Ligand-Assisted Heterolytic Activation of Hydrogen and Silanes Mediated by Nitrosyl Rhenium Complexes

Angela Llamazares, Helmut W. Schmalle, and Heinz Berke*

Anorganisch-chemisches Institut Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received May 17, 2001

Abstraction of the hydride in the dinitrosyl rhenium complexes $[Re(H)(NO)_2(PR_3)_2]$ (R = ^{i}Pr (**1a**), Cy (**1b**)) affords the dinuclear saturated compounds $[Re_2(H)(\mu,\eta^2\text{-}NO)(NO)_3(PR_3)_4][BAr_4']$ (R = ^{i}Pr, **2a**; Cy, **2b**) or the mononuclear unsaturated 16-electron derivatives $[Re(NO)_2(PR_3)_2][BAr_4']$ (R = ^{i}Pr, **3a**; Cy, **3b**). In complexes **2a**,**b** the metal centers are connected via a nitrosyl−isonitrosyl linkage. Complexes **2** and **3** react with classical two-electron donor ligands such as CH_3CN, CO, C_6H_5CHO, and THF, but also with H_2 and $HSiEt_3$. In the two latter cases heterolytic rupture of the hydrogen−hydrogen or hydrogen−silicon bonds is achieved. Complexes **2a**,**b** and **3a**,**b** are active in the catalytic scrambling of H_2/D_2 to give HD under very mild conditions. In the presence of tetramethylpiperidine as a base the reaction of these complexes with H_2 produces $[Re(H)(NO)\{NOH_2NC_5H_6(CH_3)_4\}(PR_3)_2][BAr_4']$ (R = ^{i}Pr, **9a**; Cy, **9b**). Heterolysis of $HSiEt_3$ mediated by **2a**,**b** and **3a**,**b** results in the formation of $[Re(H)(NO)(NOSiEt_3)(PR_3)_2][BAr_4']$ (R = ^{i}Pr, **8a**; Cy, **8b**). Complexes **8a** and **9b** have been characterized by X-ray diffraction studies.

Introduction

Activation of HX molecules (X = H, SiR_3) by transition metal complexes is one of the key steps in very important catalytic and stoichoimetric reactions. Cleavage of the HX bond requires the intermediacy of some hydride or dihydrogen species, either as precursors or intermediates in the reaction, and may be achieved via homolytic or heterolytic pathways.[1] Homolytic cleavage occurs normally in low-valent, electron-rich metal complexes, in which the predominant interaction after coordination of the HX substrate is the π-back-donation from metal d orbitals to the σ* orbital of the substrate. Heterolytic cleavage, on the other hand, usually requires complexes containing metals in medium or high oxidation states in which the predominant interaction is σ donation from the HX molecule to a d orbital of the metal. Heterolysis of the HX bond should be assisted by a Brönsted base, which can be externally added or "built in" in the complex. In this latter case, one of the ligands must possess a basic site easily accessible to the X^+ fragment.

The transition metal mediated heterolytic activation of small molecules such as H_2 and silanes is a topic of continuously growing interest.[1,2] A great number of studies have been carried out on octahedral compounds, and among them, special attention has been paid to those containing good π-acceptor ligands such as CO coordinated trans to HX, which is expected to greatly enhance the acidity of these units.[2a,c,e,f,j,3] On the other hand, much less is yet known about the ligand influence of other good π-acidic groups such as the strong π-acceptor NO.[4] Although most of the features of the NO bound to a metal center can be qualitatively described similarly to CO bonding,[5] the presence of nitrosyl groups in the coordination sphere should confer special properties. The NO ligand is normally regarded as a stronger π-aceptor than CO, and in addition it possesses an oxygen atom that shows a certain Lewis basic behavior forming adducts with Lewis acids.[5,6] This "intramolecular base" could therefore be exploited in heterolytic activation pathways of HX substrates. In addition, NO

* To whom correspondence should be addressed. E-mail: hberke@aci.unizh.ch. Fax: int +41-1-6356802.

(1) For reviews see: (a) Jia, G.; Lau, C.-P. *Coord. Chem. Rev.* **1999**, *190−192*, 108. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (c) Esteruelas, M. A.; Oro, L. *Chem. Rev.* **1998**, *98*, 577. (d) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1068. (e) Heinekey, D. M.; Oldham, J. W., Jr. *Chem. Rev.* **1993**, *93*, 913. (f) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 789. (g) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *92*, 289.

(2) For recent examples of heterolytic activation of H_2 and silanes see: (a) Fang, X.; Scott, B. L.; John, K. D.; Kubas, G. J. *Organometallics* **2000**, *19*, 4141. (b) Toner, A. J.; Gründemann, S.; Clot, E.; Limbach, H. H.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **2000**, *122*, 6777. (c) Fang, X.; Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *J. Organomet. Chem.* **2000**, *609*, 95. (d) Ayllon, J. A.; Sayers, S. F.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B.; Clot, E. *Organometallics* **1999**, *18*, 3981. (e) King, A. W.; Scott, B. L.; Eckert, J.; Kubas, G. J. *Inorg. Chem.* **1999**, *38*, 1069. (f) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chim. Acta* **1999**, *294*, 240. (g) Fong, T. P.; Forde, C. E.; Lough, A. J.; Morris, R. H.; Rigo, P.; Rocchini, E.; Stephan, T. *J. Chem. Soc., Dalton Trans.* **1999**, 4475. (h) Sweeney, Z. K.; Polse, J. L.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1999**, *18*, 5502. (i) Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. *Inorg. Chem.* **1998**, *37*, 3982. (j) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1998**, *120*, 6808.

(3) (a) Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. *J. Am. Chem. Soc.* **1997**, *119*, 4172. (b) Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711.

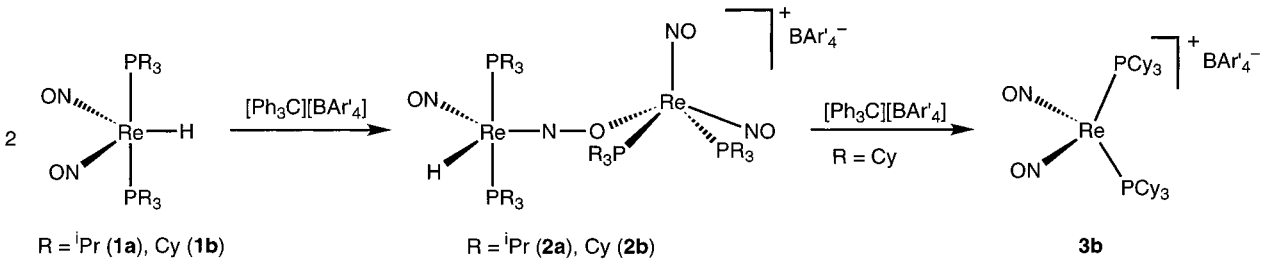
(4) Yaundolov, D. V.; Steib, W. E.; Caulton, K. G. *Inorg. Chim. Acta* **1998**, *280*, 125.

(5) Richter-Addo, G. B.; Legzdins, P. *Metal Nytrosyls*; Oxford University Press: New York, 1992.

(6) (a) Böhmer, J.; Haselhorst, G.; Wieghart, K.; Nuber, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *14*, 1473. (b) Gusev, D.; Llamazares, A.; Artus, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 75. (c) Jacobsen, H.; Heinze, K.; Llamazares, A.; Schmalle, H. W.; Artus, G.; Berke, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1717. (d) Llamazares, A.; Artus, G.; Berke, H. Manuscript in preparation. (e) Legzdins, P.; Sayers, S. F. *Chem. Eur. J.* **1997**, *3*, 1579.

10.1021/om010409c CCC: $20.00
Publication on Web 11/10/2001

Scheme 1



is known to be a noninnocent ligand able to act as a three- (linear) or one-electron donor (bent).[5] Bending a NO group at a coordinatively saturated metal center creates a vacancy for HX coordination without the requirement of previous ligand dissociation. Bending also causes a formal oxidation of the metal center, a fact that will have great consequences for the subsequent activation process. The possibility of a reversible linear to bent conversion might be of special relevance since it allows a modification of the electronic properties of the metal without the need of externally added reagents.

The rhenium(−I) hydride complexes $[Re(H)(NO)_2(PR_3)_2]$ (R = ^{i}Pr, **1a**; Cy, **1b**), which have been recently prepared in our group,[6b] are expected to display an enhanced hydridic reactivity mainly attributed to the influence of the NO groups. The "nitrosyl effect" in transition metal hydride complexes produces a strong polarization of the M−H bond which results in a higher partial negative charge at the hydride group.[7] This is also reflected in an increased propensity toward insertions of polar unsaturated organic substrates into the metal−hydrogen bond.[8] Taking advantage of this property, we were interested in the possibility of abstracting the hydride from **1a** or **1b** to generate 16-electron cationic species. These in turn were expected to coordinate H_2 or silanes. Indeed we have found that this is possible. Our current work has also revealed an unexpected nitrosyl reactivity caused by the greatly enhanced basicity of the oxygen atom of the NO group. Thus, the possibility of coordination of 1 or 2 equiv of the Lewis acid BF_3 to one NO ligand of **1a** or **1b** was discovered taking place in a reversible way.[6b,d] In these molecules therefore, two preferred reactive sites are available: the hydride and the nitrosyl groups. Consequences of this particular feature on the reactivity of such complexes will be discussed in this paper.

Results and Discussion

Reactivity of 1a,b toward $[Ph_3C][BAr'_4]$ and $H(OEt_2)_2[BAr_4']$. As already anticipated by theoretical calculations and measurements of bond ionicities,[6b,c] the hydridic character of the rhenium-bonded hydrogen in complexes **1a**,**b** facilitates hydride abstraction upon treatment with $[Ph_3C][BAr'_4]$ (Ar′ = [3,5-$(CF_3)_2C_6H_3$]).[9] The products that are obtained depend on the nature of the phosphine substituent as well as on the $[Ph_3C][BAr'_4]$/complex ratio employed in the reaction. The geometrical and structural details concerning the X-ray diffraction study of some of these compounds have already been published earlier.[6c] The present paper mainly refers to the reacitivity of the former and other species and in this context also to structural parameters crucial to it.

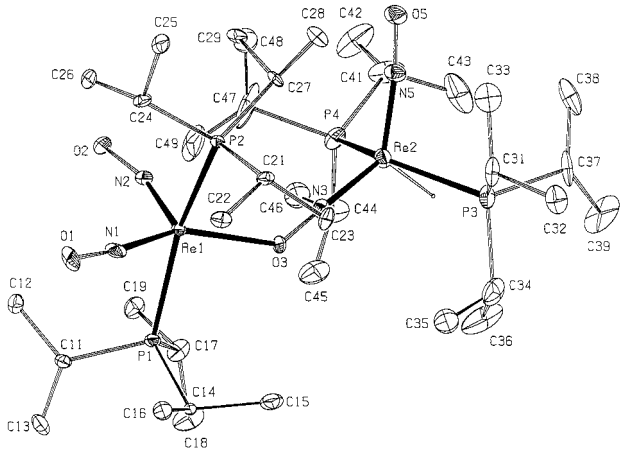


Figure 1. Molecular structure of complex **2a**.[6c] Displacement ellipsoids are shown at the 20% level. Hydrogen atoms are omitted for clarity, except for the hydride ligand, which is displayed as a sphere with arbitrary size. Not shown is the counterion. Selected bond distances (Å) and angles (deg): Re(1)−N(1) = 1.78(1); Re(1)−N(2) = 1.80(2); Re(1)−O(3) = 2.199(9); P(1)−Re(1)−P(2) = 162.8(1); Re(1)−N(1)−O(1) = 172(1); Re(1)−N(2)−O(2) = 158(1).

Reaction of **1a**,**b** with half an equivalent of $[Ph_3C][BAr_4']$ produces the binuclear derivatives $[Re_2(H)(\mu,\eta^2\text{-}NO)(NO)_3(PR_3)_4][BAr_4']$ (R = ^{i}Pr, **2a**; Cy, **2b**) (Scheme 1). An X-ray diffraction study carried out on the triisopropylphosphine derivative **2a**[6c] reveals an isonitrosyl linkage connecting the two rhenium centers, and the compound may be described as composed of the neutral $Re(H)(NO)_2(P^iPr_3)_2$ molecule and a cationic $Re(NO)_2(P^iPr_3)_2^+$ fragment (Figure 1). The coordination geometry around the rhenium atoms are trigonal pyramidal and tetragonal pyramidal, respectively. The latter unit shows a nitrosyl ligand occupying the apical position with a comparatively strong bend (Re−N(5)−O(5) = 158(1)°).

Reaction of **1b** with 1 equiv of $[Ph_3C][BAr_4']$ affords the unsaturated rhenium complex $[Re(NO)_2(PCy_3)_2]$-

(7) Ledzgins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250. (b) Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554. (c) Bursten, B. E.; Gatter, M. G.; Goldberg, K. I. *Polyhedron* **1990**, *16*, 279. (d) Jacobsen, H.; Berke, H. *Hydridicity of Transition Metals and its Implications for Reactivity.* In *Recent Advances in Hydride Chemistry*; Poli, R., Peruzzi, M., Eds.; Elsevier: New York, 2001; in press.

(8) (a) Höck, J.; Jacobsen, H.; Schmalle, H. W, Artus, G. R.; Fox, T.; Amor, J. I.; Bäth, F.; Berke, H. *Organometallics* **2001**, *20*, 1533. (b) Liang, F.; Jacobsen, H.; Schmalle, H. W.; Fox, T.; Berke, H. *Organometallics* **2001**, *19*, 1950. (c) Nietlischpach, D.; Bosch, H. W.; Berke, H. *Chem. Ber.* **1994**, *127*, 2403. (d) Van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 2051. (e) Van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Inorg. Chim. Acta* **1992**, *11*, 563. (f) Van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 563.

(9) Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545.

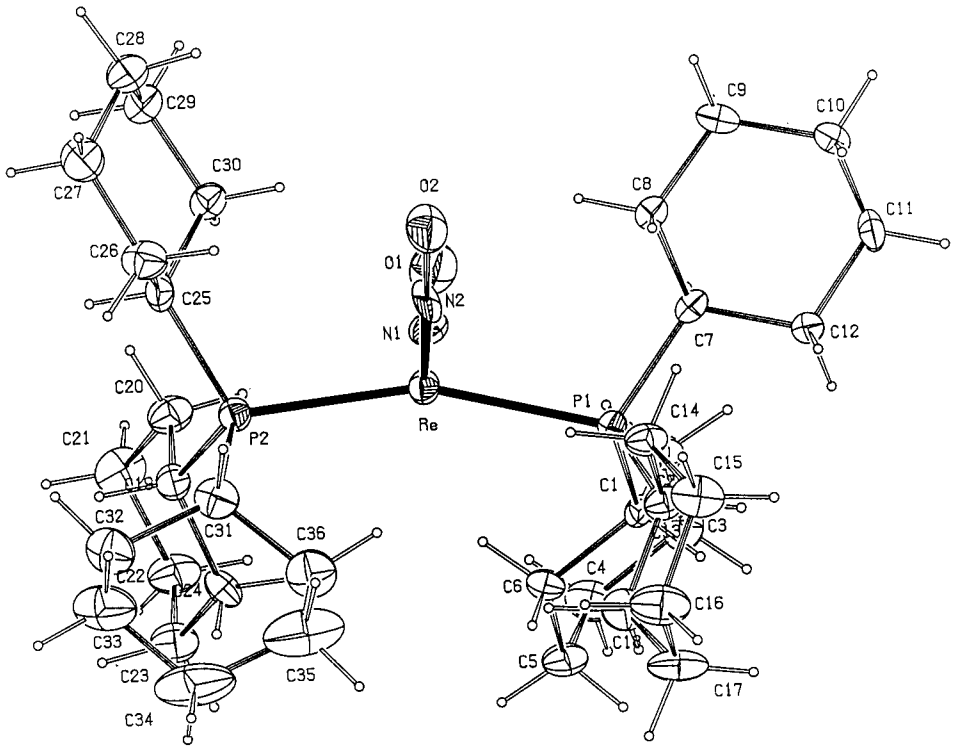


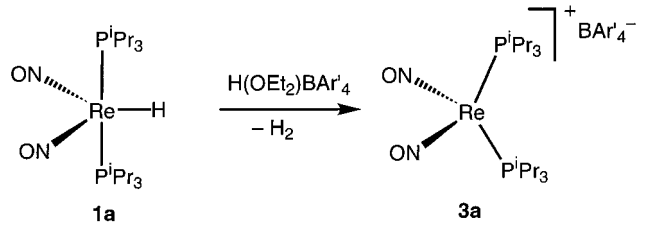
Figure 2. Molecular structure of complex **3b**.[6c] Displacement ellipsoids are shown at the 30% level. Not shown is the counterion and solvate molecules. Selected distances (Å) and angles (deg): Re−N(1) = 1.735(10); Re−N(2) = 1.766(8); P(1)−Re−P(2) = 159.93 (8); N(1)−Re−N(2) = 115.9(4); Re−N(1)−O(1) = 166.9(9); Re−N(2)−O(2) = 165.7(9).

$[BAr_4']$ (**3b**), which constitutes the first example of a 16-electron dinitrosyl compound (Scheme 1). The X-ray diffraction study[6c] reveals a butterfly-like C_{2v} geometry for the compound (Figure 2). This structure bears a great resemblance with that of the isoelectronic ruthenium complex $[Ru(NO)(CO)(PMe^tBu_2)_2][BAr_4']$.[10] At least in the solid state, **3b** displays agostic interactions that take place between the transition metal and two carbon−hydrogen bonds belonging to different tricyclohexylphosphine groups (distances of 2.637 and 2.886 Å have been determined between the rhenium and the agostic hydrogen atoms). In solution, however, confirmation of these interactions using variable-temperature (VT) ^1H NMR failed. Spectra recorded in C_6D_5Cl showed no changes for the cyclohexyl protons in the temperature range between −40 and +60 °C. Deuterated solvents that would allow a study at lower temperatures could not be employed, since the compound decomposes in CD_2Cl_2 and is not soluble in nonpolar solvents such as Tol-d_8. Furthermore it reacts with donor molecules such as THF-d_8.

Applying the same conditions as for **1b**, the reaction of **1a** with 1 equiv of $[Ph_3C][BAr_4']$ does not produce mononuclear compounds analogous to **3b**, instead it yields the binuclear complex **2a** plus unreacted $[Ph_3C][BAr_4']$. Nevertheless the 16-electron triisopropylphosphine derivative $[Re(NO)_2(P^iPr_3)_2][BAr_4']$ (**3a**) could finally be isolated from the reaction of **1a** with $H(OEt_2)_2[BAr_4']$.[11] This process takes place instantaneously in solution and is accompanied by hydrogen evolution (Scheme 2).

Some closer insight into the different reactivities of compounds **1a**,**b** toward $[Ph_3C][BAr_4']$ is provided by the VT NMR studies of the binuclear complexes **2a**,**b**, which revealed that the isonitrosyl linkage is stronger for the

Scheme 2



complex containing P^iPr_3 than for the one with PCy_3. At −40 °C complex **2a** shows in C_6D_5Cl a $^{31}P\{^1H\}$ NMR spectrum consisting of one singlet and two doublets in a 2:1:1 ratio, which correspond to an A_2MX spin system (Figure 3). Upon warming, the two doublets start to broaden until they finally collapse at higher temperatures giving a singlet resonance.

Although in the solid state the molecule does not have symmetry properties that could account for the equivalence of any of the four phosphorus nuclei, it is very likely that in solution a geometry of higher symmetry like the one shown in Figure 4 could be adopted. This would explain the observed chemical equivalence of two of the phosphorus atoms through a equatorial mirror plane. Whether the actual geometry of the NO−Re−$(NO)_2(P^iPr_3)_2$ moiety resembles more a tetragonal pyramid or a trigonal bipyramid could not be derived from the spectra. A situation, like the one shown in Figure 4, in which the phosphines of both metal fragments are staggered to minimize steric repulsions, could therefore

(10) Ogasawara, M.; Huang, D.; Streib, W. E.; Huffman, J. C.; Gallego-Planas, N.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 8642.

(11) Brookhart, M.; Grant, B.; Volpe, F. *Organometallics* **1992**, *11*, 3920.

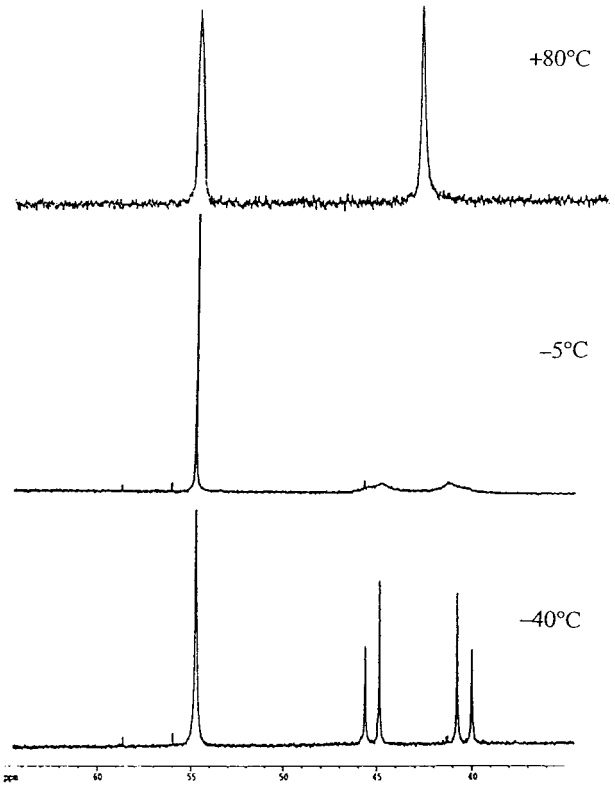


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (C_6D_5Cl) of complex $[Re_2(H)(\mu,\eta^2\text{-}NO)(NO)_3(P^iPr_3)_4]BAr'_4$ (**2a**) recorded on a Bruker DRX 500.

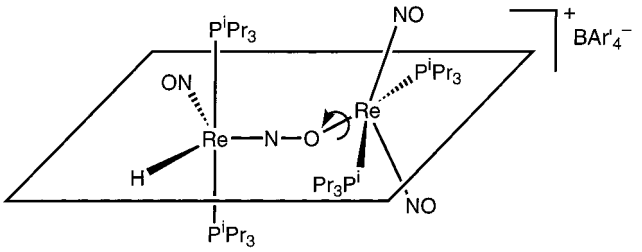


Figure 4. Proposed structure in solution for complex $[Re_2(H)(\mu,\eta^2\text{-}NO)(NO)_3(P^iPr_3)_4]BAr'_4$ (**2a**).

very likely be adopted in solution. Broadening and final collapse of the two doublets into a singlet upon warming can be explained on the basis of progressively free rotation of the $Re(NO)_2(P^iPr_3)_2^+$ fragment around the NO−Re dative bond.

A similar temperature dependence of the $^{31}P\{^1H\}$ NMR spectra is displayed by compound **2b** except for the difference that in this case two very broad singlets and two doublets are observed in C_6D_5Cl (−40 °C). This indicates that the structure is one in which none of the phosphorus nuclei are related by symmetry. As an additional phenomenon, dissociation of **2b** into **1b** and **3b** was recognized upon warming of the solution (Scheme 3). At 90 °C the signals of the ^1H and $^{31}P\{^1H\}$ NMR spectra correspond in fact to those of the independent $Re(H)(NO)_2(PCy_3)_2$ and $Re(NO)_2(PCy_3)_2^+$ species. In contrast to this, the isonitrosyl linkage of **2a** remains under the same conditions. This observation may be explained on the basis of steric arguments due to the larger cone angle of PCy_3 or, otherwise, by the fact of the agostic interactions in **3b** providing extra stabilization for the 16-electron species.

The given picture of dissociation of **2b** against nondissociation of **2a** explains also why **1a** does not react with $[Ph_3C][BAr_4']$ to afford **3a**. The nondissociating **2a** cannot release reactive **1a**, nor does it allow any further attack of the metal−hydride bond. The rhenium- and the metal-bound hydrogen atom in **2a** have a reduced basicity caused by coordination of one of the nitrosyl ligands. This prevents the second hydride abstraction by the trityl cation. On the other hand, the analogous binuclear derivative with PCy_3 **2b** with a less robust isonitrosyl linkage allows dissociation of the "free" hydride **1b** subsequently available for further reaction with $[Ph_3C][BAr_4']$. Curiously and despite the known capability of nitrosyl ligands to interact with Lewis acids via the oxygen atom,[5,6] only two other examples of isonitrosyl linkages between transition metal moieties have structurally been characterized in the solid state; both of them are clusters containing molybdenum/cobalt[12a] in one case and rhenium in the other.[12b]

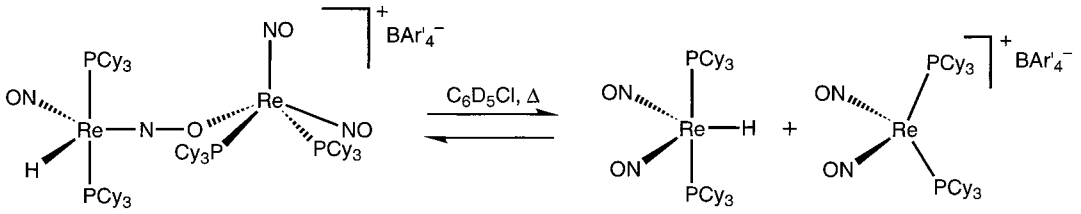
Reactivity of 3a,b toward Two-Electron Donors. Due to their coordinative unsaturation, compounds **3a**,**b** react readily in solution with two electron donor ligands to yield the corresponding addition derivatives $[Re(NO)_2(PR_3)_2L][BAr_4']$ (R = ^{i}Pr, L = CH_3CN, **4a**; CO, **5a**; C_6H_5CHO, **6a**; THF, **7a**) (R = Cy, L = CH_3CN, **4b**; CO, **5b**; C_6H_5CHO, **6b**; THF, **7b**) (Scheme 4), which can be isolated as pure solids. Except for THF, all these ligands appear to be strongly bound to the metal. No decomposition takes place after long periods of treatment under vacuum, and there is no indication of significant dissociation in solution. Structural details concerning the X-ray diffraction studies of the carbonyl and benzaldehyde complexes **5b** and **6b** have been reported.[6c] Compound **5b** displays a rather regular trigonal bipyramidal geometry around the rhenium center, while **6b** can be better described as a tetragonal pyramid (Figure 5). As in the case of **2a**, the NO group of complex **6b** is located in the apical position and shows a significant bend (Re−N−O = 150.9(3)°). The geometry changes exhibited by compounds **5b** and **6b** confirm that the fragment $[Re(NO)_2(PR_3)_2]^+$ is extremely flexible in adjusting itself to the particular stereoelectronic demands of the incoming ligands.

Addition of the above-mentioned ligands to solutions of the binuclear complexes **2a**,**b** affords 1:1 mixtures of **1a**,**b** and the corresponding $[Re(NO)_2(P^iPr_3)_2L][BAr_4']$ species. There is however one exception to this series. When **2a** is dissolved in THF, an equilibrium is established showing predominantly starting material and minor amounts of the dissociated species. If a large excess of THF is not present in the solution, dissociation is not observed at all. This can be taken as an additional proof that the isonitrosyl bridge is stronger in **2a** than in **2b**.

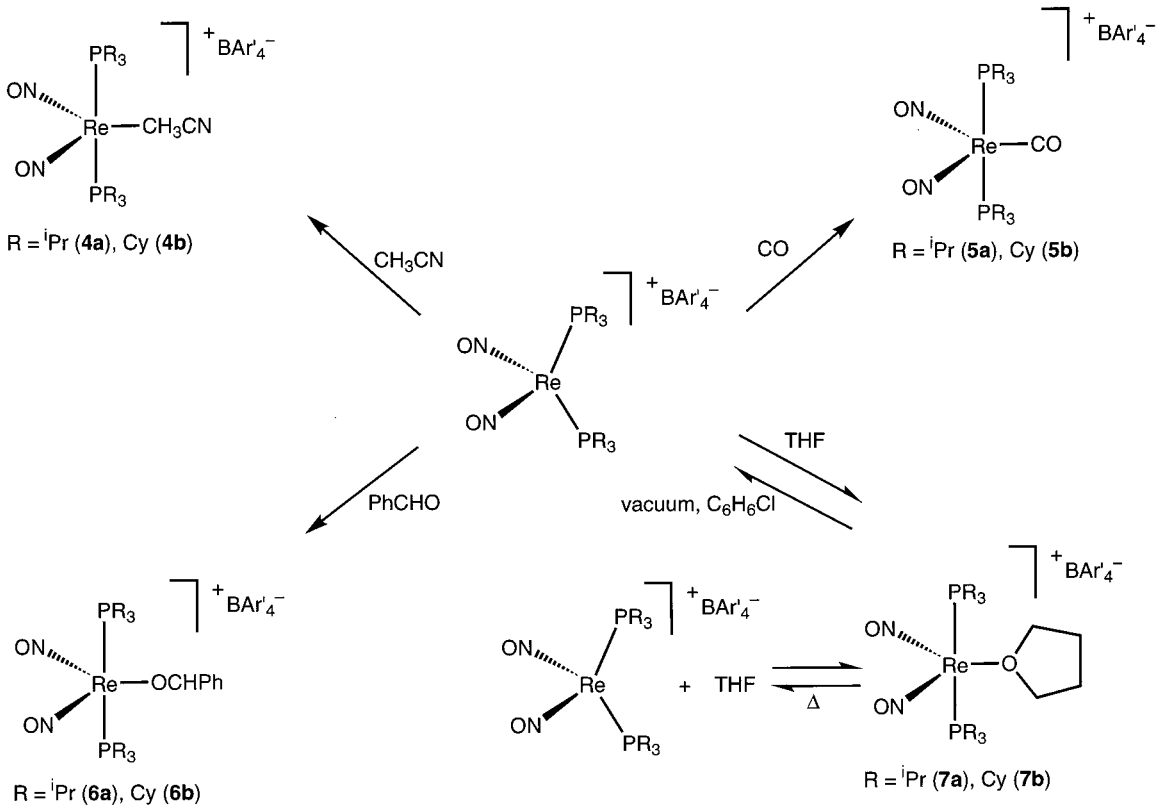
Coordination of THF is in any case a reversible temperature-dependent process for both **7a** and **7b**, as demonstrated by VT NMR experiments. Dissociation of THF does not occur in the pure yellow solids, which are stable for hours under vacuum and give rise to satisfactory elemental analyses, indicating that the ligand is not easily released. However, in solution unless an

(12) (a) Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Mountzouris, J. A.; Davis, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 905. (b) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1327.

Scheme 3



Scheme 4



excess of the ligand is present, an equilibrium between the 16- and 18-electron species can be traced. As expected from entropy considerations, the unsaturated species **3a**,**b** are preferred at higher temperatures, while at low temperatures association of a THF molecule prevails to give the 18-electron complex. Thus, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_5Cl of a freshly prepared solution of complex **7b** presents at 70 °C a signal at 46 ppm ($\delta = 47$ ppm for **3b** under the same conditions). At 20 °C a very broad signal at 42 ppm is detected, while at −40 °C the signal sharpens and shifts to 35 ppm. This latter chemical shift is also obtained when **3b** is dissolved in pure THF. The described process is accompanied by a color change of the solution, which is yellow at low temperatures and becomes dark red at temperatures higher than 60 °C, reflecting the colors of the THF and the unsaturated complexes, respectively. A similar behavior is observed for complex **7a** except that in this case the affinity for THF is greater and the temperature required to favor unsaturated **3a** over the saturated species **7a** is higher. At +30 °C the $^{31}P\{^1H\}$ chemical shift of a solution of **7a** in C_6D_5Cl is 47 ppm, still closer to the signal at 44 ppm corresponding to the THF compound **7a** than to the signal of the 16-electron species **3b**, which appears at 57 ppm. In the given range of temperatures the ^1H NMR spectra (C_6D_5Cl) show no significant shift of the THF resonances. The signals corresponding to free and coordinated THF can however be distinguished in CD_2Cl_2 at −80 °C when a slight excess of this ligand is present. Further evidence for the THF lability comes from the fact that when solutions of **7a**,**b** in C_6H_5Cl are placed under vacuum, the color of them gradually darkens apparently due to loss of THF and when the process is repeated several times the unsaturated complexes **3a**,**b** can be recovered.

Reactivity of 3a,b toward $HSiEt_3$ and H_2. In the molecules **3a** and **3b** a free basic site provided by the oxygen atom of a nitrosyl group and a free acidic site provided by the transition metal center coexist and allow the possibility of ligand-mediated heterolytic cleavage of nonpolar substrates such as hydrogen or organosilanes. With this in mind, we set out to investigate the reactions of compounds **3a** and **3b** with $HSiEt_3$ and H_2. Coordination of these molecules to the metal center might be followed by heterolytic splitting assisted by the built-in NO Brönsted base (Scheme 5).

At room temperature addition of an excess of $HSiEt_3$ to a solution of **3a**,**b** results in clean formation of $[Re(H)(NO)(NOSiEt_3)(PR_3)_2][BAr_4']$ (R = iPr, **8a**; Cy, **8b**) (Scheme 6). If only stoichoimetric amounts of $HSiEt_3$ are employed, heating of the reaction mixture is required for the process to be completed. The reaction also

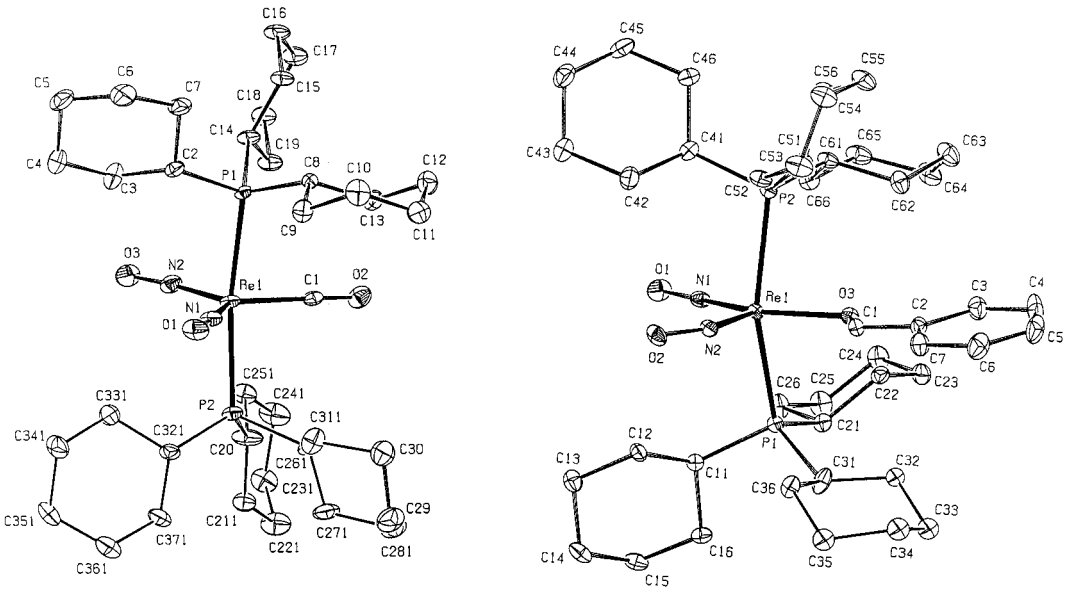
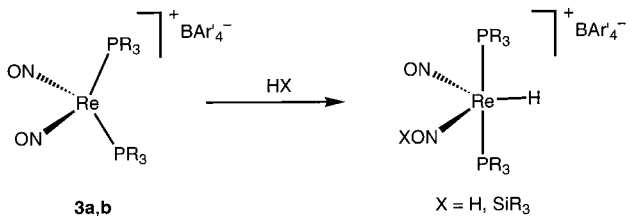
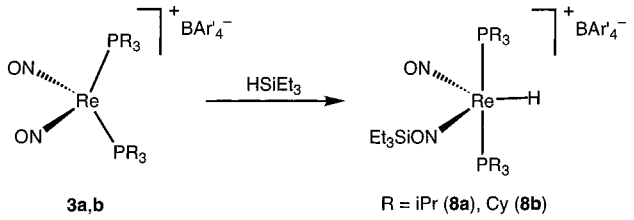


Figure 5. Molecular structure of complexes **5b** (left) and **6b** (right).[6c] Displacement ellipsoids are shown at the 20% level. Hydrogen atoms are omitted for clarity. Not shown is the counterion. Selected distances (Å) and angles (deg): For **5b**: (Re(1)−N(1) = 1.790(7); Re(1)−N(2) = 1.825(5); Re(1)−C(1) = 1.979(6); P(1)−Re(1)−P(2) = 169.62(5); Re(1)−N(1)−O(1) 174.0(6); Re(1)−N(2)−O(3) = 176.3(6). For **6b**: (Re(1)−N(1) = 1.758(4); Re(1)−N(2) = 181.1(4); Re(1)−O(3) = 218.8(3); P(1)−Re(1)−P(2) = 158.40(4); Re(1)−N(1)−O(1) = 175.9(4); Re(1)−N(2) = 150.9(3).

Scheme 5



Scheme 6



occurs with the binuclear complexes **2a**,**b**, but as expected in this case, it is accompanied by formation of the corresponding $[Re(H)(NO)_2(PR_3)_2]$. The ^1H NMR spectra of **8a** and **8b** show a resonance for a metal-bonded hydride which appears as a triplet due to the coupling with the phosphorus nuclei. In addition, signals for a triethylsilyl fragment can be detected, in which the coupling between the CH_2 groups and the terminal H−Si protons is no longer observable. These two facts together seem to indicate that cleavage of the H−Si bond has occurred. On the basis of the known marked oxophilicity of silicon and the observed basicity of the oxygen NO atom, the cationic Et_3Si^+ fragment is anticipated to be now bonded to this oxygen atom, while the hydrogen atom binds the transition metal center. This has been confirmed by an X-ray diffraction study carried out on derivative **8a** (Figure 6). Suitable crystals were obtained from a mixture of C_6H_5Cl and $HSiEt_3$. The structure displays a highly distorted trigonal pyramidal coordination geometry with the two "trans" phosphines strongly bent toward the position of the hydride. However, the most remarkable observations are as follows: (i) coordination of the $SiEt_3$ moiety to the nitrosyl produces a very significant lengthening of the respective N−O bond, (ii) only a slight shortening of the corresponding Re−N distance is observed, (iii) a N−O−Si angle close to 120° supports an sp^2 hybridization at this oxygen atom, (iv) the average C−Si−C angle is 113.3°, which is closer to a tetrahedral silicon species than to a trigonal planar three-coordinated Si cation, although given this geometry, a certain degree of remaining silylium character has to be assumed.[13]

The lengthening of the N−O bond is interpreted in terms of increased electronic donation from the metal center to the NO unit initiated by the attachment of the Et_3Si^+ fragment. Donation of electronic density from the metal to the NO is further enforced by a more pronounced phosphine bending away from the nitrosyls in the direction of the hydride ligand. This is a process that has a low energetic barrier as has been analyzed by DFT calculations on related model systems.[6c] Complex **8a** shows a resonance at 42.1 ppm (C_6D_5Cl, TMS) in the ^{29}Si NMR spectrum, a chemical shift that compares well with other oxygen-coordinated silylium species reported in the literature.[14] Remarkably and contrary to what is observed for silylium-ether adducts, which are only stable at low temperatures, complexes **8a** and **8b** remain unchanged in solution at room temperature for long periods of time, confirming the considerable basicity of the $[Re(H)(NO)(NO)(PR_3)_2]$ unit.

It is reasonable to assume that the first step in the reactions of **3a**,**b** with $HSiEt_3$ should be the coordination of the silane to the vacant rhenium site. However, extensive VT NMR studies have failed to detect any intermediates on the way to **8a** or **8b**. This seems to

(13) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325.
(14) (a) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697. (b) MacLachlan, M. J.; Bourke; S. C.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 2126.

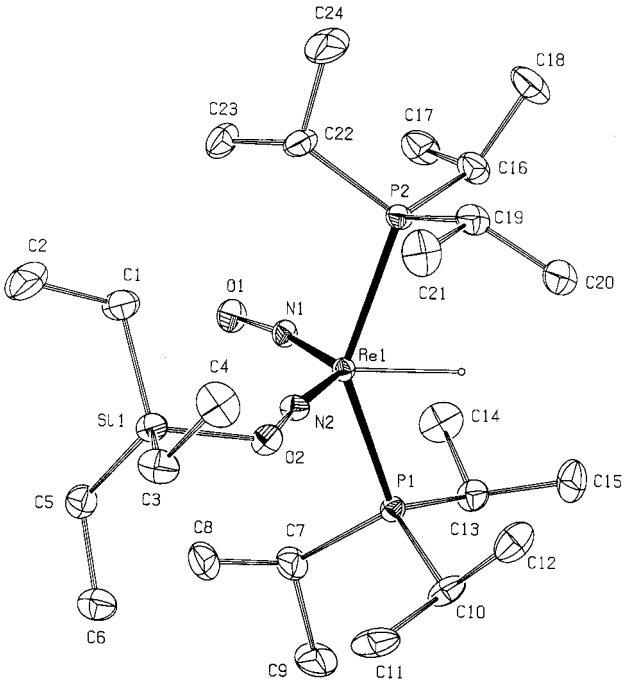
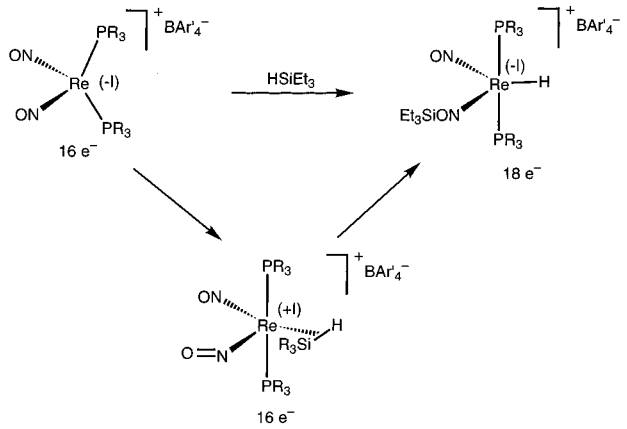


Figure 6. Molecular structure of **8a**. Displacement ellipsoids in the PLATON[24] plot are shown at the 30% probability level. Not shown is the counterion. Hydrogen atoms are omitted for clarity, except for the hydride ligand H1, which is displayed as a sphere with arbitrary size. Selected distances (Å) and angles (deg): Re(1)−P(1) = 2.4224(11), Re(1)−P(2) = 2.4346 (12), Re(1)−N(1) = 1.790(4), Re(1)−N(2) = 1.765(4), Re(1)−H(1) = 1.75(6), N(1)−O(1) = 1.194-(5), N(2)−O(2) = 1.321(5), O(2)−Si(1) = 1.744(4), Si(1)−C(1) = 1.857(7), Si(1)−C(3) = 1.845(7), Si(1)−C(5) = 1.856(7), P(1)−Re(1)−P(2) = 141.50(4), N(2)−Re(1)−N(1) = 128.1(2), O(1)−N(1)−Re(1) = 167.7(4), O(2)−N(2)−Re-(1) = 174.0(4), N(2)−O(2)−Si(1) = 119.3(3), C(3)−Si(1)−C(5) = 113.6(3), C(3)−Si(1)−C(1) = 114.0(4), C(5)−Si(1)−C(1) = 112.4(4).

indicate that coordination of the silane to the metal is the rate-limiting step in the process and that heterolytic cleavage of the Si−H bond takes place very fast after that. Further support for this hypothesis is provided by the fact that the reaction rate increases considerably with the concentration of $HSiEt_3$, indicating that the initial adduct formation significantly contributes to the rate law.

The reactions of the $[Re(NO)_2(PR_3)_2]^+$ fragments with $HSiEt_3$ are unique in various ways. First, it should be mentioned that there are only few examples of transition metal mediated heterolytic cleavage of silanes reported, and remarkably they are accomplished by electron-deficient, poor π-donating systems which greatly increase the acidity of the $HSiR_3$ molecule upon coordination.[2a,c,f,h,15,16] Furthermore, in complexes containing electron-rich metals, homolytic cleavage is preferred. However, in the case of **3a**,**b** heterolysis of $HSiEt_3$ is achieved by an electron-rich species formally containing a d^8 rhenium(−I) center, which pressumably can act as a π-donor, as corroborated by the fact that it forms stable adducts with a strong π-aceptor ligand like CO (complexes **5a**,**b**). In the compounds **8a** and **8b** the extreme electrophilicity of the silylium ion Et_3Si^+ enables it to attack one of the nitrosyl groups that acts as a trap for this fragment. With very few exceptions,[2h,16] in the cases of other systems the silylium species are

Scheme 7



converted further in less controlled ways by reactions with the solvent, adventitious water, counteranions, or the complex itself leading usually to mixtures of silicon-containing products. The apparent contradiction of an electron-rich metal center performing heterolytic activation might be reconciled taking into account the versatility of the $[Re(NO)_2(PR_3)_2L]^+$ cations in adjusting themselves to different electronic and steric situations. Following coordination of $HSiEt_3$ and due to steric repulsions, one might envisage bending of one NO ligand induced perhaps by the proximity of the ethyl groups (Scheme 7). There is precedence for this to happen, since a similar steric response has already been observed in the cases of complexes **2a** and **5a** upon coordination of benzaldehyde or $[Re(H)(NO)_2(PR_3)_2]$, respectively. But nitrosyl bending will also provoke a change in the formal oxidation state of the metal center from −1 to +1 and for this reason will create a new coordinative vacancy.[17] Note as well that like in compounds **2a** and **5a**, the geometry after NO bending should be closer to a tetragonal pyramid than to a trigonal bipyramid, since the former one is favored for a 16-electron complex. This would leave the linear NO as very good π-aceptor in an approximate trans position to $HSiEt_3$. It is reasonable to assume that the acidity of the resulting intermediate should be now greatly enhanced, facilitating the heterolytic rupture of the silane. It is also reasonable to propose that the Et_3Si^+ fragment interacts first with the nitrogen atom of the NO, since as a consequence of the anticlinal-type bending, the oxygen atom would slide away from the silicon. Subsequently the silicon residue could then migrate via a 1,2-shift to the O_{NO} atom to yield the observed 18-electron final products, in which in turn the rhenium possesses the oxidation state −1.

We have also investigated the reactivity of complexes **2a**,**b** and **3a**,**b** toward dihydrogen and dideuterium. Under 1 atm of these gases, the ^1H and $^{31}P\{^1H\}$ NMR spectra of these compounds in C_6D_5Cl solutions show no significant changes after a period of time varying from several hours to several days depending on the compound. Finally decomposition of the starting materi-

(15) (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *11*, 2527. (b) Scharrer, E.; Chang, E.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.

(16) Fryzuk, M. D.; Love, J. B.; Retting, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.

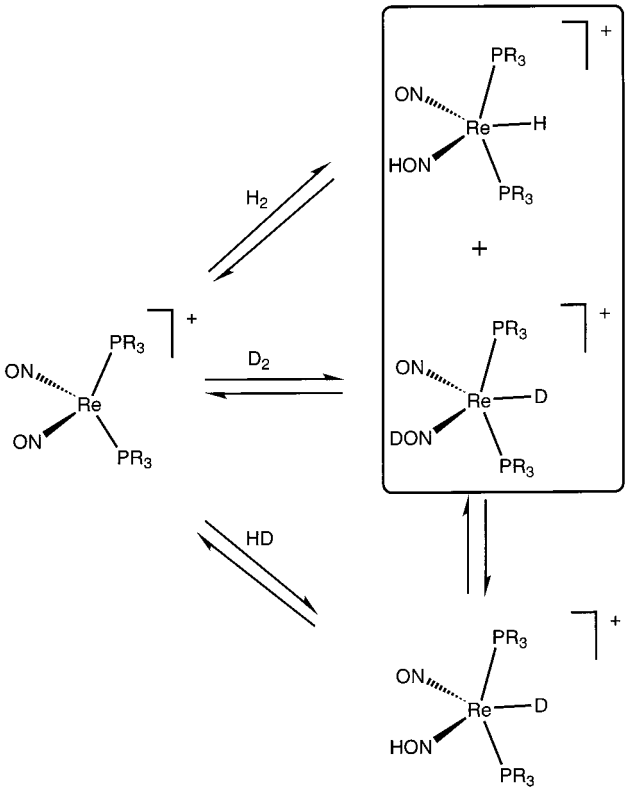
(17) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929.

als to give mixtures of unidentified products occurs. Samples of **2a**, **2b**, and **3b** decompose slowly at room temperature over a period of several days, while complex **3a** deteriorates relatively fast under H_2 atmosphere (1−2 h). Although no apparent reaction seems to take place with the complex, when identical solutions of the former compounds are exposed to 1 atm of an equimolar mixture of H_2/D_2, catalytic H/D scrambling is observed at room temperature by ^{1}H NMR. The rate of the scrambling reaction depends on the solvent, occurring very fast in C_6D_5Cl or toluene-d_8, which are considered noncoordinating molecules, and being considerably slower in donor solvents such as THF-d_8. When complexes **3a**,**b** are employed, the equilibration in toluene or chlorobenzene is finished after a few minutes. This is a high rate, especially in view of the poor solubility of these cationic derivatives in a solvent like toluene. In THF the reaction requires several hours to be completed, reflecting the lower availability of the coordinative vacancy for H_2/D_2 binding. If the binuclear derivative **2a** is used instead, equilibration in C_6D_5Cl at room temperature takes approximately 30−40 min. In addition to the scrambling processes, it has been observed that when complexes **2a**,**b** are placed under an atmosphere of D_2, replacement of the hydride ligand by deuterium is achieved to give the corresponding $[Re_2(D)(\mu,\eta^2\text{-NO})(NO)_3(PR_3)_4][BAr_4']$ (R = ^{i}Pr, **2aD**; Cy, **2bD**). In contrast exchange of the hydride ligands by deuterium does not occur under the same conditions for the mononuclear compounds **1a**,**b** after several days, suggesting that a mechanism with dissociation of the binuclear unit is operative for **2aD** and **2bD**.

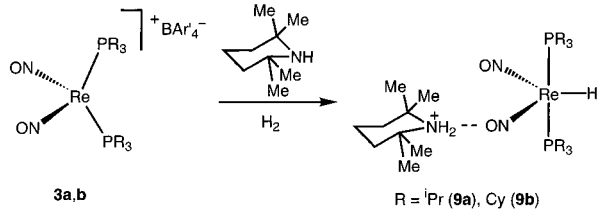
The described experiments confirm that coordination of H_2 and D_2 must indeed occur to some extent in solution, although it could not be traced by NMR spectroscopy. Derivatives analogous to those obtained in the reaction with $HSiEt_3$, namely, $[Re(H)(NO)(NOH)(PR_3)_2][BAr_4']$, are not detectable, but could very well be responsible for the observed scrambling process via a mechanism like the one proposed in Scheme 8. As in the case of the silane activation, it would involve heterolytic rather than homolytic splitting. A homolytic pathway cannot be completely excluded, but we believe it is very unlikely, since it would require simultaneous coordination of H_2 and D_2 to the same metal center. Also, although water was rigorously excluded from the reactions, the presence of trace amounts able to catalyze the exchange of protons cannot be completely ruled out. The observed final decomposition of the complexes might arise from the known instability of the BAr_4' anion over a long period of time under strong acidic conditions.[11]

Further support for the possible involvement of the nitrosyl ligands in the heterolytic cleavage of H_2 comes from the reaction of compounds **3a**,**b** with H_2 in the presence of a stoichiometric amount of the amine 1,1′,6,6′-tetramethylpiperidine. This amine was chosen because it is too bulky to be able to interact significantly with the unsaturated rhenium center but should be basic enough to abstract a proton following H_2 coordination. The ^{1}H NMR spectra of the resulting solutions (C_6D_5Cl) indicate clearly that activation of one molecule of H_2 has taken place. A signal corresponding to a metal-bonded hydride appears as a triplet at approximately

Scheme 8



Scheme 9



4.1 ppm together with another resonance assigned to a NH_2^+ fragment. The reaction is clean and almost instantaneous, but instead of the expected neutral hydrides $[Re(H)(NO)_2(PR_3)_2]$ plus the corresponding isolated ammonium salt $[H_2NC_5H_6(CH_3)_4][BAr_4']$, the new hydrogen-bonded adduct complexes $[Re(H)(NO)\{NOH_2NC_5H_6(CH_3)_4\}(PR_3)_2][BAr_4']$ (R = ^{i}Pr (**9a**), Cy (**9b**)) are isolated (Scheme 9). The source of the hydride and the proton is without doubt molecular hydrogen. This point has been confirmed by experiments carried out with D_2 in a non-deuterated solvent, which showed the formation of the corresponding isotopomers $[Re(D)(NO)\{NOHDNC_5H_6(CH_3)_4\}(PR_3)_2][BAr_4']$.

Suitable crystals of the tricyclohexylphosphine derivative **9b** were obtained in a C_6H_5Cl/pentane mixture, and an X-ray diffraction study was carried out (Figure 7). From Figure 7 it can be seen that the environment around the rhenium atom is essentially the same as the one found in the neutral hydride $[Re(H)(NO)_2(P^iPr_3)_2]$ (**1a**) and the distorted trigonal bipyramidal geometry is maintained. The structural study shows that a strong interaction between the acidic substrate, in this case the ammonium protons, and the oxygen atoms of the nitrosyl ligands takes place. In the solid state, the ammonium cation is placed in a bridging position between two NO groups connecting adjacent metal

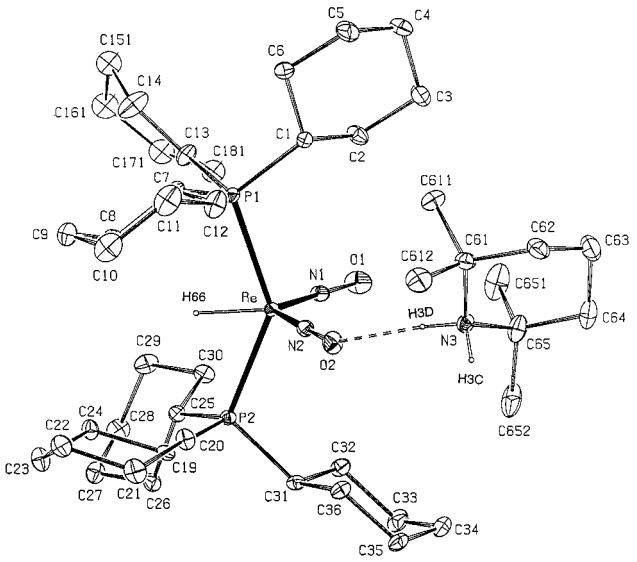


Figure 7. Molecular structure of **9b**. Displacement ellipsoids in the PLATON[24] are shown at the 20% probability level. Not shown is the counterion. Hydrogen atoms are omitted for clarity, except for the hydride ligand, H66, and ammonium hydrogens, which are shown as a spheres of arbitrary size. Selected distances (Å) and angles (deg): Re−P(1) = 2.4252(8), Re−P(2) = 2.4191(9), Re−H(66) = 1.4789, Re−N(1) = 1.782(4), Re−N(2) = 1.781(3), N(1)−O(1) = 1.213(5), N(2)−O(2) = 1.237(4), P(2)−Re−P(1) = 148.38(3), N(2)−Re−N(1) = 126.60(16), O(1)−N(1)−Re = 174.1(4), O(2)−N(2)−Re = 175.7(3).

units. Both of the ammonium hydrogen atoms are involved in hydrogen bonding in an asymmetric fashion with nitrosyl substituents which belong to two crystallographically different molecules related by the operation $1/2+x,-y,z$ (NO- -HN distances of 1.908 and 1.987 Å, respectively). Figure 8 shows the overall result of the solid-state hydrogen bonding, which occurs in parallel zigzag chains progressing in the *a*-direction of the crystal.

The great strength of the hydrogen−oxygen interaction is manifested by the fact that the ammonium salt $[H_2NC_5H_6(CH_3)_4][BAr_4']$ cannot be separated from the complex. Even in quite polar solvents such as dichloromethane it is possible to detect the existence of this linkage, because the chemical shift of the hydride in **1a**,**b** is a very sensitive probe to detect any interaction of an acidic substrate with the NO groups.[6b,d,18] Indeed a shift of about +0.3 ppm for the hydride signal is observed when a stoichiometric amount of $[H_2NC_5H_6(CH_3)_4][BAr_4']$ is added to CD_2Cl_2 solutions of **1a**,**b**.

Evolution of hydrogen gas as the result of reversal of the heterolytic splitting is not observed when solutions of **9a**,**b** are heated or placed under vacuum. Exchange with D_2 does not take place even after several hours at 70 °C in C_6D_5Cl, demonstrating that in the presence of a strong base, the activation of hydrogen is an irreversible process. This result contrasts with the observed H_2/D_2 scrambling that occurs with the 16-electron complexes **3a**,**b** and is very likely the consequence of the proton being now trapped between the amine and nitrosyl ligands. It shows that both a coordinative vacancy on the metal center and a weak base are necessary for the catalytic activation of hydrogen. The vacant position is required so that primary coordination of hydrogen can take place; when this position is already occupied by another ligand, the exchange may or may not occur depending on whether the ligand can be displaced by H_2. The base then must assist in the splitting of the bonded hydrogen molecule. If its affinity for protons is strong, the proton cannot be released anymore and the exchange between H_2 and D_2 is suppressed, but if the base is weak, as it seems to be the case with the NO groups, reversible protonation of the metal hydride as well as exchange between H^+ and D^+ can account for the observed H_2/D_2 equilibration.

Concluding Remarks

The enhanced hydridicity of the Re−H bond in the compounds $[Re(H)(NO)_2(PR_3)_2]$ makes it possible to use them as precursors for the synthesis of unsaturated rhenium dinitrosyl derivatives $[Re(NO)_2(PR_3)_2][BAr_4']$. In these complexes the phosphine seems to play a very important role in the stabilization of the molecule. Thus, the affinity of the tricyclohexylphosphine derivatives for σ-donor ligands is much lower than the affinity of the species containing triisopropylphosphine, even despite the fact that both phosphines have similar basic properties. In the earlier case, the presence of agostic interactions between the metal and two C−H bonds of the cyclohexyl groups might be responsible for this behavior.

Despite the electronic richness of the rhenium center, the unsaturated complexes **3a** and **3b** are able to perform heterolytic activation of H_2 and $HSiEt_3$ under very mild conditions. In these reactions the oxygen atom of one nitrosyl ligand appears to provide the basic site which is necessary for the process. This has been demonstrated in the reactions with $HSiEt_3$ where the driving force is presumably coming from the extreme oxophilicity of the silicon atom. Although analogous derivatives coming from the reaction with H_2 have not been isolated, the observed catalytic equilibration of H_2/D_2 mixtures could be achieved via a related mechanism. From this work it is clear that noninnocent ligands such as NO take an active part in the transformations of small molecular substrates and cannot be regarded as mere spectator groups.

Experimental Section

All operations were carried out under nitrogen atmosphere using a M. Braun 150 G-B glovebox. The solvents were dried over sodium diphenylketyl (THF, Et_2O, hydrocarbons) or P_2O_5 (CH_2Cl_2, CH_3CN, C_6H_5Cl) 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) or P_2O_5 (CD_2Cl_2, C_6D_5Cl) and vacuum transferred for storage in Schlenk flasks fitted with Teflon valves.

NMR experiments were carried out on a Varian Gemini 300, Varian Mercury 200, or Bruker DRX 500 spectrometer using 5 mm diameter NMR tubes equipped with Teflon valves, which allow degassing and further introduction of gases into the probe. 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 are relative to 85% H_3PO_4. Microanalyses were performed at the Anorganisch-chemisches Institut of the University of Zürich. IR spectra were recorded on a Bio-Rad FTS-45 spectrometer.

The following reagents were purchased from Aldrich, degassed, and used without further purification: $HSiEt_3$, PhCHO, and 2,2,6,6-tetramethylpiperidine.

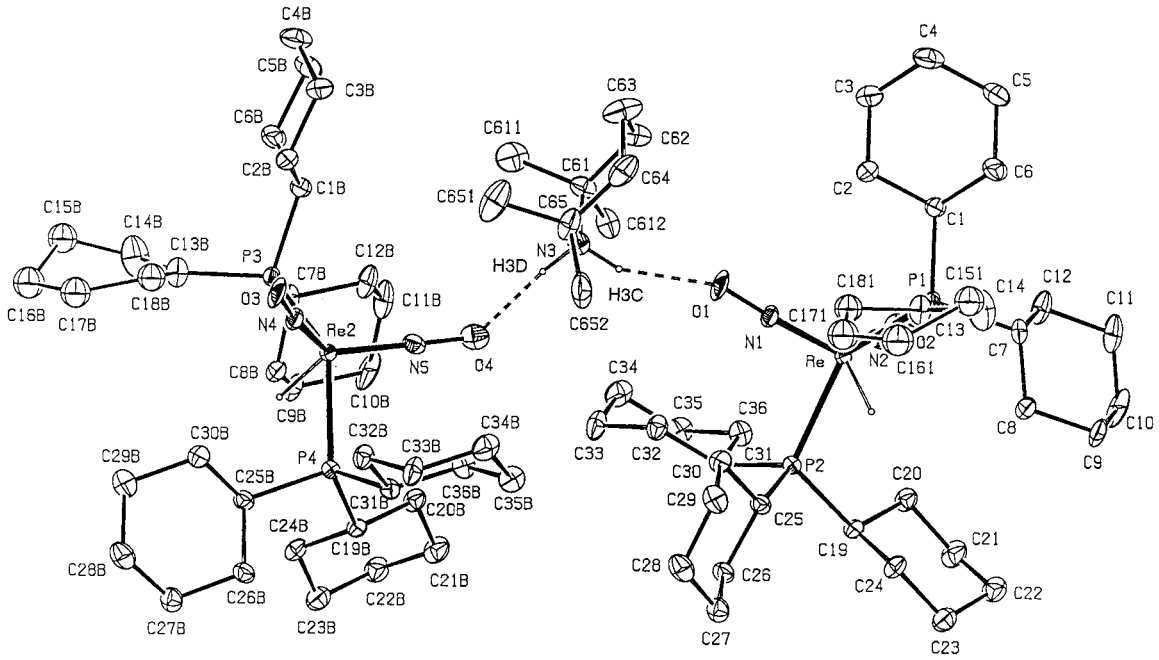


Figure 8. PLATON[24] drawing showing hydrogen bonding **9b**, which is continuing at O(2) and O(3). Selected distances (Å): O(1)−H(3C) = 1.908, O(2)−H(3D) = 1.987.

Compounds **1a**, **1b**,[6b] **2a**, **3b**, **5b**, **6b**,[6c] $[Ph_3C][BAr_4']$,[9] and $H(OEt_2)_2BAr_4'$[11] have been prepared according to the reported procedures.

X-ray Diffraction Studies of Complexes 8a and 9b. Crystallographic and experimental parameters are summarized in Table 1. Single crystals of **8a** and **9b** were mounted on top of a glass fiber using perfluoropolyether oil and immediately transferred to the diffractometer, where they were cooled at 192(2) K using an Oxford cryogenic system. Determination of the unit cell parameters and the collection of intensity data were performed with an image plate detector system (Stoe IPDS diffractometer) using the Stoe IPDS software.[19] Due to the large diffracting volume of the crystals, a colimator of 0.8 mm diameter was used. Lorentz and polarization corrections were done with INTEGRATE, and numerical absorption corrections[20] were performed with XRED, using 9 (for **8a**) and 12 (for **9b**) measured and indexed crystal faces with a video camera installed at the IPDS diffractometer. Both structures were solved with direct methods using SHELXS-97.[21] The refinements were performed with SHELXL-97.[22]

In complex **8a**, the hydride H1 was found by difference electron density calculations. Its coordinates and the isotropic displacement parameters could be refined. For complex **9b**, the hydride H66 was also found in a difference Fourier map; however its positional parameters had to be restrained at a distance of 1.700(0.025) Å during the refinement and resulted in a relatively short Re−H distance of 1.47 Å. The displacement parameters were refined isotropically. Flack's *x*-parameter was −0.014(3), confirming the absolute configuration of the structure **9b**.[23] One of the disordered cyclohexyl rings in **9b** had to be refined with split atomic positions using the PART and EADP instruction of SHELXL-97.[22] The two hydrogens of the ammonium cation have been calculated, and therefore the O··H distances of the N−H··O hydrogen bonds are indicated without standard uncertainties.

Other crystallographic data for the structures reported in this paper are included as Supporting Information.

Preparation of the Complexes. $[Re_2(H)(\mu,\eta^2\text{-}NO)(NO)_3(PCy_3)_4][BAr_4']$ (2b). Route A. A mixture of 50 mg of **1b** (0.0619 mmol) and 31 mg of $[Ph_3C][BAr_4']$ (0.0280 mmol) in 5 mL of benzene was stirred for 1 h. The solvent was removed under vacuum, and then the residue was washed once with pentane at −35 °C to facilitate the transformation of the oil into a solid. After that, the yellow-orange solid was washed with pentane at room temperature (2 × 10 mL) and dried several hours in vacuo to give 50 mg of **2b** 90% pure by NMR. Recrystallization of this material did not afford analytically pure material, and therefore route B is recommended for this synthesis.

Route B. A mixture of 40 mg of **3b** (0.0239 mmol) and 19.3 mg of **1b** (0.239 mmol) was dissolved in 0.75 mL of chlorobenzene. Pentane was layered over this solution and the mixture placed in the freezer at −35 °C during 5 days. A crop of orange crystals was collected, washed with cold pentane (2 × 4 mL, −35 °C), and dried under vacuum to give 40 mg of **2b** (67.4%). Anal. Calcd for $C_{104}H_{145}N_4O_4P_4BF_{24}Re_2$: H, 5.90; C, 50.40; N, 2.26. Found: H, 5.70; C, 50.66; N, 2.26. IR (Nujol, ν_{NO}): 1688 (m), 1640(s), 1594(s). ^{1}H NMR (C_6D_5Cl, 300 MHz), T = −40 °C: 8.42 (br, m, 8H, BAr_4'), 7.58 (br, m, 4H, BAr_4'), 1.00−3.00 (m, 132H, P*Cy*$_3$) (the hydride signal was not observed under these conditions); T = 0 °C: 8.33 (br, m, 8H, BAr_4'), 7.61 (br, m, 4H, BAr_4'), 3.35 (t, br, J_{H-P} = 46.2 Hz), 1.05−2.60 (m, 132H, P*Cy*$_3$); T = 80 °C: 8.15 (br, m, 8H, BAr_4'), 7.62 (br, m, 4H, BAr_4'), 4.23 (t, J_{H-P} = 36.9 Hz), 1.05−2.60 (m, 132H, P*Cy*$_3$). ^{31}P{^{1}H} NMR (C_6D_5Cl, 121.5 MHz), T = −40 °C: 42.6 (s, br, 1P), 37.2 (s, br, 1P), 33.5 (2P, d, J_{P-P} = 162 Hz), 28.5 (d, 2P); T = 0 °C: 39.8 (s, br, 2P), 34.7 (s, br, 2P); T = +70 °C: 46.0 (s, 2P), 38.5 (s, 2P).

$[Re(NO)_2(P^iPr_3)_2][BAr_4']$ (3a). A 190 mg sample of **1a** (0.335 mmol) and 339 mg of $H(OEt_2)_2BAr_4'$ (0.335 mmol) were dissolved in 5 mL of C_6H_5Cl. Immediate evolution of H_2 takes place, and a dark red solution is obtained. The solvent is removed under vacuum and the oily residue washed with

(18) Compare also the shift of the hydride signal of complexes **1a**,**b** with respect to complexes **8a**,**b**, in which a $^+SiEt_3$ fragment is coordinated.

(19) Stoe IPDS sofware for data collection, cell refinement and data reduction, Version 2.90; Stoe&Cie: Darmstadt, Germany, 1998.

(20) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(21) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(22) Sheldrick, G. M. *SHELXL 97*; University of Göttingen: Germany, 1997.

(23) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876. Bernardinelli, G.; Flack, H. D. *Acta Crystallogr.* **1985**, *A41*, 500.

(24) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.

Table 1. Crystal Data and Structure Refinement Parameters for 8a and 9b

	8a	9b
formula	$C_{56}H_{70}BF_{24}N_2O_2P_2ReSi$	$C_{77}H_{99}BF_{24}N_3O_2P_2Re$
M_r	1546.18	1813.54
cryst habit	yellow prism	yellow prism
cryst size	0.67 × 0.65 × 0.34	0.76 × 0.31 × 0.27
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*Ia*[a]
a (Å)	12.6986(7)	16.1372(10)
b (Å)	15.8124(6)	26.0691(19)
c (Å)	34.375(2)	20.8115(14)
α (deg)	90.00	90.00
β (deg)	105.217(7)	109.410(7)
γ (deg)	90.00	90.00
V (Å3)	6660.4(6)	8257.4(10)
ρ_{calc} (g cm^{-3})	1.542	1.459
Z	4	4
F(000)	3104	3696
temp (K)	193(2)	193(2)
μ (mm^{-1})	1.998	1.610
abs corr	numerical	numerical
T_{min}/T_{max}	0.3479/0.5499	0.3742/0.6704
θ range (deg)	2.79 < *θ* < 30.46	2.56 < *θ* < 28.95
hkl range	−18 < *h* < 17	−21 < *h* < 21
	−22 < *k* < 22	−35 < *k* < 35
	−48 < *l* < 48	−28 < *l* < 28
data measd	57 177	32 429
unique data	19 791	19 635
data obs ($I \geq 2\sigma(I)$)	14 829	17 560
parameters	806	985
max. shift/s.u.	0.003	0.003
resd *d* (e Å^{-3})	+1.799, −2.050	+0.864, −1.253
R1 (obs)	0.0571	0.0293
wR2 (obs)	0.1507	0.0710
GooF	1.093	0.994

[a] Baur and Kassner (1992)[25] and Marsh (1997)[26] have shown that many structures published in the non-centrosymmetric space group *Cc* were in fact misidentified and should be better described in a higher true symmetry, e.g., *C*2/*c*. Compound **9b** with the space group *Ia*, which is another setting for the space group *Cc*, was therefore checked for a higher symmetry with the program MISSYM, but no additional symmetry elements were found.[24]

pentane (3 × 20 mL) to give a dark red solid, which was dried under vacuum, leaving 440 mg of **3a** (91.8%). Anal. Calcd for $C_{50}H_{54}N_2O_2P_2BF_{24}Re$: H, 3.81; C, 42.03; N, 1.96. Found: H, 4.11; C, 41.94; N, 1.95. IR (Nujol, ν_{NO}): 1712 (s), 1654 (s). ^{1}H NMR (C_6D_5Cl): 8.23 (br, m, 8H, BAr$_4'$), 7.62 (br, m, 4H, BAr$_4'$), 2.22 (m, 6H, P(C*H*Me$_2$)$_3$), 0.92 (m, 36H, P(CH*M*e$_2$)$_3$). ^{31}P{^{1}H} NMR (C_6D_5Cl): 58.2 (s, br).

[Re(NO)$_2$(CH$_3$CN)(P^{i}Pr$_3$)$_2$][BAr$_4'$] (4a). From 3a. A 50 mg sample of **3a** (0.0350 mmol) was dissolved in 0.75 mL of CH_3CN. The yellow solution was evaporated and the residue washed with pentane (3 × 10 mL) to give a yellow-orange solid, which was dried in vacuo, leaving 47 mg of **4a** (91.4%). Anal. Calcd for $C_{52}H_{57}N_3O_2P_2BF_{24}Re$: H, 3.91; C, 42.46; N, 2.86. Found: H, 3.66; C, 42.26; N, 2.82. IR (Nujol): 2273 (w, ν_{CN}), 1675 (s, ν_{NO}), 1634 (s, ν_{NO}). ^{1}H NMR (CD_2Cl_2): 7.72 (br, m, 8H, BAr$_4'$), 7.57 (br, m, 4H, BAr$_4'$), 2.76 (s, 3H, C*H*$_3$CN), 2.58 (m, 6H, P(C*H*Me$_2$)$_3$), 1.32 (m, 36H, P(CH*M*e$_2$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 34.0 (s). ^{13}C{^{1}H} NMR (THF-d_8): 3.2 (s, *C*H$_3$CN), 146.7 (s, CH$_3$*C*N).

From 2a. A 44 mg sample of **2a** (0.022) mmol in C_6H_6 (2 mL) was treated with an excess of CH_3CN (3 drops added with a Pasteur pipet). The resulting orange solution was dried under vacuum and the oily residue washed with pentane (3 × 10 mL) to give a yellow-orange solid. The solid was recrystallized in C_6H_5Cl/pentane, leaving a fraction of orange crystals, which were washed with pentane (2 × 5 mL) and dried in vacuo to afford 25 mg of **4a** (77.2%).

(25) Baur, W. H.; Kassner, D. *Acta Crystallogr.* **1992**, *B48*, 356.
(26) Marsh, R. E. *Acta Crystallogr.* **1997**, *B53*, 317.

[Re(NO)$_2$(CH$_3$CN)(PCy$_3$)$_2$][BAr$_4'$] (4b). A heterogeneous mixture containing 30 mg of **3b** (0.0180 mmol) in C_6H_6 (1 mL) was treated with one drop of CH_3CN. A yellow solution was immediately obtained, and pentane was layered over it. After some hours yellow crystals were formed. The crystals were washed with pentane (2 × 5 mL) and dried under vacuum to give 20 mg of **4b** (65.1%). Anal. Calcd for $C_{70}H_{81}N_3O_2P_2BF_{24}Re$: H, 4.77; C, 49.13; N, 2.46. Found: H, 4.73; C, 49.04; N, 2.45. IR (Nujol): 2279 (w, ν_{CN}), 1663 (s, ν_{NO}), 1625 (s, ν_{NO}). ^{1}H NMR (CD_2Cl_2): 7.73 (br, m, 8H, BAr$_4'$), 7.57 (br, m, 4H, BAr$_4'$), 2.79 (s, 3H, C*H*$_3$CN), 2.40−1.05 (m, 66H, PCy$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 27.2 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): 4.3 (s, *C*H$_3$CN), 140.2 (s, CH$_3$*C*N).

[Re(NO)$_2$(CO)(P^{i}Pr$_3$)$_2$][BAr$_4'$] (5a). From 3a. A 50 mg sample of **3a** (0.0350 mmol) in 3 mL of C_6H_5Cl was placed in a 25 mL flask equipped with a Teflon valve. The solution was placed under 1 atm of CO. Immediately a yellow-brown solution was formed. By addition of 15 mL of pentane a yellow solid precipitated. The solid was washed with pentane (3 × 10 mL) and dried in vacuo to give 40 mg of **5a** (78.5%). Anal. Calcd for $C_{51}H_{54}N_2O_3P_2BF_{24}Re$: H, 3.73; C, 42.02; N, 1.92. Found: H, 3.81; C, 42.00; N, 1.87. IR (Nujol): 2029 (s, ν_{CO}), 1726 (s, ν_{NO}), 1682 (s, ν_{NO}). ^{1}H NMR (CD_2Cl_2): 7.73 (br, m, 8H, BAr$_4'$), 7.57 (br, m, 4H, BAr$_4'$), 2.65 (m, 6H, P(C*H*Me$_2$)$_3$), 1.32 (m, 36H, P(CH*M*e$_2$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 31.6 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): 202.8 (t, 1C, *C*O, J_{P-C} = 9.8 Hz).

From 2a. A 70 mg sample of **2a** (0.035 mmol) was placed in a 25 mL flask equipped with a Teflon valve and then 3 mL of C_6H_6 added. The mixture was placed under 1 atm of CO and shaken until all the starting material dissolves. The solvent was removed under vacuum and the oily residue washed with pentane (2 × 10 mL), leaving a brown solid, which was recrystallized from C_6H_5Cl/pentane. After 24 h brown crystals were collected, washed with pentane (2 × 5 mL), and dried in vacuo to give 35 mg of **5a** (68.5%).

[Re(NO)$_2$(PhCHO)(P^{i}Pr$_3$)$_2$][BAr$_4'$] (6a). From 3a. A 50 mg sample of **3a** (0.0350 mmol) in C_6H_6 (3 mL) was treated with 50 *μ*L of PhCHO. Immediately a yellow solution and a brown oil formed. A 10 mL portion of pentane was added, and the liquid was discharged. The residue was washed with more pentane (2 × 10 mL) until a yellow-orange solid was obtained and dried in vacuo to give 46 mg of **6a** (85.7%). Anal. Calcd for $C_{57}H_{60}N_2O_3P_2BF_{24}Re$: H, 3.94; C, 44.57; N, 1.82. Found: H, 4.09; C, 44.95; N, 1.82. IR (Nujol): 1674 (s) 1618 (s), 1593 (s), 1573 (s). ^{1}H NMR (CD_2Cl_2): 9.95 (s, 1H, C$_6$H$_5$C*H*O), 7.99 (m, 3H, C$_6$*H*$_5$CHO), 7.72 (br, m, 10H, BAr$_4'$ + C$_6$*H*$_5$CHO), 7.56 (br, m, 4H, BAr$_4'$), 2.45 (m, 6H, P(C*H*Me$_2$)$_3$), 1.31 (m, 36H, P(CH*M*e$_2$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 42.3 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): 207.0 (br, s, 1C, C$_6$H$_5$*C*HO).

From 2a. A 70 mg sample of **2a** (0.0350 mmol) in C_6H_6 (3 mL) was treated with an excess of PhCHO (1 drop added with a pipet). The mixture was shaken until the starting material dissolved and a brown solution with some brown oil was obtained. The solution was filtered and pentane layered over it. After 24 h brown crystals were collected, washed with pentane (2 × 5 mL), and dried in vacuo to give 30 mg of **6a** (55.8%).

[Re(NO)$_2$(THF)(P^{i}Pr$_3$)$_2$][BAr$_4'$] (7a). A 75 mg sample of **3a** (0.0524 mmol) was dissolved in 0.75 mL of THF and then 15 mL of pentane added. The light yellow flakes that precipitated were collected, washed with pentane, and dried 2 h in vacuo to give 70 mg of **7a** (88.8%). Anal. Calcd for $C_{54}H_{62}N_2O_3P_2BF_{24}Re$: H, 4.16; C, 43.18; N, 1.87. Found: H, 4.45; 43.37; N, 1.74. IR (Nujol, ν_{NO}): 1678 (s), 1630 (s). ^{1}H NMR (CD_2Cl_2, 25 °C, 3 equiv of THF): 7.73 (br, m, 8H, BAr$_4'$), 7.57 (br, m, 4H, BAr$_4'$), 3.83 (br, m, 12H, THF), 2.59 (m, 6H, P(C*H*Me$_2$)$_3$), 1.91 (br, m, 12H, THF), 1.35 (m, 36H, P(CH*M*e$_2$)$_3$). ^{1}H NMR (CD_2Cl_2, −80 °C, 3 equiv of THF): 7.73 (br, m, 8H, BAr$_4'$), 7.55 (br, m, 4H, BAr$_4'$), 4.13 (br, m, 4H, coord. THF), 3.65 (br, m, 8H, noncoord. THF), 2.49 (m, 6H, P(C*H*Me$_2$)$_3$), 2.06 (br, m, 4H, coord. THF), 1.78 (br, m, 8H, noncoord. THF), 1.35 (m,

36H, P(CH*Me*$_2$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): 45.9 (br, s). ^{31}P{^{1}H} NMR (CD_2Cl_2, −80 °C): 44.2 (s). ^{31}P{^{1}H} NMR ($C6D_5$-Cl, 80 °C): 56.3 (s, br).

[Re(NO)$_2$(THF)(PCy$_3$)$_2$][BAr$_4$′] (7b). A heterogeneous mixture containing 30 mg of **3b** (0.0180 mmol) in C_6H_6 (1 mL) was treated with an excess of THF (4 drops added with a pipet). A yellow solution was obtained, and pentane was layered over it. Small yellow crystals were collected after 12 h, washed with pentane (5 mL), and dried 15 min in vacuo to give 28 mg of **7b** (89.5%). Anal. Calcd for $C_{72}H_{86}N_2O_3P_2BF_{24}$-Re: H, 4.97; C, 49.63; N, 1.61. Found: H, 5.06; C, 49.68; N, 1.47. IR (Nujol, ν_{NO}): 1664 (s), 1585(s). ^{1}H NMR (CD_2Cl_2, 25 °C, 1.5 equiv THF): 7.73 (br, m, 8H, BAr$_4$′), 7.57 (br, m, 4H, BAr$_4$′), 3.77 (br, m, 6H, THF), 2.50−1.05 (m, 72H, PCy$_3$ + THF). ^{1}H NMR (CD_2Cl_2, −80 °C, 1.5 equiv THF): 7.73 (br, m, 8H, BAr$_4$′), 7.57 (br, m, 4H, BAr$_4$′), 4.10 (br, m, 4H, coord. THF), 3.66 (br, m, 2H, noncoord. THF), 2.60−1.05 (br, m, 72H, PCy$_3$ + THF). ^{31}P{^{1}H} NMR (THF, 25 °C): 36.2 (br, s). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): 44.4 (br, s). ^{31}P{^{1}H} NMR (CD_2Cl_2, −80 °C): 35.3 (br, s). ^{31}P{^{1}H} NMR (C_6D_5Cl, 70 °C): 46.0 (s, br).

[Re(H)(NO)(NOSiEt$_3$)(P^{i}Pr$_3$)$_2$][BAr$_4$′] (8a). From 3a. A 75 mg sample of **3a** (0.0524 mmol) was dissolved in 2 mL of C_6H_5Cl and then 2 mL of $HSiEt_3$ added. After 15 min the yellow solution was filtered, and 10 mL of pentane was layered over it. The mixture was kept at −35 °C for 24 h. After this time, a yellow crystalline solid was collected, washed with pentane (3 × 10 mL), and dried in vacuo to give 70 mg of **8a** (86.3%). Anal. Calcd for $C_{56}H_{70}N_2O_2SiP_2BF_{24}Re$: H, 4.56; C, 43.50; N, 1.81. Found: H, 4.39; C, 43.70; N, 1.86. IR (Nujol, ν_{NO}): 1667 (s). ^{1}H NMR (C_6D_5Cl): 8.23 (br, m, 8H, BAr$_4$′), 7.62 (br, m, 4H, BAr$_4$′), 4.53 (t, 1H, Re*H*, J_{H-P} = 41.0 Hz), 2.14 (m, 6H, P(C*H*Me$_2$)$_3$), 0.98 (m, 36H, P(CH*Me*$_2$)$_3$), 0.90 (t, 9H, Si(CH$_2$C*H*$_3$)$_2$), 0.70 (q, 6H, Si(C*H*$_2$CH$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_5-Cl): 57.8 (s). ^{29}Si NMR (C_6D_5Cl, TMS): 42.1 (m, br).

From 2a. A 85 mg sample of **2a** (0.0425 mmol) was dissolved in 1 mL of C_6H_5Cl and then 1 mL of $HSiEt_3$ added. The brown solution turns slowly red and finally yellow-brown. After 1 day yellow crystals were collected, washed with pentane (3 × 5 mL), and dried under vacuum, leaving 61 mg of **8a** (92.7%).

[Re(H)(NO)(NOSiEt$_3$)(PCy$_3$)$_2$][BAr$_4$′] (8b). A 50 mg sample of **3b** (0.0299 mmol) was dissolved in 0.5 mL of C_6H_5Cl and then 0.5 mL of $HSiEt_3$ added. The dark red solution became even darker, then gradually lighter and finally yellow. The solution was placed at −35 °C, and after 3 days yellow crystalls were collected, washed with pentane (3 × 5 mL), and dried in vacuo, leaving 45 mg of **8b** (84.25%). Anal. Calcd for $C_{74}H_{93}N_2O_2$-$SiP_2BF_{24}Re$: H, 5.25; C, 49.78; N, 1.57. Found: H, 5.02; C, 49.48; N, 1.52. IR (Nujol, ν_{NO}): 1677 (s). ^{1}H NMR (CD_2Cl_2): 7.72 (br, m, 8H, BAr$_4$′), 7.57 (br, m, 4H, BAr$_4$′), 4.74 (t, 1H, Re*H*, J_{H-P} = 41.8 Hz), 2.37−1.10 (m, 66H, PCy$_3$), 1.06 (t, 9H, Si(CH$_2$C*H*$_3$)$_2$), 0.94 (q, 6H, Si(C*H*$_2$CH$_3$)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): 46.8 (br, s). ^{13}C{^{1}H} NMR (C_6D_5Cl): 3.9 (s, Si(CH$_2$CH$_3$)$_3$, 6.2 (s, Si(CH$_2$*C*H$_3$)$_3$).

[Re(H)(NO){NOH$_2$NC$_5$H$_6$(CH$_3$)$_4$}(P^{i}Pr$_3$)$_2$][BAr$_4$′] (9a). From 3a. A solution of 50 mg of **3a** (0.0350 mmol) in 2 mL of C_6H_5Cl was placed in a 100 mL flask equipped with a Teflon valve. A 6 μL portion of 2,2,6,6-tetramethylpiperidine (0.0355 mmol) was then added and the solution placed under 950 mbar of H_2. The red solution turned brown immediately. The solvent was removed under vacuum and the oily residue recrystallized in CH_2Cl_2/pentane at −35 °C. After 2 days yellow crystals were collected, washed with pentane (3 × 10 mL), and dried in vacuo to give 45 mg of **9a** (70.9%). Anal. Calcd for $C_{59}H_{79}N_3O_2P_2$-$BF_{24}Re$: H, 5.05; C, 44.93; N, 2.66. Found: H, 4.90; C, 44.65; N, 2.82. IR (Nujol, ν_{NO}): 1561 (m), 1503 (m). ^{1}H NMR (CD_2Cl_2): 7.72 (br, m, 8H, BAr$_4$′), 7.57 (br, m, 4H, BAr$_4$′), 5.75 (br, s, 2H, *H*$_2$NC$_5$H$_6$(CH$_3$)$_4$), 4.30 (t, 1H, Re*H*, J_{H-P} = 37.5 Hz), 2.43 (m, 6H, P(C*H*Me$_2$)$_3$), 1.80−1.62 (m, 5H H$_2$NC$_5$*H*$_6$(CH$_3$)$_4$), 1.46 (s, 12H, H$_2$NC$_5$H$_6$(C*H*$_3$)$_4$), 1.26 (m, 36H, P(CH*Me*$_2$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 51.3 (s).

From 2a. A solution of 80 mg of **2a** (0.0400 mmol) in 2 mL of C_6H_5Cl was placed in a 100 mL flask equipped with a Teflon valve. A 7 μL portion of 2,2,6,6-tetramethylpiperidine (0.0403 mmol) was then added and the solution placed under 950 mbar of H_2. After some minutes the solution was concentrated under vacuum until 1 mL of C_6H_5Cl was left and then pentane layered. A microcrystalline yellow solid was collected in 24 h, washed with pentane (2 × 10 mL), and dried in vacuo to give 50 mg of **9a** (79.1%).

[Re(H)(NO){NOH$_2$NC$_5$H$_6$(CH$_3$)$_4$}(PCy$_3$)$_2$][BAr$_4$′] (9b). A heterogeneous mixture containing 54 mg of **3b** (0.0323 mmol) and 5.7 μL of 2,2,6,6-tetramethylpiperidine (0.0328 mmol) in 5 mL of C_6H_6 was placed in a 100 mL flask equipped with a Teflon valve and placed under 900 mbar of H_2. Upon stirring for 20 min the starting material dissolved and an oily residue precipitated. The solvent was removed under vacuum and the residue crystallized at −35 °C in CH_2Cl_2/pentane. After 3 days yellow crystals were collected, washed with pentane (2 × 10 mL), and dried in vacuo to give 35 mg of **9b** (60.6%). The crystals used for the X-ray diffraction study were obtained by slow vapor diffusion of pentane into a C_6H_5Cl solution of the complex. Anal. Calcd for $C_{77}H_{99}N_3O_2P_2BF_{24}Re$: H, 5.50; C, 51.00; N, 2.32. Found: H, 5.50; C, 51.09; N, 2.40. IR (Nujol, ν_{NO}): 1556 (m), 1506 (s). ^{1}H NMR (CD_2Cl_2): 7.72 (br, m, 8H, BAr$_4$′), 7.57 (br, m, 4H, BAr$_4$′), 5.51 (br, s, 2H, *H*$_2$NC$_5$H$_6$(CH$_3$)$_4$), 4.20 (t, 1H, Re*H*, J_{H-P} = 39.6 Hz), 2.20−1.10 (m, 66H, PCy$_3$), 1.48 (s, 12H, H$_2$NC$_5$H$_6$(C*H*$_3$)$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): 41.2 (br, s).

H$_2$/D$_2$ Equilibration Experiments. The equilibration was assumed to be complete when the ratio between the integrals of the H_2 and HD molecules in the ^{1}H NMR spectra of the solution remained constant. The equilibration times should be considered only as approximations, since accurate integral values of such low intensity signals are difficult to determine.

Using 2a. In two separate experiments 30 mg (0.0150 mmol) and 20 mg (0.0100 mmol) of **2a** in C_6D_5Cl or toluene-d_8, respectively (0.5 mL), were placed in NMR tubes which were degassed and filled with 1000 mbar of a 1:1 mixture of H_2 and D_2. At room temperature the ^{1}H NMR spectra showed that the equilibration was finished after 30 min in C_6D_5Cl and 10 min in toluene-d_8.

Using 3a. In an NMR tube 20 mg of **3a** (0.0140 mmol) dissolved in C_6D_5Cl (0.5 mL) was degassed and placed under 1000 mbar of a 1:1 mixture of H_2 and D_2. At room temperature the ^{1}H NMR spectrum showed that the equilibration was completed after 10 min.

Using 3b. In three separate experiments 20 mg of **3b** (0.0120 mmol) in toluene-d_8, C_6D_5Cl, or THF-d_8 (0.5 mL) was placed in NMR tubes which were degassed and filled with ca. 950 mbar of a 1:1 mixture of H_2 and D_2. At room temperature the ^{1}H NMR spectra showed that the equilibration was finished after 10 min in toluene and chlorobenzene. In the case of THF-d_8 only after 5 h formation of small amounts of HD was detected.

Acknowledgment. This work has been supported by the Swiss National Science Foundation (SNSF). We would like to thank Dr. Thomas Fox for his very valuable help in recording some of the NMR spectra included in this publication.

Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for **8a** and **9b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010409C