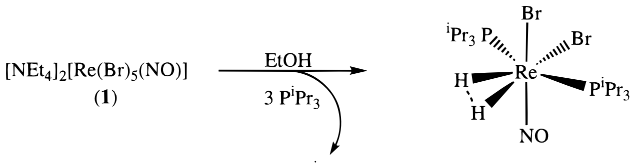
Results and Discussion

Paramagnetic rhenium salts of the formula $[A]_2[Re(X)_5(NO)]$ (A = Cs, NEt$_4$; X = Cl, Br) have been known for 30 years.[9] The synthesis of the tetraethylammonium derivatives was first reported by Giusto and Cova starting from $K_2[ReX_6]$ and NO, although with poor yields, especially for the chlorine derivative (15%).[9a] In our search for a suitable key compound to establish the desired nitrosyl hydride chemistry, we considered using these salts, since they have been successfully employed before in the preparation of a variety of mononitrosyl rhenium complexes. We have found that the bromine derivative $[NEt_4]_2[Re(Br)_5(NO)]$ (**1**) can be obtained in a more convenient way by a two-step procedure starting directly from rhenium metal. This includes first oxidation of the metal with H_2O_2 and then reduction of the thus formed oxoanion $[ReO_4]^-$ by H_3PO_2 in the presence of HBr, $[NEt_4]Br$, and bubbling NO at 110 °C. This new synthetic approach to complex **1** is a great improvement over the one reported previously, because it provides large amounts of analytically pure material in yields higher than 90%. In the former preparation[9a] the product was furthermore suspected to contain large amounts of KBr generated in the reaction, since the residue was only washed with acetone and employed without further purification.

Giusto et al. have also described the reactions of the complexes $[NEt_4]_2[Re(X)_5(NO)]$ (X = Cl, Br) with PPh$_3$. Here, the paramagnetic neutral rhenium(II) compounds $[Re(X)_3(NO)(PPh_3)_2]$[9a] were obtained, which resulted from exchange of two bromine ligands by two phosphine groups. We expected a similar behavior with bulkier phosphines such as P^{i}Pr$_3$ or PCy$_3$. Furthermore, subsequent reduction of the thus obtained $[Re(X)_3(NO)(PR_3)_2]$ could lead to the desired new hydrido nitrosyl rhenium species. With this in mind, we initially investigated the reactivity of these salts with the abovementioned phosphines.

1. $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(PR_3)_2]$ Complexes. Under conditions almost identical to those reported for the reaction of complex **1** with PPh$_3$, it was found that the reaction with P^{i}Pr$_3$ affords instead the diamagnetic complex $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(P^iPr_3)_2]$ (**2a**) as the major product (75−80% yield) (Scheme 1). In contrast to the

Scheme 1



2a

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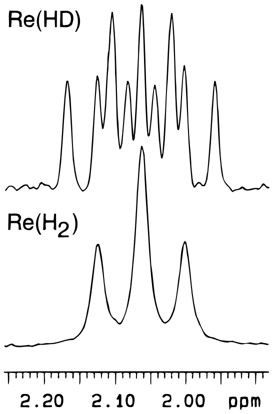

Figure 1. Resonances corresponding to the dihydrogen moiety in the ^{1}H NMR spectra of [Re(Br)$_2$(η^2-H$_2$)(NO)(P^{i}Pr$_3$)$_2$] (**2a**) (bottom) and [Re(Br)$_2$(η^2-HD)(NO)(P^{i}Pr$_3$)$_2$] (top) recorded in C$_6$D$_6$.

reaction with PPh$_3$[9a] now further reduction of the [Re(Br)$_3$(NO)(PR$_3$)$_2$] has taken place.

The ^{1}H NMR spectrum of compound **2a** (Table 1) shows an unusual low-field resonance for the dihydrogen ligand (2.07 ppm, C$_6$D$_6$) which appears as a broad triplet due to coupling with the phosphorus nuclei. The observation of relatively short longitudinal relaxation times, T_1 (45.7 ms/−30 °C; 29.0 ms/−60 °C; 26.7 ms/−70 °C; 29.4 ms/−80 °C at 300 MHz in CD$_2$Cl$_2$), and a detectable hydrogen−deuterium coupling constant ($J_{(\mathrm{H-D})}$ = 12.8 Hz) in the mixed hydrogen−deuterium isotopomer [Re(Br)$_2$(NO)(η^2-HD)(P^{i}Pr$_3$)$_2$] (Figure 1) suggest that this complex contains an elongated H$_2$ moiety. Therefore it may be better formulated as a dihydrogen complex rather than a dihydride isomer. An H···H distance of 1.27 Å can be estimated from the temperature-dependent minimum value of T_1 taking the dipole interactions to the phosphines (ca. 3.4 s^{-1})[10] and to the metal (ca. 3.2 s^{-1})[11] into account. A similar distance of 1.21 Å is calculated from a recently suggested empirical correlation between r(H···H) and ^1J(H−D) in the form $r(\mathrm{H\cdots H}) = 1.42 - 0.0167\,^1J(\mathrm{H-D})$.[12] No decoalescence of the Re(η^2-H$_2$) resonance was observed in CDClF$_2$ at −130 °C. The ^{31}P{^{1}H} NMR spectrum of **2a** also displays a broad signal. This broadening is likely caused by the quadrupolar ^{185}Re (I = 5/2, 37%) and ^{187}Re (I = 5/2, 63%). Analogous broadening is observed with other quadrupolar metals, such as ^{55}Mn (I = 5/2, 100%) and ^{59}Co (I = 7/2, 100%). The extent of this broadening depends on the magnitude of the scalar spin−spin interaction and the quadrupolar relaxation rate, and both parameters vary greatly in different spin systems.

Figure 2 shows the result of an X-ray diffraction study performed for complex **2a**. The heavy ligand atoms are in an octahedral arrangement around the metal center with the two bulky phosphine groups in a trans disposition and the π-acceptor nitrosyl placed trans to the π-donor bromine. Unfortunately the exact location of the metal-bound hydrogens in [Re(Br)$_2$(η^2-H$_2$)(NO)(P^{i}Pr$_3$)$_2$] remains uncertain, since they could not be found in the difference Fourier maps. From Figure 2 it seems clear that they should be placed in the apparent vacant site trans to the other bromine atom Br2. The rather regular octahedral geometry around the rhenium does not support a preferred rotameric conformation of the H$_2$ ligand, eclipsing either the P−Re−P or the N1−Re−Br1 moieties. However, a structural arrangement with the H$_2$ eclipsing the two rhenium phosphorus bonds would profit from an enhanced back-donation of the appropriate nonbonding metal d orbital to the σ antibonding orbital of the dihydrogen.[13]

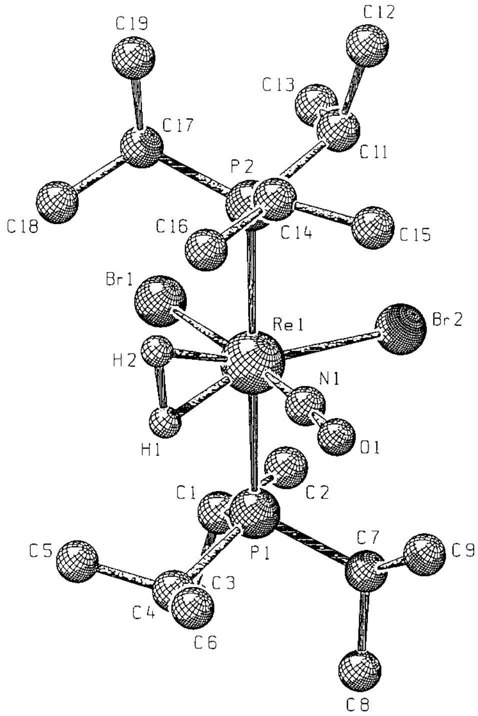

Figure 2. SCHAKAL[41] drawing of **2a**. Hydrogen atoms of the phosphines omitted for clarity. H1 and H2 were calculated.

Further support for this hypothesis is provided by the result of DFT calculations performed for the molecule **2a** as well as for similar model [Re(Br)$_2$(η^2-H$_2$)(NO)(PR$_3$)$_2$] systems.

There exist different possibilities for the binding of the HH unit to a metal center. In general, one might consider side-on as well as end-on coordinated dihydrogen. For the first case, in [Re(Br)$_2$(η^2-H$_2$)(NO)(PR$_3$)$_2$] complexes, one can further differentiate rotational isomers depending on whether the HH ligand lies in or perpendicular to the P−Re−P plane. These three types of coordination, side-on in-plane **I**, side-on perpendicular **II**, and end-on **III**, are displayed in Figure 3.

Qualitative molecular orbital considerations[14] reveal the essential bonding features of the HH ligand. For side-on coordination, the main bonding interaction stems from σ donation from the σ_{HH} orbital to a metal-based d$_\sigma$ orbital. In addition, there also exists back-bonding from d$_\pi$ to σ^*_{HH}. For end-on coordination, only

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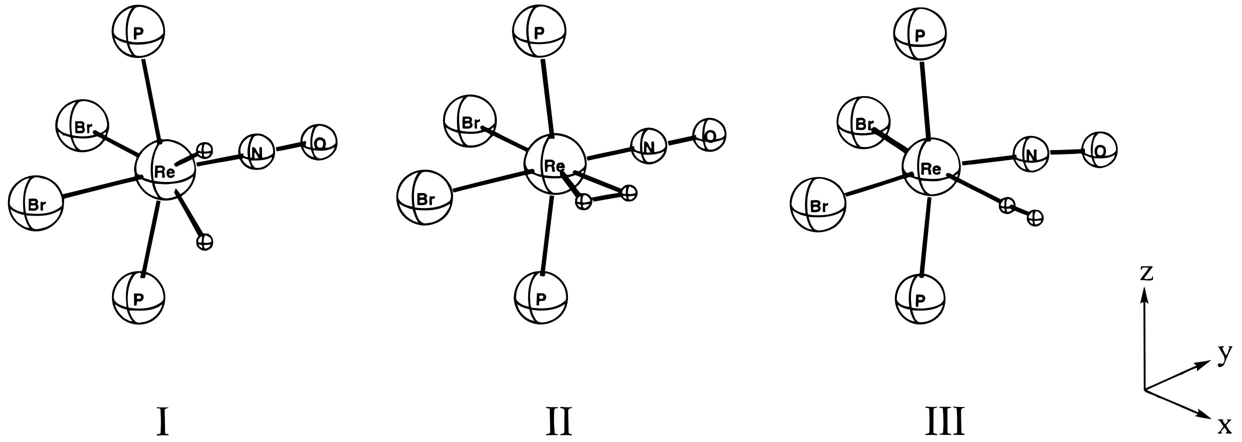
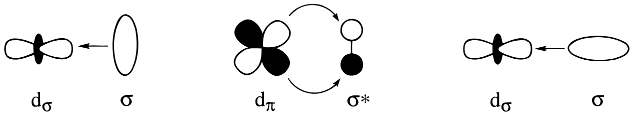
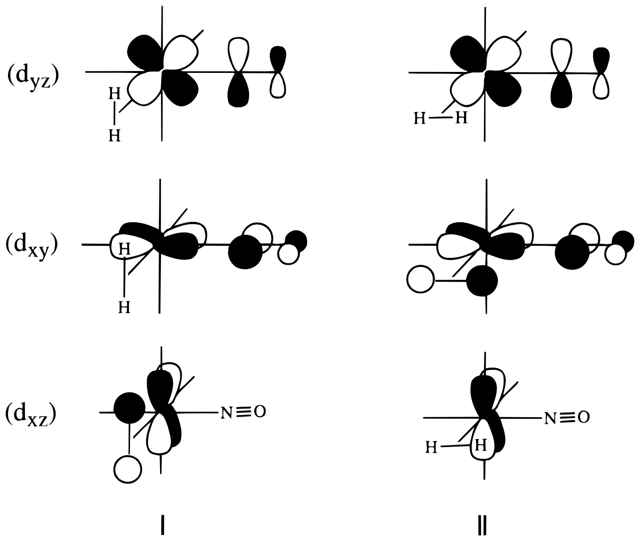


Figure 3. Different coordination geometries for the HH ligand in $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(PR_3)_2]$.

Scheme 2



Scheme 3



the σ_{HH} to d_σ interaction is possible. These different (HH)−M orbital interactions are depicted in Scheme 2.

On the basis of this bonding analysis, it becomes obvious that whenever π back-bonding can occur, side-on coordination should clearly be in favor over end-on coordination. The basic bonding characteristics of the HH ligand have been reproduced and quantified by first-principles quantum mechanical calculations.[15]

We now proceed with the problem of whether the in-plane geometry **I** or the perpendicular geometry **II** might be more stable in energy. To decide this question, we focused on the bonding of the HH unit to the metal center. Since the character of the σ bond does not change under rotation, we restricted the analysis to π back-bonding into the σ^*_{HH} orbital. In C_s symmetry, this orbital is of a″-type in the case of **I** and belongs to the completely symmetrical representation a′ in the case of **II**. The metal center is Re-d^6, and we have the typical three below two pattern for the metal d orbitals, the lower three d_{yz}, d_{xy}, and d_{xz} being fully occupied and available for back-bonding. We further have to consider that we have another strong π acceptor in our system, the nitrosyl ligand, with which the HH ligand will compete for back-bonding. The import orbital interactions are presented in Scheme 3.

For the d_{yz} orbital, only interaction with π^*_{NO} is possible in both case **I** and case **II**. For the d_{xy} orbital, the HH ligand in the perpendicular arrangement can now accept electron density from the metal center, but has to compete for back-bonding with another π^*_{NO} orbital. The d_{xz} orbital cannot undergo any interactions in the perpendicular geometry, but is solely available for π back-donation to σ^*_{HH} in the in-plane case. It follows that the HH ligand should be more strongly bound in the case of **I**, since there is no competition for back-bonding with the NO ligand. From our qualitative arguments, we cannot conclude whether classical or nonclassical coordination is preferred, but it becomes clear that **I** should exhibit more dihydride character, whereas the case **II** can be expected to be more similar to dihydrogen coordination.

To get a more detailed picture of the HH bonding in $[Re(Br)_2(\eta^2\text{-}H_2)(NO)(PR_3)_2]$ complexes, we employed density functional calculations[16] for a series of type **I** and type **II** structures with R = H, **a**; Me, **b**; Et, **c**; and ^{i}Pr, **d**. As expected, the structures of type **I** with an HH in-plane geometry are in general more stable, and the energy differences between the two geometric arrangements amount to 48 kJ/mol, **a**, 63 kJ/mol, **b**, 63 kJ/mol, **c**, and 59 kJ/mol, **d**. These values are of comparable size in any case and can be looked at as estimates for the barrier of rotation of the HH ligand. In addition, for $[Re(Br)_2(\eta^2\text{-}H_2)(NO)(PH_3)_2]$ we also performed calculations on a hypothetical end-on geometry **IIIa**, which is 97 kJ/mol higher in energy compared to **Ia**, and which is energetically the least favorable coordination mode. Selected bond distances and angles for the optimized complexes are collected in Table 2. The most interesting parameter is the H−H distance of the coordinated HH ligand. For type **I** structures, d_{HH} lies in the range between 1.28 and 1.43 Å, which at the lower end corresponds to a dihydrogen coordination with an

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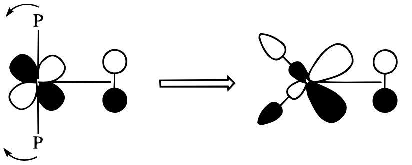
Table 2. Selected Geometric Parameters[a] for Optimized $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(PR_3)_2]$ Complexes (a, R = H; b, R = PMe_3; c, R = Et_3; d, R = P^iPr_3) with the HH Ligand in Side-On in-Plane I and Side-On Perpendicular II

	I				II			
	a	**b**	**c**	**d**	**a**	**b**	**c**	**d**
d(HH)	1.331	1.426	1.394	1.285	0.838	0.839	0.839	0.844
∠(HReH)	46.8	51.8	49.6	45.5	25.8	26.0	26.0	26.5
d(ReP)	2.460	2.507	2.530	2.584	2.431	2.468	2.489	2.536
∠(PReP)[b]	157.0	161.6	166.5	175.8	165.3	168.6	173.5	173.8
d(Re-*t*-Br)[c]	2.655	2.685	2.680	2.667	2.585	2.605	2.605	2.609
d(Re-*c*-Br)[c]	2.600	2.625	2.621	2.617	2.619	2.646	2.643	2.631
d(ReN)	1.800	1.790	1.789	1.787	1.803	1.794	1.793	1.794
d(NO)	1.180	1.186	1.188	1.189	1.180	1.187	1.188	1.188

[a] Distances in Å, angles in deg. [b] In general, ∠(PRe-*t*-Br) < 90°, except for **IId**, where ∠(PRe-*t*-Br) > 90°. Compare also footnote *c*. [c] *t*-Br denotes the bromine ligand trans to the HH group; *c*-Br is the ligand in cis position.

Scheme 4



elongated H−H bond, and at the upper end comes close to the typical H−H separation in dihydride complexes.[17] Thus, the nature of the HH bond to the transition metal center might be tuned selectively by varying the phosphine ligands. In case of alkylphosphines, we observe a decrease of the HH bond distance with increasing steric bulk of the phosphine ligand. This corresponds with a change in the angle ∠PReP, which increases on going from **Ib** to **Id**. Distorting this angle from its ideal value of 180° in a pseudo-octahedral arrangement by bending the phosphine ligand away from the HH ligand leads to a polarization of the Re d_{xz} orbital,[18] as indicated in Scheme 4.

This in turn enhances the back-bonding into the σ^* orbital of the dihydrogen ligand, leading to an elongation of the HH distance. The size of the phosphine ligands therefore determines the extent of the angle distortion, thereby influencing d_{HH}. The calculated HH distance of 1.285 Å for **Id** corresponds well with the experimentally determined values of 1.27 and 1.21 Å for complex **2a** (vide supra).

Although $[Re(Br)_2(\eta^2\text{-}H_2)(NO)(PH_3)_2]$ (**Ia**) has the smallest PReP angle, it does not exhibit the longest HH bond. The donor capability of the phosphine ligands seems to be another factor that determines the bonding to the HH ligand. The stronger the σ donor, the higher the electron density at the metal center and the stronger the back-donation to the dihydrogen. Weak donors favor dihydrogen coordination, whereas stronger donors induce a cleavage of the HH bond.

In type **II** structures, where the HH ligand is in competition with the nitrosyl group for back-bonding, we find an elongation of the H−H bond only by roughly 0.1 Å compared to free H_2. This is a typical case for dihydrogen coordination.[17] With the exception of the Re−P distance, the geometric parameters are very similar for the four complexes **IIa**−**IId**.

The synergic nature of the combined σ/π bonding mode manifests itself in the Re−Br distance of the bromine ligand in trans position to HH. This Br ligand binds mainly through σ donation and is in competition with the HH moiety. In type **II** structures, where we have a long Re−H separation, we find the shortest Re−Br distances in the range 2.58−2.61 Å. Allowing back-donation to the HH ligand strengthens and shortens the Re−H bond and also leads to enhanced σ donation. As a consequence, the Re−Br distances increase with increasing amount of back-bonding and range from 2.65 to 2.67 Å for type **I** structures.

Finally, we note that the coordination of the nitrosyl ligand does not depend on the nature of the phosphine ligands, and only small variations in ReN and NO bond lengths occur when the PR_3 ligands are altered.

The mechanism that accounts for the transformation of compound **1** into **2a** is not clear. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy established that along with coordination of the two molecules of phosphine another transformation takes place, which produces a molecule of $[HP^iPr_3]Br$. In addition, consumption of the starting material $[NEt_4]_2[Re(Br)_5(NO)]$ (**1**) is not complete unless a minimum of 3 equiv of the phosphine is used. A paramagnetic and NMR unobservable $[Re(Br)_3(NO)(P^iPr_3)_2]$ complex could be a possible intermediate, since preparation of the analogous triphenylphosphine derivative $[Re(Br)_3(NO)(PPh_3)_2]$ has been achieved under virtually identical conditions of reacting complex **1** with an excess of PPh_3. Further transformation in the isopropylphosphine case might proceed via the nondetectable ethoxy intermediate $[Re(Br)_2(OEt)(NO)(PR_3)_2]$, the formation of which would indeed be accompanied by the production of 1 equiv of $[HP^iPr_3]Br$. Similar paramagnetic rhenium(II) alkoxide complexes have been isolated by different procedures.[19a]

Concerning the reactivity of complex **2a**, it should be pointed out that the elongated dihydrogen ligand is strongly bound. The complex is stable toward hydrogen loss and even appears to be air stable in the solid state, although it slowly decomposes under air in solution. A change in color from the original light brown to purple takes place also in solution after several days, but no significant differences in the NMR spectra are observed. ^{13}C-enriched carbon monoxide can irreversibly displace the hydrogen molecule from its coordination site leaving the corresponding carbonyl derivative $[Re(Br)_2(NO)(^{13}CO)(P^iPr_3)_2]$ (Scheme 5). The reaction of **2a** with deuterium gas is interesting, but difficult to understand. There is no detectable hydrogen/deuterium scrambling in samples prepared in halogenated solvents such as CH_2Cl_2, CF_2Cl_2, or $CDFCl_2$ after several days. On the

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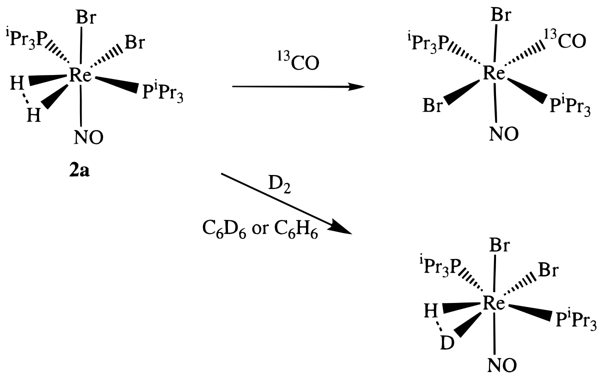
(17) Morris, R. H. *Can. J. Chem.* **1996**, *74*, 1907.

(18) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry;* John Wiley: New York, 1985; Chapter 15.4.

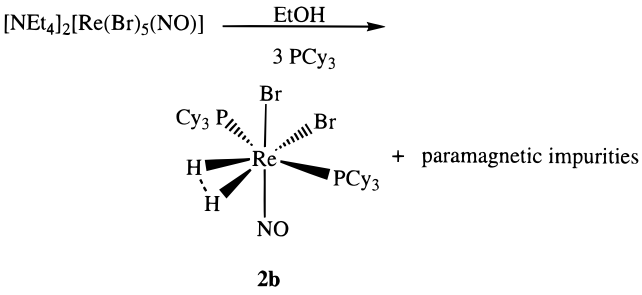
Scheme 5



contrary, formation of the mixed hydrogen−deuterium isotopomer **$2aD_1$** is observed in a few hours when C_6D_6 or C_6H_6 solutions of **2a** are kept under an atmosphere of deuterium (Scheme 5). In Figure 1 the ^1H NMR spectrum of **$2aD_1$** has been obtained in an inversion−recovery experiment eliminating the $Re(H_2)$ component derived from **2a** with a shorter T_1 time. The ^1H NMR experiment could not detect the $Re(D_2)$ compound, but it is likely that all three isotopomers were present in solution, since exchange of H_2 by D_2 has been observed in samples of **2a** prepared under a deuterium atmosphere in a nondeuterated solvent. It is noticeable that no variation in the chemical shift of the Re(H−D) resonance with respect to the $Re(H_2)$ signal is detected. Although isotopic shifts in the NMR spectra of different magnitude (both low-field or high-field in direction) have been observed, no theory is yet available that could predict their magnitude or allow a meaningful treatment of the experimental findings.

In a fashion similar to that described for the triisopropylphosphine complex **2a**, the reaction of $[NEt_4]_2$-$[Re(Br)_5(NO)]$ (**1**) with PCy_3 produces a dihydrogen derivative $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(PCy_3)_2]$ (**2b**) (Scheme 6).

Scheme 6

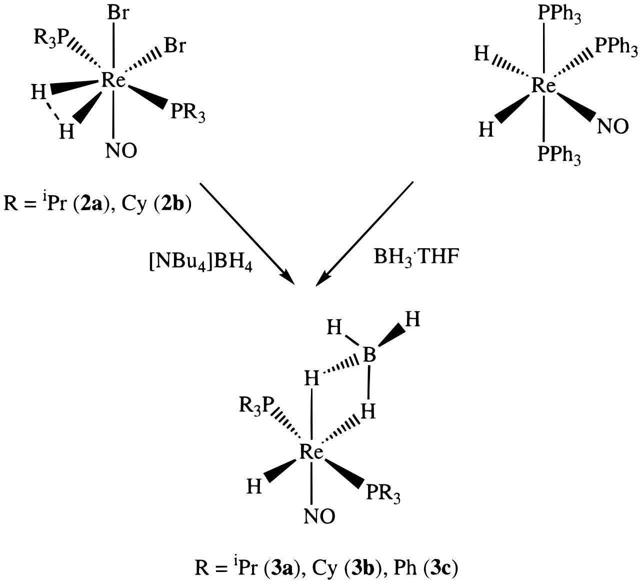


Unfortunately, in this case the solubility of all constituents is dramatically reduced and prevents the isolation of pure **2b**. The brown solid shows in the ^1H and ^{31}P-$\{^1H\}$ NMR spectra in C_6D_6 solution signals undoubtedly assignable to complex **2b**, although the ^1H NMR resonances of the diamagnetic **2b** are resting now on a very broad spectral component (pedestal). This is clearly distinguishable in the ^1H NMR spectrum and arises from some paramagnetic impurities that could not be separated.

The rate of formation of $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(PCy_3)_2]$ is reduced substantially and still incomplete in 48 h (sufficient time for the reaction of P^iPr_3), presumably because of a low solubility of the $[Re(Br)_3(NO)(PCy_3)_2]$ or $[Re(OEt)(Br)_2(NO)(PCy_3)_2]$ intermediates. Longer reaction times (3−6 days) have not improved the preparation, since complex **2b** was then already slowly losing H_2 to yield increasing amounts of ethoxy rhenium derivatives detectable by ^1H NMR spectroscopy. Isolation of pure **2b** has not been pursued further, because we have found in subsequent experiments that this complex together with the paramagnetic admixtures can be cleanly converted to the borohydride complex $[ReH(BH_4)(NO)(PCy_3)_2]$ (**3b**) by treatment with $[NBu_4][BH_4]$.

2. $[Re(H)(BH_4)(NO)(PR_3)_2]$ Complexes. Complex **2a** and the mixture containing the PCy_3 derivative **2b** react in several organic solvents with an excess of $[NBu_4][BH_4]$ to quantitatively yield the orange borohydride derivatives $[Re(H)(BH_4)(NO)(PR_3)_2]$ (R = ^{i}Pr, **3a**; R = Cy, **3b**) (Scheme 7). The reactions take place within minutes in solvents such as THF or C_6H_6. A longer period of time is required in diethyl ether, where neither of the reactants is very soluble. Diethyl ether is however a useful solvent when the isolation of pure **3a**,**b** is sought. In the case of **3a** the product is separated from insoluble $[NBu_4]Br$ by filtration and evaporation, followed by recrystallization from ether/pentane. For complex **3b** the residue of the reaction is washed with CH_3CN, affording analytically pure material.

Scheme 7



The analogous derivative containing triphenylphosphine, $[Re(H)(BH_4)(NO)(PPh_3)_2]$ (**3c**), has to be prepared in a different manner, reacting the known dihydrido complex $[Re(H)_2(NO)(PPh_3)_3]$[19] with an excess of BH_3·THF (Scheme 7). In the former process, 1 equiv of BH_3 is needed to remove the phosphine in the form of the borane adduct, and a second one coordinates to the metal yielding **3c**. These complexes have to be handled under nitrogen atmosphere, because they decompose slowly when exposed to air even in the solid state.

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[19] (a) Cameron, T. S.; Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1982**, *21*, 4149. (b) We have prepared the compound $[Re(H_2)(NO)(PPh_3)_2]$ by the method employed by Giusto et al.: Giusto, D.; Ciani, G.; Manasero, M. *J. Organomet. Chem.* **1976**, *105*, 91, although in this publication no amounts of the reagents employed were specified. Therefore we include the synthesis of this compound in the Experimental Section of the present work.

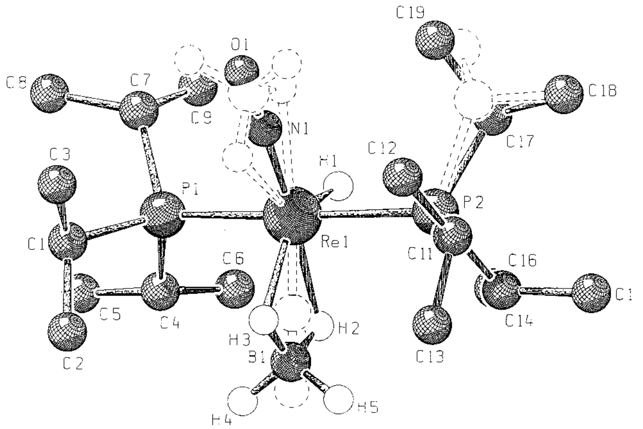


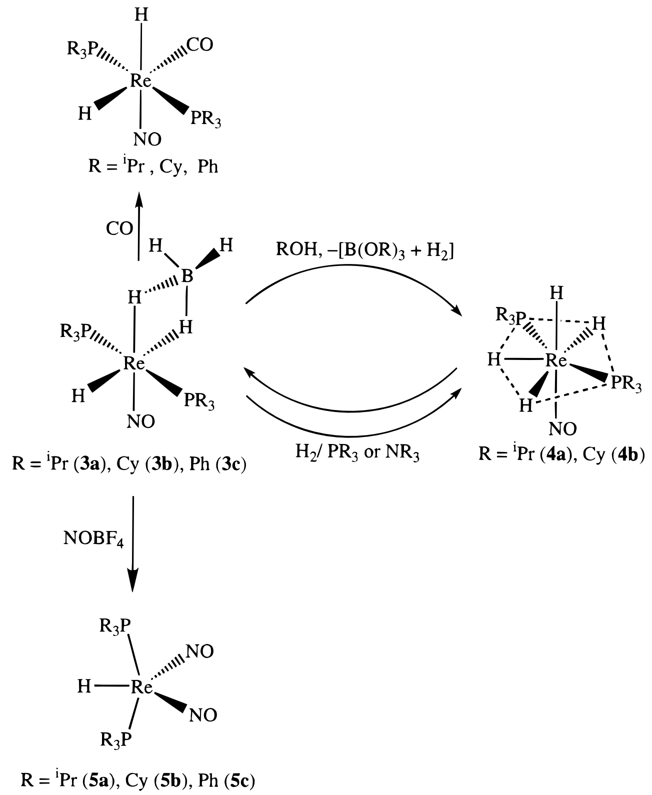
Figure 4. SCHAKAL[41] drawing of **3a**. Hydrogen atoms of the phosphines omitted for clarity.

The borohydrides **3** do not display fluxional behavior in solution at room temperature, and no exchange of the hydrido ligands was observed under such conditions, as reflected by their ^{1}H NMR spectra (Table 1). In all the cases the hydride region shows a very similar pattern with three resonances in a 1:1:1 ratio. Two of the signals are coupled to the boron spins and are characteristically broadened by the fast boron relaxation corresponding to the boron–rhenium-bridging hydrogen nuclei. A doublet of triplets is assigned to the terminal hydride bonded to rhenium, which is coupled to the two phosphorus atoms and to one of the bridging hydrides. The remaining two terminal protons on the boron atom appear in the aromatic region of the spectrum as a very broad signal.

To complete the characterization of the former species, an X-ray diffraction study was carried out on the complexes [Re(H)(BH$_4$)(NO)(P^{i}Pr$_3$)$_2$] (**3a**) (Figure 4) and [Re(H)(BH$_4$)(NO)(PPh$_3$)$_2$] (**3c**). Compounds **3a** and **3c** are isostructural and may be viewed in two ways, depending on the number of coordination sites occupied by the BH$_4^-$ ligand. If the bridging BH$_4^-$ is considered to occupy a single site in the coordination polyhedron, the structure of the complexes consists of an approximately trigonal bipyramidal arrangement of the ligands around the central metal atom. Alternatively, the structure might also be referred to as a very distorted octahedral environment around the rhenium and with the bridging borohydride filling two coordination positions. The two phosphine ligands in the molecule are placed trans to each other in axial positions, and the NO group, the terminal hydride, and the bridging borohydride form the equatorial plane. Unfortunately, both X-ray diffraction studies are affected by a major disorder phenomenon due to positional exchange of the borohydride and the nitrosyl ligands. The disorder therefore does not allow further discussion of geometrical data, although the actual coordination environment around the transition metal is clearly established.

3. Reactivity of [Re(H)(BH$_4$)(NO)(PR$_3$)$_2$]. Synthesis of [Re(H)$_4$(NO)(PR$_3$)$_2$] and the Dinitrosyl Complexes: [Re(H)(NO)$_2$(PR$_3$)$_2$] and [Re(H)(NOBF$_3$)(NO)(PR$_3$)$_2$]. Compounds **3a**–**c** are very reactive species due to the fact that the BH$_3$ moiety can easily be displaced, leaving a vacanct coordination site. Some characteristic reactions are illustrated in Scheme 8.

Scheme 8



Borane is irreversibly displaced from **3** within minutes in the presence of CO, and the known dihydrides [Re(H)$_2$(CO)(NO)L$_2$][7a,20] (L = P^{i}Pr$_3$, PCy$_3$, PPh$_3$) are formed.

The tetrahydride species of the formula [Re(H)$_4$(NO)L$_2$] (L = P^{i}Pr$_3$, **4a**; PCy$_3$, **4b**) can be generated from **3a**,**b** in two different ways (Scheme 8). Thus dissolving these complexes in methanol or ethanol produces **4a** and **4b** directly. Their formation is probably a consequence of the reaction of free borane with the alcohol to give the corresponding alkyl orthoborates and hydrogen, which is then incorporated in the complex. These molecules are, however, subject to some further unidentified transformations in both of these solvents. A clean formation of both species **4** is observed in the bulkier alcohol 2-propanol. Formation of **4a** was then also recognized in the reaction of [Re(Br)$_2$(NO)(η^2-H$_2$)(PCy$_3$)$_2$] (**2a**) with [NBu$_4$][BH$_4$] carried out in acetone-d_6, probably due to the presence of 2-propanol generated from acetone.

Another approach to produce complexes **4** involves removal of BH$_3$ in the form of the corresponding phosphine or amine adducts under hydrogen atmosphere. These reactions are, in principle, reversible, because species **4** are susceptible to H$_2$ loss and the highly reactive 16-electron species [ReH$_2$(NO)L$_2$] are expected to compete for BH$_3$ binding with the free phosphines or amines. Consistent with this idea, we tried a series of reagents of different basicity to achieve a complete removal of BH$_3$. The results show that PPh$_3$ or NEt$_3$ is appropriate for that purpose, while only 6% of conversion to the rhenium tetrahydrides is observed with the less basic AsPh$_3$.

The structures of **4a** and **4b** could only be established by NMR spectroscopy, because on repeated attempts to

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[20] Grundy, K.; Robertson, K. N. *Inorg. Chem.* **1985**, *24*, 3898.

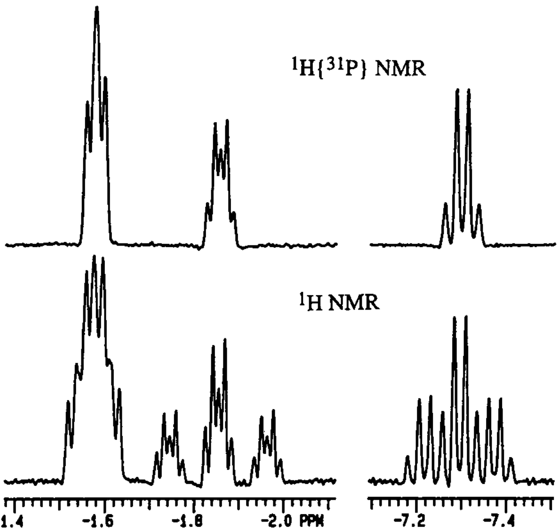

Figure 5. Hydride region of the $^1H\{^{31}P\}$ NMR (top) and ^1H NMR (bottom) spectra of complex **4a** in methylcyclohexane-d_{14} at −40 °C.

isolate both compounds, problems were encountered owing to their instability toward H_2 loss when they were placed under vacuum. Subsequent substantial decomposition takes place even when vacuum is applied only briefly (5 min). **4a** and **4b** are fluxional above −30 °C. The hydride region in the ^1H NMR spectra recorded at room temperature shows only two broad resonances (Table 1). The $^{31}P\{^1H\}$ NMR spectrum of **4a** at 20 °C presents a single line, which becomes a resolved quintet (averaged $^2J_{(P-H)} = 18$ Hz) upon selective decoupling of the protons belonging to the phosphine ligands (Table 1). This indicates that at this temperature there is a dynamic process that takes place on the NMR time scale affecting the hydride ligands. Below −30 °C three resonances in a 2:1:1 ratio are observed in the hydride region (Figure 5). Two of the metal-bonded hydrogens (δ −1.57 ppm) are chemically but not magnetically equivalent and give rise to a complicated pattern, since they represent the AA′ part of an AA′BCXX′ spin system (^1H = A, A′, B, C; ^{31}P = X, X′), which is not sufficiently resolved for reliable simulation. When decoupled from the phosphorus nuclei, the spectrum pattern becomes simpler and coupling constants of 5.4, 7.1 and 9.0 Hz can be set between the metal-bonded hydrides.

Measurements of $T_{1\min}$ relaxation times were performed for the hydride ligands of **4a**. Tumbling of this molecule in solution is anisotropic, and the minima are observed at different temperatures.[11] The shortest measured T_1 in **4a** (98 ms) is longer than the $T_{1\min} = 26.7$ ms found for **2a**, supporting the conclusion that in **4a** there are no close H···H interactions. Interpretation of the spectroscopic data in solution establishes a unique structure (Figure 6). Apparently complexes **4** have a pentagonal bipyramidal geometry around the central atom with one hydride and the NO ligand in apical positions. The other three hydrides and the phosphines lie in the pentagonal plane of the molecule. A mirror plane containing H_B, H_C, and the NO group, as well as the metal is responsible for the observed equivalence of the phosphorus nuclei and the hydrides H_A and $H_{A'}$ in the NMR spectra.

The complexes $[Re(H)_4(NO)L_2]$ are thus notably different from the isoelectronic osmium molecules $[Os(H_2)(H)_2(CO)L_2]$ (L = P^iPr_3, P^tBu_2Me).[21] Despite being originally formulated as classical polyhydride complexes, more recent studies have confirmed that they possess an octahedral geometry with trans disposed phosphines and an elongated H_2.[22]

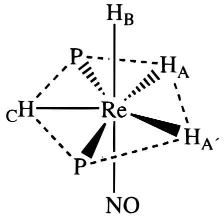

Figure 6. Proposed structure in solution for the tetrahydride **4**.

In contrast to the reactions of **3a**,**b** in alcoholic solvents described above, no such conversion was observed for the triphenylphosphine derivative **3c**. Attempts to remove the BH_3 moiety from this molecule with PPh_3 or NEt_3 under H_2 atmosphere were unsuccessful and resulted in recovering unreacted **3c**. The hypothetical $[Re(H)_4(NO)(PPh_3)_2]$ derivative was indeed never observed in solution. This can be explained in terms of a lower basicity of PPh_3 compared with P^iPr_3 or PCy_3. Thus, the PPh_3 derivative is a less electron-rich molecule and, accordingly, displays a decreased tendency to undergo oxidative H_2 addition reactions.

When compounds **3a**−**c** are treated with $NOBF_4$ in THF, the ^1H and $^{31}P\{^1H\}$ NMR spectra of the resulting solutions show the dinitrosyl hydride species $[Re(H)(NO)_2(PR_3)_2]$ (R = ^iPr, **5a**; R = Cy, **5b**; R = Ph, **5c**) as the only detectable products (Scheme 8). The structures of these formally rhenium(−I) molecules can be described as distorted trigonal bipyramids. Although in low yields, complexes **5a**−**c** can be isolated as orange solids by flash-type chromatography of the reaction solutions over silica gel columns. The triphenylphosphine derivative **5c** has already been described more than 20 years ago by La Monica et al. resulting from the reaction between $[Re(Cl)_4(PPh_3)_2]$ or $[Re(O)(I)_2(OC_2H_5)(PPh_3)_2]$ and Diazald.[23] No NMR or X-ray diffraction studies were performed at that time, and the proposed structure was merely based on the available IR data, which showed one hydride and two nitrosyl bands with an absorption pattern similar to those reported for the related $[Mn(H)(NO)_2(PPh_3)_2]$[24] and $[Re(X)(NO)_2(PPh_3)_2]$ (X = Cl,[9a] Br,[9a] I[25]) complexes.

Complexes **5a**−**c** are very sensitive toward oxygen, and in the presence of air significant decomposition of the solids takes place after some minutes. The most characteristic features of the dinitrosyl species are the exceptionally high chemical shifts displayed by the hydrido ligands in their ^1H NMR spectra (varying from +4 ppm in the case of **5a** to +6.3 ppm in the case of **5c**)

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[21] Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. Esteruelas, M. A.; Lahoz, F. J.; Lòpez, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034. Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

[22] Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775.

[23] La Monica, G.; Freni, M.; Cenini, S. *J. Organomet. Chem.* **1974**, *71*, 57.

[24] Hieber, W. H.; Tengler, H. *Z. Anorg. Allg. Chem.* **1962**, *318*, 136.

[25] Freni, M.; Giusto, D.; Valenti, V. *Gazz. Chim. Ital.* **1964**, *94*, 797.

Table 3. Selected IR Data

2a	1722 (νNO), 2052, 2039 (ν_{Re-H})[a]
2b	1706 (ν_{NO}), 2020, 2012 (ν_{Re-H})[a]
3a	1660 (ν_{NO}), 2039, 2010 (ν_{Re-H}), 2462, 2437 (ν_{B-H}), 1854, 1794 (ν_{Re-H-B})[a]
3b	1660 (ν_{NO}), 2020, 1999 (ν_{Re-H}), 2462, 2437 (ν_{B-H}), 1843, 1790 (ν_{Re-H-B})[a]
3c	1687, 1666 ($\nu_{NO,\ split}$), 1966 (ν_{Re-H}), 2482, 2446 (ν_{B-H}), 1810 (ν_{Re-H-B})[b]
5a	1604, 1554 (ν_{NO}), 1810 (ν_{Re-H})[b]
5b	1602, 1559 (ν_{NO}), 1801 (ν_{Re-H})[b]
5c	1622, 1588, 1575, 1568 (ν_{NO}, split), 1789 (ν_{Re-H})[b]
6a	1637 (ν_{N-O}), 1363 (ν_{N-OBF3}), 1851 (ν_{Re-H})[b]
6b	1646 (ν_{N-O}), 1377 (ν_{N-OBF3}), 1882 (ν_{Re-H})[b]

[a] In KBr pellets. [b] In Nujol.

(Table 1). Furthermore, the ν(NO) vibrations appear at unusually low wavenumbers, indicating an important contribution of electronic back-donation from the metal to the π^* orbitals of the nitrosyl ligands (Table 3). It has already been noted that NO substitution causes marked low-field chemical shifts for the metal-bonded hydrogens, especially for those located in a trans position with respect to that group.[7a,b] Unfortunately, no special chemical properties can be derived from this, since empirical correlations relating ^{1}H NMR data with hydride reactivity could not be established in transition metal chemistry.[3c,4,26] With respect to the IR spectra it was observed that the presence of good donor phosphines leads to lower energy vibrations for the NO groups and that their position can be used as an indication of the degree of M−H activation. Systems with NO stretching vibrations at low wavenumbers are expected to have more basic hydrides and vice versa.[2,4] Taking these criteria into account and considering the low IR wavenumbers registered for the nitrosyl substituents of complexes **5**, an enhanced hydridic reactivity is expected for the metal-bonded hydrogen of such derivatives, especially in the case of **5a** and **5b**, which contain the better σ-donor phosphines. Indeed, based on temperature-dependent measurements of the deuterium quadrupole coupling constant[27] for the D nucleus in the $[Re(D)(NO)_2(PR_3)_2]$ complexes, the bond ionicities have been calculated to be 72% (**5a**) and 70% (**5b**), respectively.

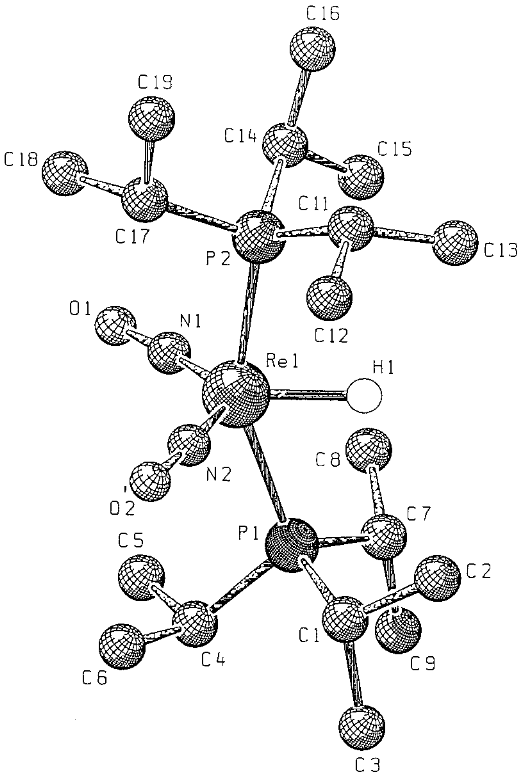

Figure 7. SCHAKAL[41] drawing of **5a**. Hydrogen atoms of the phosphines omitted for clarity.

Figure 7 shows the result of an X-ray diffraction study undertaken for the triisopropylphosphine derivative **5a**. Cooling a saturated pentane solution of the complex afforded red crystals suitable for this purpose. As mentioned before, the molecule can be considered as a very distorted trigonal bipyramid with one hydrido and two essentially linear nitrosyl ligands placed in the equatorial plane, while the phosphorus substituents occupy apical positions. The two phosphines are subjected to a commonly observed deviation with respect to the 180° angle expected for an ideal trigonal bipyramidal geometry, because the low steric demand of the hydride ligand allows a narrow P−Re−P angle of 154° (Table 4). The rhenium-bonded hydrogen atom could be located and refined. The Re−N and N−O bond distances compare well with those found for other neutral linear nitrosyl rhenium complexes (Table 5).[7a] In general, the structural features concerning compound **5a** are very similar to those reported previously for the manganese derivative $[Mn(H)(NO)_2(PMe_3)_2]$.[8]

When the THF solutions resulting from the reactions of the borohydride complexes **3a** and **3b** with $NOBF_4$ are evaporated and the residue is extracted with diethyl ether, complexes of the type $[Re(H)(NO)(NOBF_3)(PR_3)_2]$ (R = ^{i}Pr, **6a**; R = Cy, **6b**) remain after removal of the solvent (Scheme 9). These species can be described as Lewis acid/base adducts of BF_3 and the dinitrosyl derivatives **5**, in which one of the O_{NO} atoms acts as the basic site. In THF compounds **6a** and **6b** are not observed, since BF_3 then prefers coordination to the solvent molecules. When extracted with Et_2O, a mixture of the $[Re(H)(NO)_2(PR_3)_2]$ complexes and $BF_3{\cdot}OEt_2$ passes to the solution. Upon concentration or cooling, the BF_3 adduct of the corresponding dinitrosyl complexes starts to precipitate due to a concomitant increase in BF_3 concentration and/or to the fact that the solubility of the $[Re(H)(NO)(NOBF_3)(PR_3)_2]$ species is significantly decreased in ether at lower temperatures.

The extent to which the coordination of BF_3 to the nitrosyl ligands takes place in solution is strongly dependent on the solvent used. In weakly donating solvents such as toluene, benzene, or dichloromethane only the species $[Re(H)(NO)(NOBF_3)(PR_3)_2]$ are detected by ^{1}H, $^{31}P\{^1H\}$, and ^{19}F NMR spectroscopy, while in a donor solvent such as THF exclusively the BF_3-free complexes can be observed accompanied by $BF_3{\cdot}THF$ formation. An intermediate situation occurs in acetone where both the BF_3-free complex and the BF_3 adduct can be traced at −60 °C, whereas at 25 °C the spectra show only broad resonances, suggesting fast exchange of the BF_3 unit between the transition metal complex and the solvent.

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(26) Schunn, R. A. *The Hydrogen Series*; Mutterties, E. L., Ed.; Marcel Dekker: New York, 1971; Vol. 1, p 203. Kaesz, H. D.; Sallant, R. B. *Chem. Rev.* **1972**, *72*, 231.

(27) Nietlispach, D.; Bakhmutov, V. I.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 9191.

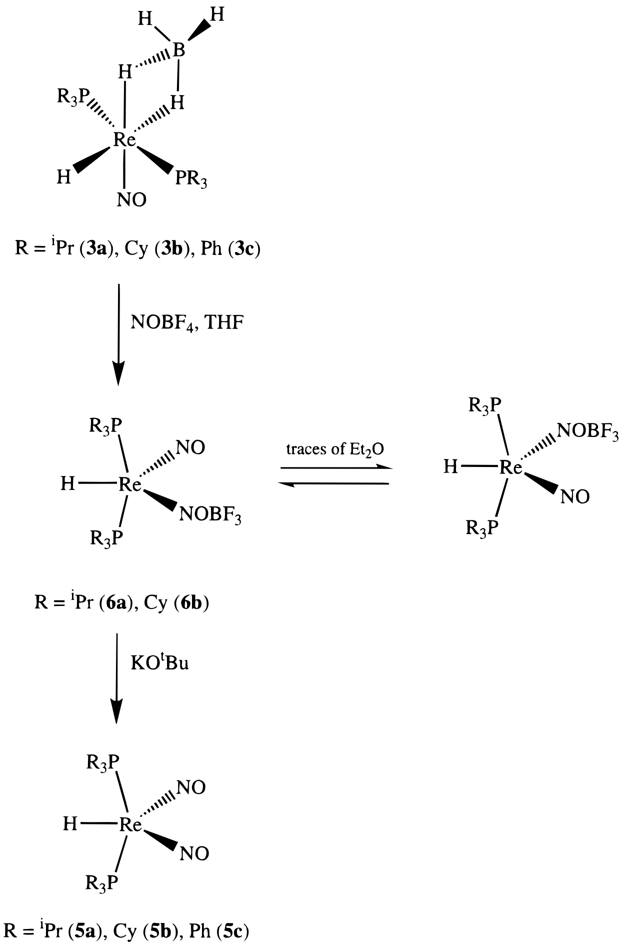
Table 4. Selected Bond Angles (deg) for Complexes 2a, 3a, 3c, 5a, and 6a

2a	3a	3c	5a	6a
Br1−Re1−Br2 = 89.50(1)	P1−Re1−P2 = 168.45(3)	P1−Re1−P2 = 170.51(8)	P1−Re1−P2 = 153.89(6)	P1−Re1−P2 = 146.60(6)
Br1−Re1−P1 = 89.51(2)	P1−Re1−N1 = 91.2(2)	P1−Re1−N1 = 90.2(4)	P1−Re1−N1 = 98.5(3)	P1−Re1−N1 = 92.2(2)
Br2−Re1−P1 = 86.41(2)	P2−Re1−N1 = 93.7(2)	P2−Re1−N1 = 90.0(4)	P2−Re1−N1 = 94.7(3)	P2−Re1−N1 = 94.1(2)
Br1−Re1−P2 = 85.94(2)	P1−Re1−N11 = 88.5(6)	P1−Re1−N11 = 95.0(7)	P1−Re1−N2 = 94.3(3)	P1−Re1−N2 = 103.2(2)
Br2−Re1−P2 = 90.19(2)	P2−Re1−N11 = 92.9(6)	P2−Re1−N11 = 89.6(7)	P2−Re1−N2 = 95.4(3)	P2−Re1−N2 = 100.5(2)
P1−Re1−P2 = 174.35(3)	Re1−N1−O1 = 176.8(6)	Re1−N1−O1 = 170.9(13)	N1−Re1−N2 = 127.4(3)	N1−Re1−N2 = 123.6(2)
Br1−Re1−N1 = 173.2(1)	Re1−N11−O11 = 178.0(15)	Re1−N11−O11 = 170.2(26)	P1−Re1−H1 = 71.31(4)	P1−Re1−H1 = 66.3(22)
Br2−Re1−N1 = 97.3(1)			P2−Re1−H1 = 82.58(4)	P2−Re1−H1 = 80.6(22)
P1−Re1−N1 = 90.8(1)			N1−Re1−H1 = 122.3(3)	N1−Re1−H1 = 108.6(23)
P2−Re1−N1 = 94.1(1)			N2−Re1−H1 = 110.2(2)	N2−Re1−H1 = 127.4(23)
Re1−N1−O1 = 176.4(4)			Re1−N1−O1 = 173.1(8)	N2−O2−B1 = 117.5(5)
			Re1−N2−O2 = 175.4(7)	Re1−N1−O1 = 168.7(5)
				Re1−N2−O2 = 170.0(4)

Table 5. Selected Bond Distances (Å) for Complexes 2a, 3a, 3c, 5a, and 6a

2a	3a	3c	5a	6a
Re1−Br1 = 2.5891(4)	Re1−P1 = 2.427(1)	Re1−P1 = 2.411(2)	Re1−P1 = 2.428(2)	Re1−P1 = 2.448(1)
Re1−Br2 = 2.6005(4)	Re1−P2 = 2.433(1)	Re1−P2 = 2.404(2)	Re1−P2 = 2.421(2)	Re1−P2 = 2.438(2)
Re1−P1 = 2.5237(8)	Re1−N1 = 1.748(6)	Re1−N1 = 1.75(2)	Re1−N1 = 1.804(7)	Re1−N1 = 1.775(5)
Re1−P2 = 2.5268(9)	Re1−N11 = 1.58(2)	Re1−N11 = 1.86(2)	Re1−N2 = 1.780(7)	Re1−N2 = 1.749(5)
Re1−N1 = 1.768(4)	O1−N1 = 1.17(1)	O1−N1 = 1.18(2)	Re1−H1 = 1.7793(2)	Re1−H1 = 1.69(7)
O1−N1 = 1.166(5)	O11−N11 = 1.27(2)	O11−N11 = 1.10(3)	O1−N1 = 1.193(9)	O1−N1 = 1.212(7)
			O2−N2 = 1.227(9)	O2−N2 = 1.304(7)
				O2−B1 = 1.54(1)

Scheme 9



At room temperature the BF_3 molecule is also exchanging positions between the two nitrosyl groups, as reflected by the ^{1}H NMR spectrum of the triisopropylphosphine derivative **6a**, which shows a unique signal for the two diastereotopic methyl groups of the phosphines. This is hardly surprising, because both ligands are chemically equivalent and there should be no preference for coordination to one over the other. The mechanism by which the hopping of the BF_3 molecule between the nitrosyl ligands takes place seems to be dependent on the presence of a donor solvent molecule. In this case catalysis of the process can be envisaged establishing an intermolecular pathway. Traces of Et_2O or THF previously employed in the reaction are very difficult to remove from the final product and appear in the ^{1}H NMR spectra even when this is dried under vacuum for hours or washed several times with noncoordinating solvents such as pentane. The former exchange, however, can be slowed and finally frozen by cooling at temperatures below −60 °C (Tol-d_8). Two broad signals are observed for the methyl groups of the isopropylphosphine substituent, which then become nonequivalent. Upon warming the probe above room temperature, the hydride resonance becomes broader, and at 50 °C coalescence is reached. The $^{31}P\{^{1}H\}$ and ^{19}F resonances are also considerably broadened. Addition of small amounts of acetone produces the same effect, while, on the contrary, introduction of a few microliters of $Et_2O\cdot BF_3$ results in sharper resonances for the hydride ligand, since dissociation of BF_3 is then less extensive. A similar phenomenon was seen for the PCy_3 complex, but in this case the pattern of the ^{1}H NMR spectrum is more complicated.

Formation of the nitrosyl linkage dramatically affects the $\nu_{(NO)}$ vibrations in the IR spectrum. The BF_3-bonded $\nu_{(NO)}$ vibration appears at lower wavenumbers by more than 250 cm^{-1} with respect to the BF_3-free nitrosyl group (Table 3). As a consequence of the interaction with the Lewis acid, electronic density is drained from the ligand and the transition metal donates further to the π^* orbital of the NO group. The result is a weaker nitrogen−oxygen bond, as reflected by the lower IR wavenumber. The BF_3-free $\nu_{(NO)}$ is shifted in the opposite direction to higher wavenumbers with respect to those of $[Re(H)(NO)_2(PR_3)_2]$ as a consequence of a decreased electronic density on the rhenium center.

Boron trifluoride can definitively be removed from the solution adding KO^tBu, which then forms insoluble

$K(BF_3O^tBu)$. Compounds **5a**,**b** are then extracted with different solvents. This procedure is the best route to these complexes when high isolated yields are considered.

The triphenylphosphine derivative $[Re(H)(NO)(NOBF_3)(PPh_3)_2]$ (**6c**) could not be detected spectroscopically in solution, nor could it be isolated. Despite this, its presence cannot be ruled out because there is evidence to suggest the existence of an equilibrium. However, this seems to be shifted much further to the dissociated side of BF_3 and **5c** than those of **5a,b**. Complex $[Re(H)(NO)_2(PPh_3)_2]$ (**5c**) is also isolated in good yield by treatment of the reaction mixture with KO^tBu. This indicates that BF_3 is present in solution. In fact, when the ^1H NMR spectrum of the reaction residue is recorded in CD_2Cl_2, no hydride signal is observed, while in THF-d_8 the hydride signal is present parallel to the observations for **5a,b**. The anticipated fast BF_3 exchange in the CD_2Cl_2 spectrum is then further supported by a similar observation in Tol-d_8. When a small amount of $BF_3{\cdot}OEt_2$ is added to a Tol-d_8 solution of complex **5c**, immediate disappearance of the hydrido signal occurs and very broad resonances appear in the $^{31}P\{^1H\}$ and ^{19}F NMR spectra. However, no significant changes in the shape of the resonances are observed upon cooling to −90 °C.

Once again, the experimental results suggest that the lower basicity of PPh_3 compared with P^iPr_3 or PCy_3 results in an electronically less rich molecule, which displays a reduced tendency to form the Lewis acid nitrosyl adduct. The broad signals in the NMR spectra suggest an equilibrium involving fast coordination/decoordination of the BF_3 between the nitrosyl ligands and the donor solvent. While in solutions of **6a** and **6b** in nondonor organic solvents, there seems to be a preference of the BF_3 for binding to the nitrosyl groups of the molecule (even in the presence of traces of Et_2O or THF), this preference is inverted or at least not pronounced with the PPh_3 derivative.

In a way it was surprising to us that the strong Lewis acid BF_3 formed in the process does not attack the hydride group of the dinitrosyl molecules **5**, especially in the absence of donor solvents. However, small amounts of $[Re(BF_4)(NO)_2(PCy_3)_2]$[28] have been observed by NMR spectroscopy contaminating the $[Re(H)(NO)(NOBF_3)(PCy_3)_2]$ derivative (ca. 10%). Formation of $[Re(BF_4)(NO)_2(PCy_3)_2]$ can be explained as a consequence of hydride abstraction by 1 equiv of BF_3 followed by coordination of BF_4^- to the unsaturated species. The reduced reactivity of the hydride substituent toward BF_3 in complexes **5a**−**c** may be explained either by the relatively congested environment of the H_{Re} atom or by the higher basicity of the O_{NO} sites. It is proposed that the nitrosyl ligand−Lewis acid interaction in **6** can support the opening up of a new metal site by bending of the $NOBF_3$ moiety. Thus, molecules **5** would possess an open basic and a hidden acidic site. This property is deemed to be very useful for the activation of polar organic substrates. The reactions of complexes **5** and **6** with acids, as well as organic substrates, are indeed currently under investigation.

The following stoichiometric equation may be formulated for the transformation of complexes of type **3** into **6**:

$$3\,\mathbf{3} + 3\,[NO]BF_4 \rightarrow 3\,\mathbf{6} + 3\,H_2 + 2\,BH_3 + 4\,BF_3 \quad (1)$$

This equation would account for the observed gas evolution and the BF_3 formation from the BF_4^- anion. It remains unexplained why only THF and not other organic solvents such as C_6H_6, Et_2O, CH_2Cl_2, CH_3CN, or acetone can be used to prepare complexes **6** in good yields. From another point of view THF is not a perfect choice, since polymerization of this solvent by the NO^+ cation is known to occur.[29] However, it has been experimentally verified that the reactions of complexes **3** with $[NO][BF_4]$ proceed faster than the reaction between the nitrosonium salt and THF. In this context it may also be important to note that other nitrosylating agents such as Diazald or NO gas have failed to yield the dinitrosyl hydrides. From the latter experiments it may be concluded that in the reactions of **3** with $[NO]BF_4$ a NO molecule is not involved, which might have been formed by reduction of $[NO]^+$.

From these observations it can be assumed that a mechanism for eq 1 would include in a first step displacement of BH_3 by NO^+ with formation of cationic $[Re(H_2)(NO)_2(PR_3)_2][BF_4]$ intermediates (it has been shown previously that BH_3 in the molecule is easily replaced by several donor ligands). As conjugate acids of compounds **5**, these cations are in turn expected to act as proton donors toward BH_3 to produce the short-lived, but known BH_2^+ cation with evolution of H_2.[30a30] The BH_2^+ species could then attack the BF_4^-, affording BF_3 and BFH_2. This latter compound is known to disproportionate in solution at room temperature to give BH_3 and BF_3.[30b] BF_3 finally coordinates to the hydrides **5**. Note that the transitory existence of $[Re(H_2)(NO)_2(PR_3)_2][BF_4]$ species provides an alternative route toward the $[Re(BF_4)(NO)_2(PCy_3)_2]$ derivative, since displacement of H_2 by BF_4^- could occur.

Yellow X-ray-quality crystals of $[Re(H)(NO)(NOBF_3)(P^iPr_3)_2]$ (**6a**) were grown by slow diffusion of pentane into a C_6H_6 solution of the complex. The result of the X-ray diffraction study shown in Figure 8 allows us to establish a comparison between the structural features of the corresponding hydrido nitrosyl derivatives **5a** and **6a** and makes it possible to analyze directly the effect caused by the added Lewis acid. The ligand geometry around the transition metal in **6a** resembles that found for the BF_3-free complex **5a** and is best described as a distorted trigonal bipyramid. The NO and the hydride ligands together with the $NOBF_3$ fragment are located in the trigonal plane of the molecule, and the phosphines occupy apical positions. The typical bending of the phosphorus substituents in the direction of the hydride

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[28] This compound has been characterized by $^{31}P\{^1H\}$ and ^{19}F NMR as a side product in the reaction between **3b** and $NOBF_4$, although it could not be isolated as a pure species. The ^1H NMR signals are partially overlapped with the ones corresponding to the cyclohexyl groups of **6b**, but no hydride resonances were observed. The complex is fluxional, even at −80 °C, due to fast exchange of the fluoride atoms belonging to the BF_4^-. $^{31}P\{^1H\}$ NMR (Tol-d_8, −40 °C): 38.1 (quint, $^2J_{(P-F)} = 7.1$ Hz). ^{19}F NMR (C_6D_6): −171.0 (s, br).

[29] Dreyfuss, P.; Eckestein, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 4115. Seung, S. L. N.; Dreyfuss, P.; Fetters, L. J. *J. Polym. Bull. (Berlin)* **1985**, *13* (4), 337.

[30] (a) Nainan, K. C.; Ryschkewitsch, G. E. *Inorg. Chem.* **1968**, *7*, 1316, and references cited herein. Nainan, K. C.; Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 330. Wille, H.; Goubeau, J. *Chem. Ber.* **1972**, *105*, 2156. (b) *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emelèus, H. J., Sir Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press Ltd.: New York, 1973; Vol. 1, Chapter 11, p 742.

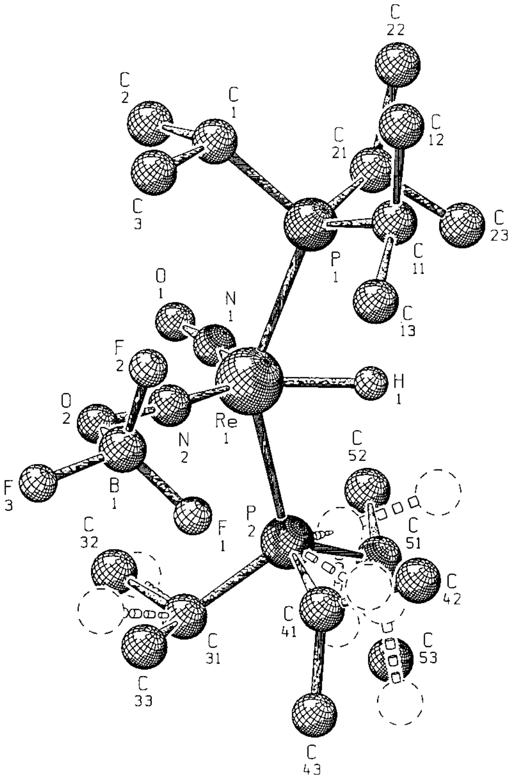

Figure 8. SCHAKAL[41] drawing of **6a**. Hydrogen atoms of the phosphines omitted for clarity.

is more pronounced in **6a** by 7.3° (Table 4). The hydrogen atom bonded to rhenium was found in difference Fourier maps, but could not be refined. The spectroscopically derived BF_3 linkage to one O_{NO} atom was confirmed by this study. Several features concerning the interaction of the Lewis acid with the metal complex deserve mentioning (Tables 4 and 5): (i) A 0.09 Å elongation of the N−O bond in the $NOBF_3$ fragment with respect to the other NO is observed. (ii) The metal nitrogen distances on the other hand are only slightly affected by the BF_3 coordination. (iii) Both nitrosyl ligands remain essentially linear after attachment of BF_3. (iv) The N−O−B linkage is sharply bent with a N−O−B angle of 116.1°. On this basis an approximate sp^2 hybridization can be assumed at this O_{NO} atom.

These latter results contrast with those found by Gladysz et al. for compound $[Re(Cp)(SiMe_2Cl)(NOBCl_3)(PPh_3)]$,[31] which is, to our knowledge, the only other example of a nitrosyl complex−Lewis acid adduct characterized by an X-ray diffraction study (although several other metal nitrosyl complexes are known to form adducts with Lewis acids via the NO linkage).[32] The adduct is formed in the reaction of the silyl rhenium derivative $[Re(Cp)(SiMe_2Cl)(NO)(PPh_3)]$ with BCl_3. Interpretation of the crystallographic data of this compound reveals a marked elongation of the N−O bond accompanied by a significant shortening of the Re−N one (more than 0.2 Å in both cases) relative to those found in other neutral $[Re(Cp)(X)(NO)(PPh_3)]$ complexes. The structural effect caused by BF_3 coordination at the nitrosyl ligand of compound **5a** is not so drastic (see (i) and (ii)). It should be mentioned that it was reported that the quality of the data set for the X-ray study of the cyclopentadienyl rhenium derivative was relatively low, which might also be seen from the published Re−N distance (1.57 Å). This is shorter than the ones found in rhenium nitride compounds with formally a Re−N triple bond.[33]

Experimental Section

Unless specified, all operations were carried out under nitrogen atmosphere using standard Schlenk and glovebox techniques. All solvents were dried over sodium diphenylketyl (THF, Et_2O, $O(SiMe_3)_2$, hydrocarbons) or P_2O_5 (CH_2Cl_2) and distilled under N_2 prior to use. The deuterated solvents used in the NMR experiments were dried over sodium diphenylketyl (C_6D_6, toluene-d_8, THF-d_8), 0.4 Å molecular sieves (acetone-d_6), or P_2O_5 (CD_2Cl_2) and vacuum transferred for storage in Schlenk flasks fitted with Teflon stopcocks. $CDFCl_2$ was prepared by a reported procedure.[34]

For the reactions studied by NMR the solids were weighed (±0.1 mg) in 5 mm NMR tubes inside the glovebox. When required, the charged tubes were tightly fitted into a small apparatus closed with a Teflon stopcock that preserved the inner space from passage of air during subsequent manipulations. This apparatus was removed from the glovebox and attached to a vacuum line and evacuated, and then the solvent was vacuum-transferred into the tube. The tube could be flame-sealed under 900 Torr of N_2, CO, or H_2 or under vacuum. In other cases NMR tubes equipped with a Teflon stopcock were employed. All NMR experiments were carried out on a Varian Gemini 300 spectrometer. Chemical shifts are given in ppm. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual proton or ^{13}C resonances of the deuterated solvent. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4 sealed in a capillary and inserted into a standard 5 mm NMR tube filled with the deuterated solvent. ^1H T_1 measurements were performed at 300 MHz using the inversion recovery method.

IR spectra were recorded in BIO RAD FTS-45 or BIO RAD FTS-15 spectrophotometers.

The following reagents were purchased from commercial suppliers and used without further purification: Re (H. C. Starck Berlin), $NOBF_4$, $[NBu_4]BH_4$ (Aldrich), P^iPr_3, $[NEt_4]Br$, H_2O_2 (30%), H_3PO_2 (50%), HBr (49%), THF·BH_3 (1 M), and KO^{t}Bu (Fluka).

X-ray Structure Analyses. Crystallographic and experimental parameters are summarized in Table 6. All crystals were mounted inside Lindemann capillaries or on top of a glass rod. Measurements were done with Mo Kα radiation (λ = 0.710 73 Å) on a Siemens P3, respectively, an upgraded Nicolet R3 (Siemens P4) (**3a**, **3c**, **5a**, **6a**), and a Nonius Kappa-CCD diffractometer (**2a**) with graphite monochromator. Cell constants for **3a**, **3c**, **5a**, and **6a** were determined with at least 39 reflections with a minimum θ value of 12.5°. For **2a** 9157 reflections in the range $5.1° < \theta < 31.0°$ were used. The data were collected with the ω-scan mode for **3a**, **3c**, **5a**, and **6a**. For **2a** 360 images with a rotating angle of 1° and an exposure time of 40 s per image at a detector to crystal distance of 41.5 mm were recorded. All data were corrected for Lorentz and

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[31] Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1990**, *29*, 2885. Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309.

[32] See for example: Onaka, S. *Inorg. Chem.* **1980**, *19*, 2132. Rausch, M. D.; Mintz, E. A.; Macomber, D. W. *J. Org. Chem.* **1980**, *45*, 689. Crease, A. E.; Legzdins, P. *J. Chem. Soc., Dalton Trans.* **1973**, 1501. Lokshin, B. V.; Rusach, E. B.; Kolobova, N. E.; Makarov, Y. V.; Ustynyuk, N. A.; Zdanovich, V. I.; Zhakaeva, A. Z.; Setkina, V. N. *J. Organomet. Chem.* **1976**, *108*, 353. Legzdins, P.; Rettig, S. J.; Sànchez, L. *Organometallics* **1988**, *7*, 2394. Ginzburg, A. G.; Setkina, V. N.; Kursanov, D. N. *Izv. Akad. Nauk SSSr Ser. Khim.* **1985**, 447. CA103-(13):105099n.

[33] Normal Re−N bond distances in neutral nitrido complexes reported in the *Cambridge Chemical Data Base* are found in the range between 1.60 and 1.67 Å.

[34] Siegel, J. S.; Anert, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

Table 6. Crystal Data and Structure Refinement Parameters for 2a, 3a, 3c, 5a, and 6a

	2a	**3a**	**3c**	**5a**	**6a**
formula	$C_{18}H_{44}Br_2NOP_2Re$	$C_{18}H_{47}BNOP_2Re$	$C_{36}H_{35}BNOP_2Re$	$C_{18}H_{43}N_2O_2P_2Re$	$C_{18}H_{43}BF_3N_2O_2P_2Re$
M_r	698.51	552.54	756.64	567.70	635.50
cryst habit	yellow single crystal	orange prism	yellow roof shaped	dark red fragment	yellow fragment
cryst size	0.12 × 0.16 × 0.18	0.14 × 0.25 × 0.42	0.13 × 0.27 × 0.36	0.30 × 0.30 × 0.30	
cryst system	monoclinic	triclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)	$P2_12_12_1$ (No. 19)	$P2_{1/n}$ (No. 14)
a (Å)	8.8016(4)	7.846(2)	17.629(4)	12.085(3)	8.028(1)
b (Å)	15.5248(8)	8.548(2)	16.887(7)	13.817(3)	15.323(3)
c (Å)	9.6736(6)	19.576(2)	22.056(5)	14.485(4)	20.752(7)
α (deg)		94.42(2)			
β (deg)	104.757(3)	98.59(2)			91.15(2)
γ (deg)		109.86(2)			
V (Å^3)	1278.23(12)	1209.4(5)	6566(3)	2418.7(10)	2552.3(10)
ρ_{calc} (g cm^{-3})	1.81	1.52	1.53	1.56	1.65
Z	2	2	8	4	4
F(000)	684	560	3008	1144	1272
temp (°C)	−120(2)	−110(5)	−80(5)	−80(5)	−120(7)
μ (cm^{-1})	80.5	52.3	38.7	52.4	49.9
abs corr	numerical[a]	ψ-scans[b]	numerical[a]	ψ-scans[b]	ψ-scans[b]
T_{min}/T_{max}	0.3304/0.5531	0.141/0.211	0.0458/0.852	0.025/0.046	0.054/0.102
θ range (deg)	$5.13 < \theta < 31.03$	$2 < \theta < 26$	$2 < \theta < 25$	$2 < \theta < 25$	$2 < \theta < 27$
hkl range	$\pm h \pm k \pm l$	$+h \pm k \pm l$	$+h +k +l$	$+h +k +l, -h -k -l$	$+h +k \pm l$
width (deg)	c	0.8	1.2	1.6	1.6
speed (deg min^{-1})	c	2−29	1−29	1−29	3−29
data meas	11 657	5094	6429	4877	6210
unique data	7179	4704	5683	4016	5435
data used	7179	4703[d]	4111	3901	5435
$I/\sigma(I) >$			1.0	0.0	
parameters	402	227	374	227	259
flack param	−0.009(6)			0.02(2)	
max. shift/esd	0.009	0.0005	0.0007	0.017	0.017
resd dens (e Å^{-3})	+2.32, −2.86	+1.59, −2.24	+1.38, −1.26	+3.42, −1.02	+1.52, −1.49
R1 (obs)[e]	0.029	0.036	0.067	0.043	0.077
wR2 (obs)[e]	0.050	0.060	0.086	0.069	0.084
GooF	1.119	1.112	1.086	1.148	1.136

[a] See ref 37. [b] See ref 35. [c] See experimental part for area detector measurement. [d] Reflection 002 was rejected because it was shaded by beam stop. [e] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

polarization terms.[35,36,37] Three reflections monitoring the intensities were collected every 97 or 147 reflections. The maximum decay observed and corrected was 3% for compound **3a**.[35] All structures were solved with the Patterson method[38,39] and standard difference Fourier techniques. Refinements were carried out against F^2.[39] The Chebyshev polynomial weighting scheme was used in all cases.[40,41] Extinction effects were not observed. The hydrides at rhenium in **5a** and **6a** could be found in difference Fourier maps. For **6a** the coordinates of the hydride could be refined; U_{iso} was kept at 0.03. The hydride in **5a** was not refined ($U_{iso} = 0.05$). The shape of one single peak appearing approximately in the middle between H1 and H2 in **2a** was used to determine the orientation of the H2 ligand. This orientation is in accord with that obtained from the theoretical calculations. Thus, the calculated geometry was used to set the restraints for the refinement of the coordinates of H1 and H2. For both hydrogen atoms, one single isotropic displacement parameter was used. All remaining hydrogen atoms in **3a**, **3b**, **5a**, and **6a** were calculated in their ideal positions ($d_{C-H}/d_{B-H}/d_{Re-H}$: 0.96/1.10/1.75 Å, $U_H = 1.3U_{C/Re}$, $U_{H-B} = 0.05$). The positions of the hydrogen atoms H3 to H44 in **2a** were calculated initially and were refined with isotropic displacement parameters. Several disorder problems occurred in the structures of **3a**, **3c**, and **6a**. Within one phosphine ligand of **6a** all three isopropyl groups are disordered. Affected carbon atoms were refined isotropically. Two groups of atoms with the same occupation factor could be distinguished. The sum of the occupation factors was constrained to 1. In the structures **3a** and **3c** the BH_4^- ligand and the NO ligand are disordered. O1, N1, and B1 in **3a** could be refined anisotropically; all other disordered oxygen, nitrogen, and boron atoms were treated isotropically. The sum of the occupation factors for both groups was constrained to 1. Additionally one isopropyl group in **3a** is disordered. Affected bond lengths and angles should be treated with care.

Crystallographic data (excluding structure factors) for the structures reported in this paper are included as Supporting Information.

Computational Methods. All calculations are based on the local density approximation (LDA) in the parametrization of Vosko, Wilk, and Nussair,[42] with the addition of gradient corrections due to Becke[43] and Perdew [44] (GGA). The calculations were carried out on a DEC AlphaStation 500, using the program system TURBOMOLE,[45] within the framework of the

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(35) Siemens SHELXTL PLUS Package; 1994.

(36) Zbyszek Otwinowski, DENZO-SMN, Version 1.8.0; 1993−1998.

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RI-J approximation.[46] For Re, effective core potentials (ECP-60) were applied, which include relativistic corrections.[47] A triple-ζ valence basis plus polarization (TZVP) was employed for the heavy metal;[48a] the remaining elements were treated with a split valence plus polarization basis set (SVP).[48b] For the numerical integration, the grid of accuracy "m3" was used.[46c] All calculations were performed in C_s symmetry.

Preparation of the Complexes. $[Re(H)_2(NO)(PPh_3)_3]$. A mixture of **1** (1 g, 1.14 mmol) and PPh_3 (1.5 g, 5.72 mmol) suspended in ethanol (30 mL) was refluxed for 25 min. $NaBH_4$ (250 mg, 6.608 mmol) was then added in small portions over a period of 45 min while still refluxing. Gradually, a pale yellow solid formed in a reaction accompanied by gas evolution. When addition of $NaBH_4$ was complete the liquid was filtered off and the solid washed with hot ethanol (70 °C, 3 × 15 mL). The product was dissolved in C_6H_6 (20 mL), filtered, and precipitated with ethanol. A pale yellow solid was collected, recrystallized in C_6H_6/ethanol, and subsequently dried under vacuum, leaving 0.81 g (ca. 70.6%) of $[Re(H)_2(NO)(PPh_3)_3]$. ^1H NMR (C_6D_6): -1.93 (dtd, 1H, $^2J_{(H-Pcis)} = {}^2J_{(H-Ptrans)} = 30.3$ Hz), -0.55 (dtd, $1H_{trans\ NO}$, $^2J_{(H-H)} = 6.0$ Hz, $^2J_{(H-Peq.)} = 34.2$ Hz, $^2J_{(H-Pap.)} = 32.4$ Hz), 6.81–7.57 (m, 45H, $P(C_6H_5)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): 28.3 (d, 2P), 20.2 (t, 1P, $^2J_{(P-P)} = 8$ Hz). IR (Nujol): 1640 (ν_{N-O}), 1950, 1800 (ν_{Re-H}). Anal. (%). Calc for $C_{54}H_{47}NOP_3Re$: C, 64.53; H, 4.71; N, 1.39. Found: C, 64.75; H, 4.39; N, 1.30.

$[NEt_4]_2[Re(Br)_5(NO)]$ (1). This preparation can be carried out under air and does not require dry solvents.

H_2O_2 (10 mL, 30%) was added dropwise to Re powder (3.0 g, 16.11 mmol) at 0 °C. $[NEt_4]Br$ (4.0 g, 19.03 mmol) was added to this solution without a further treatment. After drying the mixture by rotary evaporation (25 mbar, 80 °C) additional $[NEt_4]Br$ (4.0 g, 19.0 mmol) was added, and the solid dissolved in a 70:5 mL mixture of HBr (49%) and H_3PO_2 (50%). NO gas was bubbled through the solution at 110 °C, which turned dark green in 24 h. The reaction mixture was filtered and dried by rotary evaporation (25 mbar, 80 °C) to give a viscous dark green semisolid. This residue was well washed with THF (3 × 30 mL), suspended in ethanol, filtered off, and additionally washed with ethanol (2 × 25 mL) and acetone (2 × 25 mL). The resulting apple green powder was dried under vacuum to yield 12.76 g (ca. 90.4%) of $[NEt_4]_2[Re(Br)_5(NO)]$. IR (KBr): 1732 (ν_{N-O}). Anal. (%). Calc for $C_{16}H_{40}Br_5N_3ORe$: C, 21.93; H, 4.60; N, 4.80. Found: C, 22.04; H, 4.60; N, 4.78.

$[Re(NO)(\eta^2\text{-}H_2)(Br)_2(P^iPr_3)_2]$ (2a). A mixture of **1** (1.25 g, 1.43 mmol) and P^iPr_3 (0.79 g, 4.93 mmol) suspended in ethanol (10 mL) was stirred for 48 h at 70 °C. The reaction mixture was then left at −30 °C for 2 h and filtered cold. The residue was then washed with ethanol (2 × 5 mL) and dried under vacuum for 0.5 h to yield 0.75 g (ca. 75%) of a light brown powder. The mother liquor and washings collected after the treatment of 5 g of $[NEt_4]_2[Re(Br)_5(NO)]$ were reduced in volume to ca. 10 mL, leaving additional 0.53 g of solid. This amount was recrystallized from ethanol at 70 °C (15 mL) and afforded 0.25 g of microcrystalline $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(P^iPr_3)_2]$, increasing the overall yield to 80%. Anal. (%). Calc for $C_{18}H_{44}Br_2NOP_2Re$: C, 30.95; H, 6.35; N, 2.01. Found: C, 31.10; H, 6.28; N, 2.03.

Mixture Containing $[Re(Br)_2(NO)(\eta^2\text{-}H_2)(PCy_3)_2]$ (2b) and $[Re(Br)_3(NO)(PCy_3)_2]$. A mixture of **1** (1.0 g, 1.14 mmol) and PCy_3 (1.04 g, 3.71 mmol) suspended in ethanol (25 mL) was stirred for 48 h at 70 °C. A brown precipitate gradually formed, which was filtered off hot, washed with hot ethanol (3 × 10 mL, 70 °C), and dried under vacuum, leaving 0.99 g of a brown solid (ca. 88%).

$[Re(H)(\eta^2\text{-}BH_4)(NO)(P^iPr_3)_2]$ (3a). A mixture of **2a** (1.06 g, 1.52 mmol) and $[NBu_4]BH_4$ (1.03 g, 4.00 mmol) in Et_2O (25 mL) was stirred for 21 h. After this time the orange solution was filtered and dried under vacuum to yield 0.82 g (98%) of **3a** contaminated with ca. 6–10 mol % of $P^iPr_3{\cdot}BH_3$. Slow cooling to −65 °C of a solution of 1.06 g of **3a** in ether/pentane (20/10 mL) afforded large crystals, which were separated by removing the mother liquor via cannula and dried under vacuum, yielding 0.81 g (76%). Alternatively, **3a** can be isolated in similar yield; washing with CH_3CN (3 × 5 mL) the solid was obtained after evaporation of the diethyl ether. Anal. (%). Calc for $C_{18}H_{47}BNOP_2Re$: C, 39.13; H, 8.57; N, 2.53. Found: C, 39.39; H, 8.48; N, 2.54.

$[Re(H)(\eta^2\text{-}BH_4)(NO)(PCy_3)_2]$ (3b). The mixture containing **2b** and $[Re(Br)_3(NO)(PCy_3)_2]$ isolated as described above (0.96 g, ca. 1 mmol) was stirred in 25 mL of ether with $[NBu_4]BH_4$ (0.810 g, 3.15 mmol) for 48 h. The resulting orange solid was filtered off, well washed with acetonitrile (4 × 10 mL), and dried under vacuum. Yield: 0.72 g (81.3%, calculated on $[NEt_4]_2[Re(Br)_5(NO)]$ used for the preparation of **2b** and $[Re(Br)_3(NO)(PCy_3)_2]$). Anal. (%). Calc for $C_{36}H_{71}BNOP_2Re$: C, 54.53; H, 9.03; N, 1.77. Found: C, 54.58; H, 8.92; N, 1.76.

$[Re(H)(\eta^2\text{-}BH_4)(NO)(PPh_3)_2]$ (3c). A mixture of $[Re(H)_2(NO)(PPh_3)_3]$ (1 g, 0.995 mmol) and 1 M $THF{\cdot}BH_3$ (3.5 mL, 3.5 mmol) was stirred for 12 h. Over this period of time, the starting yellow compound disappeared and an orange precipitate gradually formed. The residue was washed with CH_3CN (4 × 10 mL) and dried under vacuum, leaving 650 mg (ca. 86.4%) of **3c** as a bright-yellow orange solid, which can be used without further purification for subsequent chemistry. Recrystallization in THF/pentane afforded analytically pure material. Anal. (%). Calc for $C_{36}H_{35}BNOP_2Re$: C, 57.15; H, 4.66; N, 1.85. Found: C, 56.79; H, 4.82; N, 1.85.

$[Re(H)(NO)_2(P^iPr_3)_2]$ (5a). A mixture of **3a** (300 mg, 0.542 mmol) and $NOBF_4$ (100 mg, 0856 mmol) was stirred in THF (40 mL) for 1 h. The resulting solution was concentrated under vacuum until 15 mL of the solvent was left. Then 15 mL of diethyl ether and KO^tBu (95 mg, 0.847 mmol) were added, and the heterogeneous mixture was stirred for an additional hour. The solvent was removed under vacuum and the residue extracted with pentane (2 × 15 mL). The red-orange solution was concentrated until approximately 4 mL of the solvent was left and then placed for 10 h at −35 °C. Red crystals were collected and dried under vacuum, affording 216 mg of **5a** (ca. 70.1%). Anal. (%). Calc for $C_{18}H_{43}N_2O_2P_2Re$: C, 38.08; H, 7.63; N, 4.93. Found: C, 37.76; H, 7.48; N, 4.84.

$[Re(H)(NO)_2(PCy_3)_2]$ (5b). A mixture of **3b** (300 mg, 0.372 mmol) and $NOBF_4$ (68 mg, 0.582 mmol) was stirred in THF (50 mL) for 1 h. KO^tBu was then added (65.4 mg, 0.582 mmol) and the heterogeneous mixture stirred for an additional hour. The solvent was removed under vacuum and the residue extracted with pentane (3 × 25 mL). Removal of the solvent left a light orange solid, which was washed with $O(SiMe_3)_2$ (2 × 5 mL) and dried under vacuum, affording 220 mg of $[Re(H)(NO)_2(PCy_3)_2]$ (**5b**) (ca. 72.0%). Anal. (%). Calc for $C_{36}H_{67}N_2O_2P_2Re$: C, 53.51; H, 8.36; N, 3.47. Found: C, 53.68; H, 8.12; N, 3.26.

$[Re(H)(NO)_2(PPh_3)_2]$ (5c). A mixture of **3c** (135 mg, 0.179 mmol) and $NOBF_4$ (41 mg, 0.351 mmol) was stirred in THF (40 mL) for 1 h. K^tOBu was then added (39.8 mg, 0.355 mmol) and the mixture stirred for an additional hour. The resulting red-brown solution was filtered and the solvent removed under vacuum, leaving a dark red solid, which was washed with THF (2 × 2 mL). A pink-red powder was collected and dried under vacuum, leaving 60 mg of **5c**. Pentane was layered over the THF solution and the mixture cooled at −35 °C. After 24 h a red microcrystalline solid formed, which was washed with diethyl ether (3 × 10 mL), affording an additional 40 mg of **5c**

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(total yield ca. 72.4%). Anal. (%). Calc for $C_{36}H_{31}N_2O_2P_2Re$: C, 56.02; H, 4.05; N, 3.63. Found: C, 55.68; H, 4.13; N, 3.61.

$[Re(H)(NO)(NOBF_3)(P^iPr_3)_2]$ (6a). A mixture of **3a** (250 mg, 0.452 mmol) and $NOBF_4$ (79 mg, 0.676 mmol) was stirred for 1 h in THF (35 mL). The solvent was removed under vacuum and the residue extracted with diethyl ether (3 × 15 mL). Upon concentration a yellow solid started to precipitate. When approximately 1 mL of solvent was left, the Et_2O was discharged, and the solid was washed with an additional 1.5 mL of Et_2O and 8 mL of pentane and dried under vacuum to give 215 mg (ca. 75%) of **6a**. Anal. (%). Calc for $C_{18}H_{43}BF_3N_2O_2P_2Re$: C, 34.02; H, 6.82; N, 4.41. Found: C, 34.25; H, 6.45; N, 4.31.

$[Re(H)(NO)(NOBF_3)(PCy_3)_2]$ (6b). A mixture of **3b** (200 mg, 0.0252 mmol) and $NOBF_4$ (48 mg, 0.410 mmol) was stirred for 1 h in THF (40 mL). The solvent was removed under vacuum and the oily residue well washed with $O(SiMe_3)_2$ (3 × 10 mL). The yellow solid was dissolved in benzene (5 mL) and filtered, and the solution was concentrated until only 1 mL of C_6H_6 was left. Addition of $O(SiMe_3)_2$ (10 mL) produced the precipitation of a light yellow powder. Evaporation of the solvent was continued until all the benzene was removed and then the $O(SiMe_3)_2$ discharged. The powder was then washed with pentane (2 × 10 mL) and dried under vacuum to give 145 mg of $[Re(H)(NO)(NOBF_3)(PCy_3)_2]$ (**6b**) contaminated with 6−10% of $[Re(BF_4)(NO)(NOBF_3)(PCy_3)_2]$.[23] Pure **6b** can be obtained by crystallization in toluene/pentane at −35 °C (120 mg, ca. 54.3%). Anal. (%). Calc for $C_{36}H_{67}BF_3N_2O_2P_2Re$: C, 49.37; H, 7.71; N, 3.20. Found: C, 49.48; H, 7.61; N, 3.31.

NMR Tube Reactions. $[Re(Br)_2(NO)(^{13}CO)(P^iPr_3)_2]$. A solution of **2a** (16 mg, 0.0229 mmol) in C_6D_6 (0.65 mL) was sealed under ^{13}CO (600 Torr). Slow displacement of H_2 and incorporation of ^{13}CO were observed by NMR monitoring (19% of conversion in 0.5 h and 73% in 2 h). ^1H NMR (C_6D_6): 1.14 (dvt, $^3J_{(H-H)} = 7.1$ Hz, 18H, $P(CH\{CH_3\}_2)_3$), 1.34 (dvt, $^3J_{(H-H)} = 7.1$ Hz, 18H, $P(CH\{CH_3\}_2)_3$), 2.87 (m, 6H, $P(CH\{CH_3\}_2)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): 6.57 (d, $^2J_{(P-C)} = 6.7$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): 19.40 (s, $P(CH\{CH_3\}_2)_3$), 20.28 (s, $P(CH\{CH_3\}_2)_3$), 24.78 (t, $P(CH\{CH_3\}_2)_3$, apt $J_{(C-P)} = 19.2$ Hz), 202.01 (t, $^2J_{(C-P)} = 6.7$ Hz, *C*O).

$[Re(H)_2(^{13}CO)(NO)L_2]$ ($L = P^iPr_3, PCy_3$). A solution of $[Re(H)(\eta^2\text{-}BH_4)(NO)(PR_3)_2]$ (**3a,b**) (20 mg, 0.0362 mmol of **3a**, 0.0252 mmol of **3b**) in THF-d_8 (**3a**) or C_6D_6 (**3b**) (0.65 mL) was sealed under ^{13}CO (900 Torr). Clean formation of known dihydrides, $[Re(H)_2(^{13}CO)(NO)L_2]$,[7a] takes place immediately upon shaking of the tubes. All NMR data are in agreement with those previously reported in the literature. The following carbon−hydride coupling constants have been included since they were not given in the former publication. ^1H NMR ($L = P^iPr_3$, THF-d_8): −5.66 (tdd, 1H, Re*H*, $^2J_{(H-C)} = 12.2$ Hz), −1.63 (tdd, 1H, Re*H*, $^2J_{(H-C)} = 6.4$ Hz). ^1H NMR ($L = PCy_3$, C_6D_6): −4.87 (tdd, 1H, Re*H*, $^2J_{(H-C)} = 12.0$ Hz), −0.99 (tdd, 1H, Re*H*, $^2J_{(H-C)} = 6.4$ Hz).

$[Re(H)_2(CO)(NO)(PPh_3)_2]$. A solution of **3c** (20 mg, 0.0264 mmol) in THF-d_8 (0.5 mL) was sealed under CO (900 Torr). After 30 min the $^{31}P\{^1H\}$ and ^1H NMR spectra of the solution are identical to those reported for the known carbonyl derivative $[Re(H)_2(CO)(NO)(PPh_3)_2]$.[20]

$[Re(H)_4(NO)(P^iPr_3)_2]$ (4a). Method A. Acetone-d_6 (0.65 mL) was vacuum transferred into an NMR tube containing **2a** (19.7 mg, 0.028 mmol) and $[NEt_4]BH_4$ (9.6 mg, 0.066 mmol), and the tube was sealed under H_2 (900 Torr). Clean formation of **4a** was completed in 1.5 h.

Method B. Methylcyclohexane-d_{14} (0.65 mL) was vacuum transferred into an NMR tube containing **3a** (15.2 mg, 0.022 mmol) and PPh_3 (7.1 mg, 0.027 mmol). The tube was sealed under H_2 (900 Torr). Formation of a mixture of $[Re(H)_4(NO)(P^iPr_3)_2]$ (75%), $[Re(H)_2(NO)(PPh_3)(P^iPr_3)_2]$ (17%), and $[ReH(BH_4)(NO)(P^iPr_3)_2]$ (8%) was observed upon vigorous shaking of the tube.

$[Re(H)_4(NO)(PCy_3)_2]$ (4b). THF-d_8 (0.65 mL) was vacuum transferred into an NMR tube containing complex **1** (20 mg, 0.023 mmol), $[NBu_4]BH_4$ (21 mg, 0.082 mmol), and PCy_3 (39 mg, 0.139 mmol). The tube was sealed under H_2 (900 Torr). Clean formation of **4b** was completed in 6 h at 60 °C.

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Supporting Information Available: Tables of crystal data and structure refinement parameters, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen coordinates of **2a**, **3a**, **3c**, **5a**, and **6a** (32 pages). Ordering information is given on any current masthead page.

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