Rhenium Nitrosyl Complexes for Hydrogenations and Hydrosilylations

A. Choualeb, E. Maccaroni, O. Blacque, H. W. Schmalle, and H. Berke*

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

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The tris(acetonitrile)dibromonitrosylrhenium(I) compound (**1a**) was obtained by reduction of the paramagnetic $[NMe_4]_2[Re(NO)Br_5]$ salt with Zn in MeCN. Subsequent reaction of **1a** with THF produced the THF derivative $[Re(NO)(THF)(MeCN)_2Br_2]$ (**1b**). Reaction of **1b** with P*i*Pr$_3$, Pcy$_3$, or P(*p*-tolyl)$_3$ yielded bis(acetonitrile)-*cis*-dibromo(nitrosyl)-*trans*-bis(phosphine)rhenium complexes (R = *i*Pr **2a**, cy **2b**, *p*-tolyl **2c**). Treatment of **2a**,**b** with excess $NaBH_4$ produced the known borohydride complexes $[Re(H)(\eta^2\text{-}BH_4)(NO)(PR_3)_2]$ (R = *i*Pr **3a**, cy **3b**). Replacement of the BH_3 moiety of **3a**,**b** in THF by ethylene (1 bar) produced the dihydride complexes $[Re(H)_2(\eta^2\text{-}C_2H_4)(NO)(PR_3)_2]$ (**4**) (R = *i*Pr **a**, cy **b**). Protonation of **4a**,**b** with $HBF_4 \cdot OEt_2$ afforded H_2 and the monohydrido tetrafluoroborato species $[Re(H)(NO)(PR_3)_2(\eta^2\text{-}C_2H_4)(BF_4)]$ (R = *i*Pr **5a**, cy **5b**). X-ray diffraction studies were carried out on **1a**, **2b**,**c**, and **5b**. Complexes **4a**,**b** are catalytically active in olefin, imine, and ketone hydrogenations and in olefin and ketone hydrosilylations, as well as in the scrambling of H_2/D_2 to give HD under mild conditions.

I. Introduction

As a "noninnocent" ligand nitrosyl may take over special roles in transition metal chemistry. It supports different oxidation states of metal centers often accompanied by different coordination modes, and furthermore it exerts a relatively strong *trans*-influence or *trans*-effect, thus activating metal−ligand bonds. Manifestations of the latter influences are nitrosyl-substituted transition metal hydrides,[1] in which the M−H bonds show increased hydride transfer activity. In the attempt to exploit the ability of NO to tune transition metal hydrides toward catalytic activity, we were specifically interested in the development of new rhenium hydride catalysts for hydrogenations and hydrosilylations of unsaturated organic molecules. Our group recently reported several examples of rhenium mono- and dinitrosyl complexes that are active in these or related catalyzes.[2,3] We also studied the ethylene chemistry of Re(I) mononitrosyl hydride complexes, which demonstrated the general disposition to coordinate ethylene and to undergo organometallic reactions. In extension of this work we wanted to further explore the hydrogen/olefin chemistry and the catalytic potential of such complexes.

II. Results and Discussion

IIa. Preparation of Phosphine-Substituted Dibromo Nitrosyl Rhenium(I) Complexes. The orange complex *mer*-$[Re(NO)(MeCN)_3Br_2]$ (**1a**) is obtained as a solvate complex **1a**·MeCN by reduction of the paramagnetic salt $[NMe_4]_2$-$[Re(NO)Br_5]$[4] with Zn in MeCN and direct crystallization from this solvent. The solvate molecule can be removed *in vacuo*. **1a** has decent solubility only in MeCN (≈17 g/L at 25 °C) and CH_2Cl_2, has low solubility in MeOH and acetone, and is only sparingly soluble in Et_2O, THF, ethanol, and dioxane. ^{1}H NMR samples of **1a** in CH_2Cl_2 indeed showed two signals at 3.02 and 2.97 ppm (1:2 ratio), confirming the presence of the *mer*-substitution pattern (Scheme 1), but revealed after approximately 15 min also a signal for free MeCN originating from decoordination and gradual decomposition in this solvent.

In the ^{1}H NMR and ^{13}C NMR spectra of **1a** distinct resonances could be detected for the two *trans* and the unique *trans* Br Me groups and CN groups of the MeCN ligands. ATR-IR spectroscopy of **1a** did not reveal bands for the *mer*-$(MeCN)_3$ rhenium unit, which presumably is due to their too low intensities. The expected ν(NO) band was found to appear at 1691 cm^{-1}.

1a was additionally characterized by an X-ray diffraction study. Single crystals were grown in an NMR tube from a MeCN solution saturated at 60 °C and slow cooling to room temperature. Selected bond lengths and angles are reported in Table 1. As shown in Figure 1, **1a** possesses a pseudo-octahedral structure with *mer*-arranged MeCN ligands. The O(1)−N(1)−Re(1) angle of around 177° and the relatively short N(1)−O(1) bond length of 1.1260(9) Å gave evidence for a linear nitrosyl ligand (average bond length 1.18−1.22 Å).[5] The three MeCN molecules are coordinated practically linear to rhenium with N(3)−Re(1)−N(2) and N(4)−Re(1)−Br(2) angles of 173.3(3)° and 174.8(2)°, respectively.

The air-stable mixed solvento complex $[Re(NO)(THF)$-$(MeCN)_2Br_2]$ (**1b**) (Scheme 1) was obtained dissolving **1a** in THF and was isolated in pure form after recrystallization from THF/pentane. The facile MeCN exchange in **1a** is thought to originate mainly from the *cis*-labilization effect exerted by one of the two bromide ligands. In the ^{1}H NMR spectrum the coordinated THF of **1b** was indicated by multiplets at 1.81 and 3.64 ppm for the methylene groups and also in the ^{13}C NMR spectrum by singlets at 26.3 and 68.3 ppm for the corresponding

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

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Scheme 1

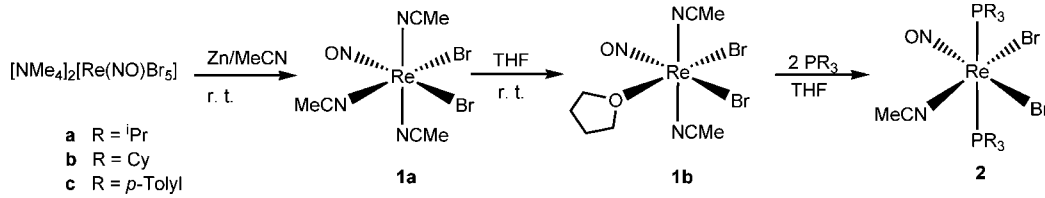


Table 1. Selected Bond Distances and Bond Angles in $ReBr_2(MeCN)_3(NO)\cdot C_2H_3N$ (1a)

bond distances (Å)		bond angles (deg)	
Re(1)−N(2)	2.073(8)	N(3)−Re(1)−N(2)	173.3(3)
Re(1)−N(3)	2.050(8)	N(4)−Re(1)−Br(2)	174.8(2)
Re(1)−N(4)	2.065(8)	N(1)−Re(1)−Br(1)	179.5(2)
Re(1)−N(1)	1.797(7)	O(1)−N(1)−Re(1)	176.7(7)
Re(1)−Br(1)	2.5672(11)	N(4)−Re(1)−N(2)	89.9(3)
Re(1)−Br(2)	2.5531(11)	N(3)−Re(1)−Br(2)	90.1(2)
N(1)−O(1)	1.126(9)	N(2)−Re(1)−Br(2)	90.4(2)

carbon atoms. The IR spectrum of **1b** reveals in the solid state a strong band at 1685 cm^{-1}, which confirms the presence of the NO ligand, and furthermore a weak band at 2277 cm^{-1}, which is assigned to the coordinated MeCN groups.

For various ligand substitution reactions **1b** turned out to be a superior starting material in comparison with **1a**, mainly because of its higher solubilities in most organic solvents. Therefore **1b** was used for the preparation of various phosphine-disubstituted complexes according to Scheme 2. Applying excess phosphine ligands at room temperature in THF allowed access to disubstituted $[Re(NO)(MeCN)(PR_3)_2Br_2]$ compounds (**2**) (R = *i*Pr **a**, cy **b**, *p*-tolyl **c**) obtained in good yields. Complexes **2a**−**c** are very air sensitive in solution, and **2b** and **2c** have low solubilities in many organic solvents.

2a−**c** were characterized by IR and ^1H NMR spectroscopy and elemental analyses. The ^1H NMR spectra in CD_2Cl_2 displayed besides the signals for the phosphine substituents singlets of the $Me_{acetonitrile}$ groups at 3.06, 3.08, and 1.77 ppm. The lower chemical shift of the Me signal of **2c** is suggested to

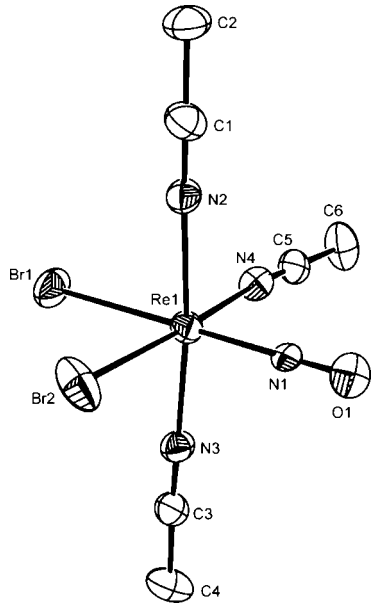
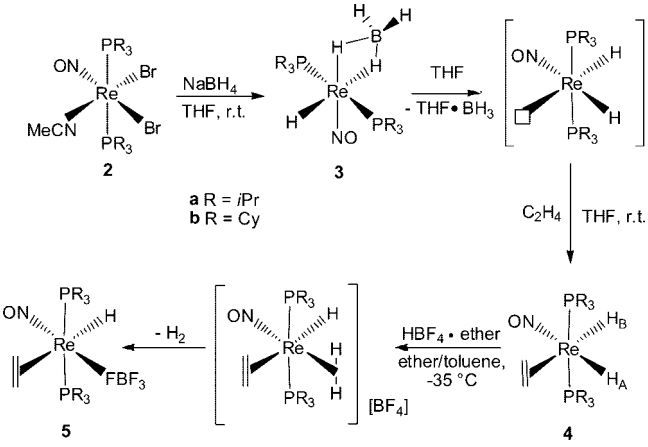


Figure 1. X-ray structure of complex **1a** (ORTEP representation with selected atomic labels). All hydrogen atoms and the MeCN solvate are omitted for clarity. The displacement ellipsoids are drawn with 50% probability.

Scheme 2



originate from aromatic shielding of the phosphine substituents. The $^{31}P\{^1H\}$ NMR spectra of **2a**−**c** each show one singlet for the two equivalent *trans*-phosphorus nuclei, and in the IR spectra strong bands in the range of 1679 − 1700 cm^{-1} were attributed to ν(NO) vibrations.

The pseudo-octahedral structures of **2b** and **2c** were determined by X-ray diffraction studies (Figure 2). Selected bond distances and angles of **2b** and **2c** are given in Table 2. **2b** crystallizes with 2 THF solvate molecules in the asymmetric unit, and in both structures NO and Br(2) are positionally disordered. The phosphine ligands are disposed approximately *trans*, slightly bending toward the bromides (P(1)−Re(1)−P(2) = 172.60(7)° (**2b**) and 173.51(3)° (**2c**); Re−P distances 2.4608(10)−2.5138(18) Å[5−7]), the bromides are located *cis*, and the MeCN and the nitrosyl ligands take places *trans* to a bromide. The MeCN moieties in **2b** and **2c** are practically linear with a Re(1)−N(2)−C(1) angle of 177.7(6)° (**2b**) and 172.2(4)° (**2c**),[8−11] and the Re−NCMe distances are 2.065(7) and 2.079(4) Å, close to the average value of 2.098 Å.[6,11] In addition the carbon−nitrogen (1.099(10) and 1.113(6) Å) and the carbon−carbon (1.488(13) and 1.464(7) Å) distances of the coordinated MeCN ligand are at the 3σ level within the average values of 1.136 and 1.470 Å.[12]

IIb. Synthesis of Di- and Monohydrido Ethylene Rhenium Complexes. Treatment of **2a** and **2b** with excess $NaBH_4$ leads to formation of the known hydride borohydride

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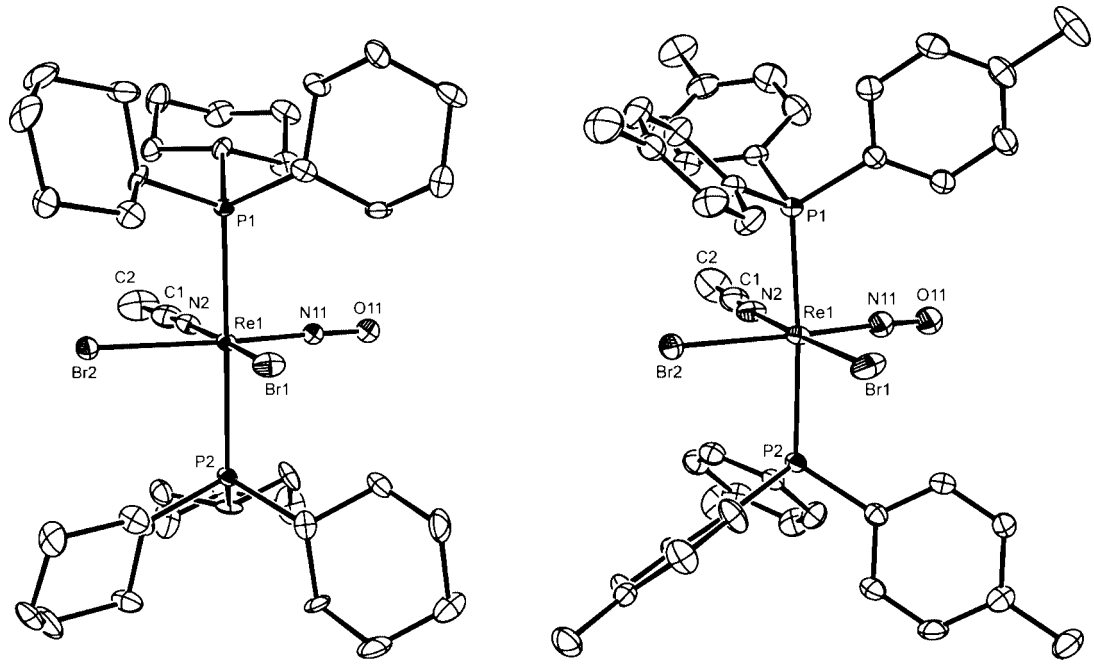

Figure 2. ORTEP drawing of the molecular structures of **2b** (left) and **2c** (right) (thermal ellipsoids are drawn at the 50% probability level). For both structures the observed disorder between the *trans* NO and Br ligands and all hydrogen atoms have been omitted for clarity. For **2b** the THF solvates are not shown, as well.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2b,c (values of disordered atoms are not given)

	2b	2c
Re(1)−P(1)	2.5138(18)	2.4760(10)
Re(1)−P(2)	2.5085(18)	2.4608(10)
Re(1)−N(2)	2.065(7)	2.079(4)
Re(1)−Br(1)	2.5804(10)	2.5608(6)
P(1)−Re(1)−P(2)	172.60(7)	173.51(3)
P(1)−Re(1)−Br(1)	86.31(5)	89.89(3)
P(1)−Re(1)−N(2)	92.74(16)	90.35(9)
P(2)−Re(1)−Br(1)	86.84(5)	87.29(3)
P(2)−Re(1)−N(2)	93.89(16)	92.81(9)
Br(1)−Re(1)−N(2)	175.83(17)	176.60(10)

complexes $[Re(H)(\eta^2\text{-}BH_4)(NO)(PR_3)_2]$ (**3**) (R = *i*Pr **a**, cy **b**) (Scheme 2). **3a**,**b** were obtained earlier by the reaction of the dihydrogen complexes $[Re(Br)_2(\eta^2\text{-}H_2)(NO)(PR_3)_2]$ with $[NBu_4]BH_4$.[4] In contrast to this reaction mode, substitution with sterically less hindered phosphines as in the $[Re(NO)(MeCN)(PMe_3)_2Cl_2]$ complex afforded in the reaction with $[BH_4]^-$ reduction of the CN triple bond[6,13] or under different reaction conditions formation of the dihydrido trisphosphine species $[Re(H)_2(NO)(PMe_3)_3]$. Removal of the BH_3 moieties of **3a**,**b** was achieved in the presence of THF, forming $H_3B\cdot$THF and ethylene (1 bar). The reactions to generate the substitution compounds $[Re(H)_2(\eta^2\text{-}C_2H_4)(NO)(PR_3)_2]$ (R = *i*Pr **4a**, cy **4b**) were instantaneous (Scheme 2).

4a,**b** were characterized by spectroscopic means (IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR). A satisfactory elemental analysis was obtained for **4a**, but not for **4b** presumably due to its liquid nature. In both cases the ATR IR spectrum and the spectrum in KBr indicated the presence of the coordinated ethylene (**4a** ν(C−H) 2925, 2875, 2835 cm^{-1}, **4b** ν(C−H), 2929, 2848 cm^{-1}). ν(C═C) bands were not detected. The coordinated NO ligand gave rise to ν(NO) bands at 1619 (**4a**) and 1614 cm^{-1} (**4b**).

The room-temperature NMR spectra of **4a**,**b** were interpreted in terms of hindered ethylene rotation and prefered alignment of the C═C bond along the P−Re−P vector.[14–17] This observation is consistent with those of the related $Re(NO)L_2Br_2(\eta^2\text{-}C_2H_4)$ structures, where the same olefin orientation was found.[7b,18–21] Two ^1H NMR resonances for two pairs of ethylene Z-protons and additionally a single ^{13}C NMR resonance provided evidence for this. The two hydride ligands H_A (*trans* to NO) and H_B (*trans* to ethylene) are observed as doublets of triplets: −0.75 Re−H_A, −5.92 Re−H_B for **4a** and −0.68 Re−H_A, −5.51 Re−H_B for **4b** (compare ref 7a[7a]).

Protonation of **4a**,**b** with an equimolar amount of $HBF_4\cdot OEt_2$ produced the monohydrido tetrafluoroborato compounds $[Re(H)(NO)(PR_3)_2(\eta^2\text{-}C_2H_4)(BF_4)]$ (R = *i*Pr **5a**, cy **5b**) (Scheme 2) presumably via initial generation of unstable cationic H_2 complexes, in which the H_2 ligands then get replaced with the BF_4^- anion. **5a**,**b** were characterized by their analytical and spectroscopic data, and their structures were confirmed by an exemplary single-crystal X-ray diffraction study of **5b**. The molecular structure is shown in Figure 3, and selected bond

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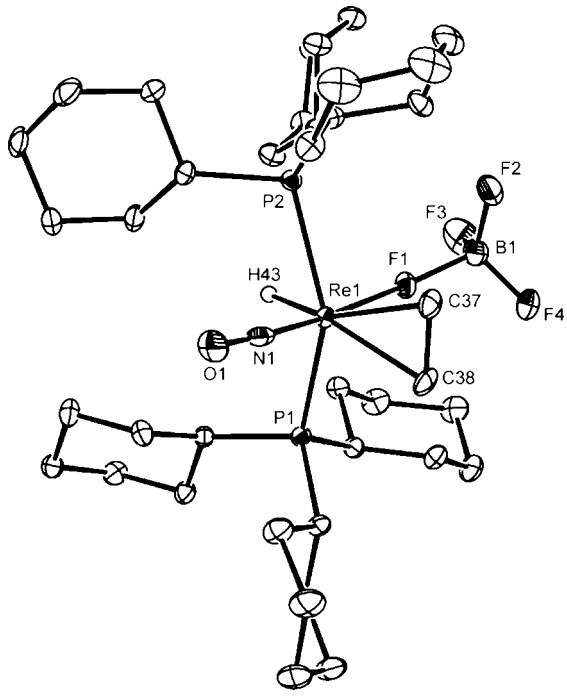

Figure 3. ORTEP drawing of the molecular structure of **5b** (thermal ellipsoids are drawn at the 30% probability level). The toluene solvate and selected hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 5b

Re(1)−P(1)	2.4813(14)	N(1)−Re(1)−P(1)	93.94(15)
Re(1)−P(2)	2.4817(13)	N(1)−Re(1)−P(2)	87.50(15)
Re(1)−N(1)	1.704(5)	F(1)−Re(1)−C(37)	81.17(17)
Re(1)−C(37)	2.215(5)	F(1)−Re(1)−C(38)	84.12(17)
Re(1)−C(38)	2.227(5)	F(1)−Re(1)−P(1)	90.85(9)
Re(1)−F(1)	2.177(3)	F(1)−Re(1)−P2	88.24(8)
C(37)−C(38)	1.404(8)	C(37)−Re(1)−C(38)	36.9(2)
N(1)−O(1)	1.219(6)	C(37)−Re(1)−P(1)	120.66(15)
F(1)−B(1)	1.485(7)	C(37)−Re(1)−P(2)	91.96(15)
P(1)−Re(1)−P(2)	146.83(4)	C(38)−Re(1)−P(1)	83.98(16)
N(1)−Re(1)−F(1)	175.19(17)	C(38)−Re(1)−P(2)	128.81(16)
N(1)−Re(1)−C(37)	96.8(2)	Re(1)−N(1)−O(1)	175.6(4)
N(1)−Re(1)−C(38)	96.8(2)	Re(1)−F(1)−B(1)	152.3(4)

distances and bond angles are given in Table 3. The coordination sphere of **5b** is pseudo-octahedral with the hydride *cis* to NO, which became evident from the X-ray diffraction study showing vacancy at this location. The phosphine ligands in **5b** are markedly bent toward the H ligand (P(1)−Re−P(2) = 146.83(4)°) favored by steric and electronic factors.[25,26] The C═C distance of 1.404(8) Å is close to that in the complex [Re($cy_2PCH_2SiMe_2$-$NSiMe_2CH_2Pcy_2$)(C-CH_3)(C_2H_4)][27] (1.422(3) Å) and is substantially elongated compared to free ethylene (1.337(2) Å).[28] The ethylene ligand is found in a conformation parallel to the P−Re−P axis, maximizing π back-bonding in this orientation. The nitrosyl ligand is approximately linear (Re−N−O angle of 175.6(4)°) with a Re−N distance of 1.704(5) Å in accordance with the values found in the literature.[5] Related to this, the N(1)−O(1) distance of 1.219(6) Å lies in the range 1.10−1.38 Å expected for linear NO^+ type binding.[5,29]

The ^{1}H NMR spectra of compounds **5a**,**b** showed unusual low-field resonances for the hydride ligands at 6.38 and 6.58 ppm, which appeared as doublets of triplets due to coupling with one fluorine atom and two magnetically equivalent phosphine ligands. This together with doublets observed at 32.5 and 26.2 ppm in the ^{31}P{^{1}H} NMR spectra suggests that BF_4^- coordination is persistent in solution. Hindered rotation of the Re-bound ethylene at room temperature as perhaps suggested by the X-ray structure of **5b** is not supported by the ^{1}H NMR spectra of **5a**,**b**, since for **5a** the corresponding resonances are broad and have no specific structure, and in the case of **5b** they are buried under the signals of the cyclohexyl groups. In the IR spectra of **5a**,**b** the ν(NO) absorptions are shifted by 65 and 62 cm^{-1} to higher wavenumbers in comparison with **4a**,**b**, confirming the cationic nature of these species.

The protonation of **4a**,**b** occurred regioselectively in accord with the findings for the protonation of the structurally related trisphosphine rhenium dihydride with $HClO_4$, giving the [Re(H)(NO)(CO)(PPh_3)$_3$(ClO_4)] complex with the hydride ligand assigned also *cis* to NO.[22] The protonation of the phosphonite dihydride complex [Re(H)$_2$(NO)(PPh_2OEt)$_3$] applying again strong acids such as $HBF_4 \cdot OEt_2$ and CF_3SO_3H was found to produce the thermally unstable *cis*-[Re(H)(NO)(PPh_2OEt)$_3$(Y)] species (Y = BF_4 or CF_3SO_3), which were trapped in its stereochemistry by regiospecific replacement of the Y group with hydrazines, forming *cis*-[Re(H)(NO)(NH_2NHR)(PPh_2OEt)$_3$] compounds.[23] However, in the case of the [Re(H)$_2$(NO)(CO)(PR_3)$_2$] compounds (R = Me, *i*Pr, O*i*Pr) the protonation with the weaker acid CF_3COOH was stereochemically different, generating *trans* H/NO complexes of the [Re(H)(NO)(CO)(PR_3)$_2$($OOCF_3$)][24a] type. Summarizing these observations it is anticipated that the regioselectivity of the protonation of *cis*-$ReH_2(NO)(PR_3)_2L$ compounds follows roughly the acid strength. Stronger acids protonate the H ligand *trans* to NO, which appears to be the slightly more negatively charged ("hydridic") H positions, as established by measurements of the deuterium quadrupole coupling constants of the corresponding deuterides.[24b] Weaker acids protonate and substitute *trans* to L.

III. Catalytic Explorations

IIIa. Reactions of 4a,b with Hydrogen and H_2/D_2 Scrambling. 4a,**b** were reacted at room temperature with H_2 in benzene or toluene with hydrogenation of the ethylene ligand to ethane and formation of the classical tetrahydride species [Re(H)$_4$(NO)(PR_3)$_2$] (R = *i*Pr **6a**, cy **6b**)[4] (Scheme 3). ^{31}P NMR monitoring at room temperature revealed that the reaction time is dependent on the H_2 pressure: it took 30 min with a $p(H_2)$ of 1.4 bar, but approximately 90 min when $p(H_2)$ was 0.7 bar. The formation of ethane was confirmed by a singlet at 0.76 ppm in the ^{1}H NMR spectrum.

Scheme 3 sketches a possible mechanism for the hydrogenation process of the ethylene ligand. The pathway is assumed to start with C_2H_4 insertion into a Re−H bond of **4a**,**b** and subsequent oxidative addition of H_2. The formed ethyl trihydrides undergo reductive elimination of C_2H_6, leaving a vacant site, to which H_2 can eventually be added, forming **6a**,**b**. Previous studies on **6a**,**b** made it plausible that these compounds have approximate pentagonal-bipyramidal geometries with a hydride and the NO group in apical positions and three hydrides and the two phosphines in the equatorial plane. The ^{1}H NMR spectrum of **6a**,**b** showed at room

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Scheme 3

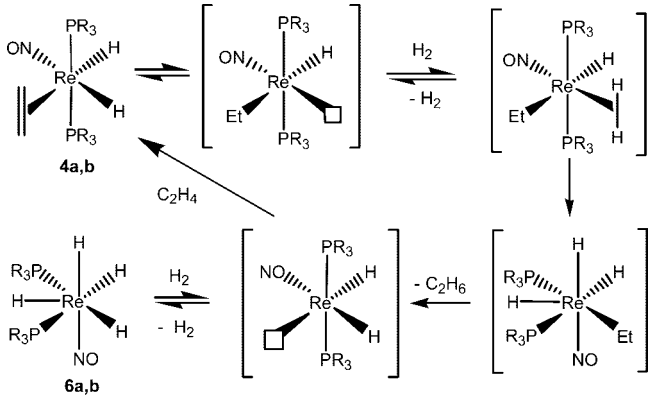

Table 4. Results of Catalytic Hydrogenation of Alkenes, Alkynes, Ketones, And Imines with H_2 under Pressure

substrate	cat.	cat./sub (mol %)	$p(H_2)$ (bar)	T (°C)	time (h)	TOF (h^{-1})	conv (%)
1-hexene	**4a**	1.7	68	75	3	17	85
	4b	1.2	75	70	1.5	47	92.5[a]
cyclohexene	**4a**	1	70	80	14	0.8	24
	4b	1.2	75	70	1	24	29
Ph-CH═N-Me	**4a**	1.8	65	80	17.5	1	33
	4b	1.2	65	80	22.0	0.6	16
Ph-CO-Me	**4a**	1.2	65	80	2.33	16	46
	4b	1.2	68	80	5	17	100
Ph-C≡CH	**4a**	0.6	65	80	5	31	92
	4b	0.6	65	80	2	3.3	4

[a] Mixture with *trans*-2-hexene (7.5%).

temperature in toluene-d_8 two broad high-field signals at −1.45 and −7.2 ppm, indicating at least two types of hydride ligands, and the broadness of the signals points to dynamic behavior. Indeed at −50 °C and below, the spectra split further into three resonances (multiplets) in a 2:1:1 ratio at −1.55, −1.80, and −7.09 ppm. Under C_2H_4 **6a**,**b** were converted back to **4a**,**b**, promoting again hydrogenation of C_2H_4 to C_2H_6 with the characteristics of a catalytic reaction (*vide infra*). This chemistry contrasts somewhat the H_2/C_2H_4 reaction found for the [($cy_2PCH_2SiMe_2NSiMe_2CH_2Pcy_2$)-$ReH_4$] complex, leading eventually to a [($cy_2PCH_2SiMe_2NSiMe_2$-CH_2Pcy_2)$ReH(C\text{-}CH_3)$] ethylidyne species involving C−H activation steps.[27,30]

In addition to hydrogenation observed for **4a**,**b**, instantaneous H_2/D_2 scrambling was observed to give HD at room temperature when solutions of **4a**,**b** were placed under 1.2 bar of an equimolar mixture of H_2 and D_2. The ^{1}H NMR spectra proved equilibration to form HD, which can be explained assuming an equilibrium between the coordinatively unsaturated [ReH_2-$(NO)(PR_3)_2$] derivatives (R = *i*Pr, cy) and the dihydrides **6a**,**b**.[4] Toggling back and forth between these species is accompanied by addition and elimination of the various isotopomers of H_2 (Scheme 3).

IIIb. Catalytic Activity of 4a,b in Homogeneous Hydrogenations. Using **4a**,**b** catalytic hydrogenations of several olefins, alkynes, ketones, and imines were explored in benzene in a steel autoclave at 70 or 80 °C and under pressures of around 70 bar of H_2 (Table 4). For volatile, liquid substrates and products the catalysts were separated by vacuum transfer or by exposing the reaction mixture to air and filtration through silica. For linear olefins, ketones, and alkynes the hydrogenations furnished moderate turnover frequencies with however satisfying conversions. The hydrogenation of acetophenone revealed with **4b** good activity with 100% conversion. Monitoring the catalytic hydrogenation reaction of phenyl acetylene with ^{1}H NMR spectroscopy revealed selective formation of styrene, and under the given conditions styrene could not be hydrogenated further to ethyl benzene. For the cyclic olefin cyclohexene the reaction time was quite long without reaching completion of the conversion. Hydrogenation of the imine PhCH═NPh was sluggish, with both derivatives **4a**,**b** generating the corresponding amine at such a slow pace that the reaction could not easily be distinguished from a stoichiometric process. The catalytic performances of **4a**,**b** were moderate, and as far as the small number of selected substrates allows to conclude some chemoselectivity can be deduced in favor of olefinic species and ketones. There was no great difference in the performance of **4a** and **4b**.

Table 5. Results of Catalytic Hydrosilylation of Cyclohexene and Ketones

substrate	cat.	cat/sub (mol %)	temp (°C)	time (h)	TOF (h^{-1})	conv (%)
cyclohexene/Et_3SiH	**4a**	0.5	80	3	54	81
PhCOMe/Ph_3SiH	**4a**	0.1	70	2	500	100
PhCOMe/Ph_3SiH	**4b**	0.5	70	2	100	100
PhCOMe/Et_3SiH	**4a**	0.5	70	0.25	800	100
PhCOMe/Et_3SiH	**4b**	0.5	70	0.25	800	100

IIIc. Catalytic Activity of 4a,b in Homogeneous Hydrosilylations. The catalytic activity of **4a**,**b** in hydrogenations prompted us to study also hydrosilylations, which are considered to be related to hydrogenations.[31] Traditional hydrosilylation catalysts are Pt-[32] or Rh-based,[33] although several highly active early transition metals[34,35] and lanthanide-based catalysts[36] have also been reported. In contrast, efforts to develop homogeneous rhenium-based catalysts for hydrosilylations with rhenium in low oxidation states have been limited. For instance the rhenium dinitrosyl complexes [$Re(P\textit{i}Pr_3)_2(NO)_2$][$B(C_6F_5)_4$], [Re(H)-$(P\textit{i}Pr_3)_2(NO)(NOB(C_6F_5)_3]$, and [$Re(H)(P\textit{i}Pr_3)_2(NO)(NOEt)$]-[$(B(C_6F_5)_4$] were found to be effective in ketone hydrosilylation.[2]

The progress of each reaction according to Table 5 was monitored by NMR spectroscopy, and the identity of each hydrosilylation product was assured by ^{1}H NMR spectroscopy and GC-MS. As a general manifestation the rates of hydrosilylations normally do not follow the same trends as for hydrogenations. This is also seen in this work. For instance hydrosilylation of the linear olefin 1-hexene and the imine of Table 4 could not be achieved at all, while these substrates showed at least some hydrogenation activities. On the other hand the catalytic hydrosilylations of cyclohexene and benzophenone with either Et_3SiH or Ph_3SiH and **4a**,**b** showed much better performances than in the hydrogenation cases. The hydrosilylations of acetophenone even rapidly and selectively produced products over the course of 15 to 20 min in the case of Et_3SiH and 2 h in the case of Ph_3SiH (Table 5).

IIId. Mechanism of the Hydrogenations and Hydrosilylations with 4a,b. A generalized catalytic cycle for the hydrogenation and hydrosilylation with **4a**,**b** is suggested in Scheme 4. Starting from **4a**,**b** the catalytic hydrogenations and

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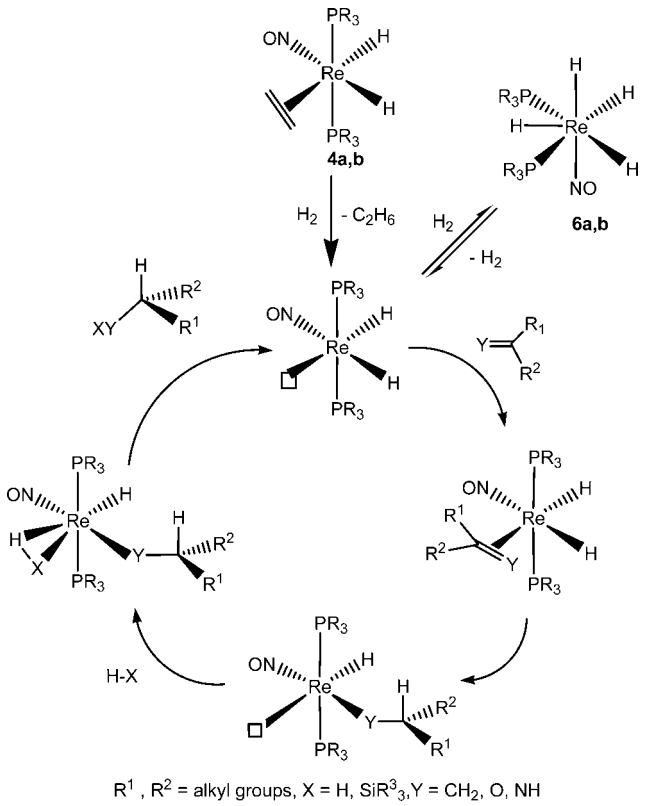
Scheme 4



hydrosylilations proceed first with insertion of the ethylene ligand into the Re−H bond, and subsequently loss of ethane occurs to give the $16e^-$ species $[ReH_2(NO)(PR_3)_2]$. On a sidetrack the $[ReH_2(NO)(PR_3)_2]$ derivatives and **6a**,**b** are in equilibrium with each other following the H_2/D_2 scrambling pathway of Scheme 3. The substrates $Y = CR^1R^2$ ($Y = CH_2$, NH_2, O) are then added to the unsaturated species $[ReH_2(NO)(PR_3)_2]$, which then undergoes insertion into the $Re-H_{cis}$ bond, leaving again a vacant site, to which H_2 is supposed to be added. Reductive elimination leads to liberation of the hydrogenated/hydrosilated alkane/amine/alcohol products.

IV. Conclusion

In this paper the syntheses of the new rhenium precursors $[Re(NO)(MeCN)_3Br_2]$, $[Re(NO)(THF)(MeCN)_2Br_2]$, and $[Re(NO)(MeCN)(PR_3)_2Br_2]$ were developed to establish a reactive hydride chemistry with nitrosyl phosphine rhenium derivatives. Key compounds were the dihydride-ethylene complexes $[Re(H)_2(\eta^2\text{-}C_2H_4)(NO)(PR_3)_2]$. Exploratory studies revealed a quite unexpected olefin and hydrogen chemistry, which could be turned into catalytic hydrogenations and hydrosilylations based on the $[Re(H)(NO)(PR_3)_2]^+$ fragments as the persistent and invariant units in these catalyses. Although the performance of these reactions was not yet optimum and comparable to the level of full competitiveness with existing such processes, these findings further promote rhenium as a metal with potential in homogeneous catalysis.

V. Experimental Section

All operations were carried out under a nitrogen atmosphere using a M. Braun 150 G-B glovebox. The solvents were dried over sodium/benzophenone (THF, Et_2O, hydrocarbons) or P_2O_5 (CH_2Cl_2, MeCN) and distilled under N_2 prior to use. The deuterated solvents used in the NMR experiments were dried over sodium/benzophenone (C_6D_6, toluene-d_8, THF-d_8) or P_2O_5 (CD_2Cl_2, CD_3CN) 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 NMR resonances of the deuterated solvent. ^{31}P chemical shifts are relative to 85% H_3PO_4. Microanalyses were carried out at the Anorganisch-chemisches Institut of the University of Zürich. IR spectra were recorded on a Bio-Rad FTS-45 spectrometer. $[NMe_4]_2[ReBr_5(NO)]$ was prepared analogous to ref 4.

Preparation of *mer*-$[Re(NO)(MeCN)_3Br_2]$ (1a). A mixture of $[NMe_4]_2[ReBr_5(NO)]$ (3.0 g, 3.9 mmol) and an excess of Zn powder (2.56 g, 39 mmol) in 50 mL of MeCN was stirred for 3 days at room temperature. After filtration the residue was washed with MeCN (4 × 5 mL) and the solvent was removed *in vacuo* to leave behind an orange solid, which was washed with water (3 × 10 mL) and dried *in vacuo*, which removes the MeCN solvate. Yield of **1a**: 1.45 g (73.8%). IR (ATR, cm^{-1}): 1691 (vs, ν(NO)). ^1H NMR (300.1 MHz, CD_3CN, ppm): δ 2.96 (s, 6H), 2.94 (s, 3H). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_3CN, ppm): δ 4.23 (s, CH_3), 133.7 (s, 2 CN), 134.3 (s, CN). Anal. Calcd for $C_6H_9N_4OBr_2Re$: C, 14.44; H, 1.82; N, 11.22. Found: C, 14.60; H, 1.77; N, 11.14.

Preparation of $[Re(NO)(THF)(MeCN)_2Br_2]$ (1b) from $[NMe_4]_2[ReBr_5(NO)]$ via 1a. An excess of Zn (0.80 g, 12.3 mmol) was added to a solution of $[NMe_4]_2[ReBr_5(NO)]$ (1.3 g, 1.7 mmol) in 100 mL of MeCN. The mixture was stirred at room temperature for 3 days, the orange solution of **1a** was filtered, the residue was washed with MeCN (4 × 5 mL), and the solvent was evaporated *in vacuo*. The solid was extracted with THF and recrystallized at room temperature from THF/pentane to afford red crystals of **1b** (0.63 g, 1.26 mmol, 73%) after 2 days. IR (ATR, cm^{-1}): 2277 (w, ν(MeC≡N)), 1685 (vs, ν(NO)). ^1H NMR (500.25 MHz, CD_3CN, ppm): 3.64 (m, 4H, (CH_2CH_2O)-Re), 2.98 (s, 6H, MeCN-Re), 1.81 (m, 4H, (CH_2CH_2O)-Re). ^{13}C NMR (125.8 MHz, CD_3CN, ppm): 133.9 (s, Me*C*N), 68.3 (s, (CH_2CH_2O)-Re), 26.3 (s, (CH_2CH_2O)-Re) 4.3 (s, *Me*CN-Re). Anal. Calcd for $C_8H_{14}Br_2N_3O_2Re$ (530.23): C, 18.12; H, 2.66; N, 7.92. Found: C, 18.4; H, 2.60; N, 8.03.

Preparation of $[Re(NO)(P\mathit{i}Pr_3)_2(MeCN)Br_2]$ (2a). A solution of $[Re(NO)(THF)(MeCN)_2Br_2]$ (0.22 g, 0.42 mmol) and excess P*i*Pr_3 (0.42 mL, 2.2 mmol) was heated in 40 mL of THF for 12 h. The solution was filtered through Celite, and the solvent and the excess phosphine were removed *in vacuo*. Recrystallization of the residue from THF/pentane afforded light orange crystals after 1 week at −30 °C. Yield of **2a**: 0.25 g, 0.33 mmol, 80%. IR (ATR, cm^{-1}): 2266(w, ν(MeC≡N)), 1684 (vs, ν(NO)). ^1H NMR (300.1 MHz, CD_2Cl_2, ppm): 3.07 (s, 3H, MeCN-Re), 3.03−2.86 (m, 6H, $(CH_3)_2CHP$), 1.47−1.34 (m, 36H, $(CH_3)_2CHP$). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6, ppm): −7.2 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, ppm): 24.4 (t, J(PC) = 10.7 Hz, $(CH_3)_2CHP$), 20.1 and 19.5 (2s,$(CH_3)_2CHP$). Anal. Calcd for $C_{20}H_{45}Br_2N_2OP_2Re$ (737.546)·$^1/_4$pentane: C, 33.78; H, 6.40; N, 3.71. Found: C, 33.92; H, 6.30; N, 3.80.

Preparation of $[Re(NO)(Pcy_3)_2(MeCN)Br_2]$ (2b). A solution of $[Re(NO)(THF)(MeCN)_2Br_2]$ (0.11 g, 0.21 mmol) and excess Pcy_3 (0.30 g, 1.0 mmol) was heated in 35 mL of THF overnight. The solution was filtered through Celite, and about 70 mL of hexane was layered over this solution. After 1 week at room temperature, light orange crystals were collected, washed with MeCN, cold toluene (2 × 5 mL), cold THF (2 × 5 mL), and pentane, and dried *in vacuo* to give **2b** (0.14 g, 0.15 mmol, 71%). IR (KBr, cm^{-1}): 2259(w, ν(MeC≡N)), 1679 (vs, ν(NO)). ^1H NMR (300.1 MHz, CD_2Cl_2, ppm): 3.08 (s, 3H, MeCN-Re), 2.78−1.27 (m, 66H, $P(C_6H_{11})_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, ppm): −19.1 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 35.5 (t, J(PC) = 10.1

Hz, $P(C_6H_{11})_3$), 29.5, 28.4 and 27.1 (3s, $P(C_6H_{11})_3$). Anal. Calcd for $C_{38}H_{69}Br_2N_2OP_2Re$ (977.93): C, 46.67; H, 7.11; N, 2.86. Found: C, 46.93; H, 7.00; N, 2.95.

Preparation of [Re(NO){P(*p*-tol)$_3$}$_2$(MeCN)Br$_2$] (2c). A solution of $[Re(NO)(THF)(MeCN)_2Br_2]$ (0.078 g, 0.147 mmol) and excess of P(*p*-tol)$_3$ (0.234 g, 0.772 mmol) was heated in 40 mL of THF for 15 h. The solution was then concenterd, filtered over Celite, and recrystallized at room temperature from THF/pentane to afford after 5 days light orange crystals of **2c**, which were dried *in vacuo* (0.117 g, 0.114 mmol, 77%). IR (KBr, cm^{-1}): 2279(w, ν(MeC≡N)), 1700 (vs, ν(NO)). ^1H NMR (300.1 MHz, CD_2Cl_2, ppm): 7.75−7.19 (m, 24H, P(*p*-$(C_7H_7)_3$), 2.37 (s, 18H, P(*p*-$(C_7H_7)_3$), 1.77 (s, 3H, MeCN-Re). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, ppm): −6.3 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 140.6 (s), 135.17 (m), 129.6 (t, *J*(PC) = 24.1 Hz, 129.01 (m), 21.6 (s, P(*p*-$(C_7H_7)_3$), 14.4 (s, Me*C*N-Re), 3.7 (s, *Me*CN-Re). Anal. Calcd for $C_{44}H_{45}Br_2N_2OP_2Re$ (1025.8): C, 51.51; H, 4.42; N, 2.73. Found: C, 51.41; H, 4.48; N, 3.15.

Preparation of [Re(H)(η^2-BH$_4$)(NO)(P*i*Pr$_3$)$_2$] (3a). A solution of **2a** (0.157 g, 0.21 mmol) and excess of $NaBH_4$ (0.036 g, 0.95 mmol) in 20 mL of THF was stirred at room temperature for 12 h. The orange solution was filtered over Celite, and the solvent was evaporated under vacuum. Extraction with pentane affords pure [Re(H)(η^2-BH_4)(NO)(P*i*Pr$_3$)$_2$] (**3a**) (0.095 g, 0.17 mmol, 81%). All the spectroscopic data are in agreement with those previously reported in the literature.[4]

Preparation of [Re(H)(η^2-BH$_4$)(NO)(Pcy$_3$)$_2$] (3b). A solution of **2b** (0.082 g, 0.08 mmol) and excess $NaBH_4$ (0.015 g, 0.40 mmol) in 20 mL of THF was stirred at room temperature for 24 h. The orange solution was filtered over Celite, and the solvent was evaporated under vacuum. Extraction with a mixture of pentane/toluene (9:1) affords pure [Re(H)(η^2-BH_4)(NO)-(Pcy$_3$)$_2$] (**3b**) (0.06 g, 0.08 mmol, 92%). All the spectroscopic data are in agreement with those previously reported in the literature.[4]

Preparation of [Re(H)$_2$(η^2-C$_2$H$_4$)(NO)(P*i*Pr$_3$)$_2$] (4a). The complex **3a** (0.08 g, 0.15 mmol) was dissolved in 15 mL of THF in a 60 mL Young tap Schlenk vessel and sealed under 1 bar of C_2H_4. The solution was stirred for 1 h, and then the solvent and the gas were removed under reduced pressure. The residue was extracted with pentane to give pure pale yellow, viscous **4a** (0.068 g, 0.12 mmol, 83%). IR (ATR, cm^{-1}): 2925, 2875, 2835 (s, ν(C−H)), 1843 (w, ν(Re−H)), 1619 (vs, ν(NO)). ^1H NMR (500.2 MHz, C_6D_6, ppm): 2.24, (br, 2H, H_2C=CH_2), 2.12 (br, 2H, H_2C=CH_2), 3.07−2.97 (m, 6H, $(CH_3)_2CHP$), 1.57−1.41 (m, 18H, $(CH_3)_2CHP$), 1.39−1.31 (m, 18H, $(CH_3)_2CHP$), −0.75 (dt, ^1H, ^2J(HH) = 6.9 Hz, ^2J(PH) = 35.9 Hz), Re−H_A, −5.92 (dt, ^1H, ^2J(HH) = 8.1 Hz, ^2J(PH) = 28.0 Hz, Re−H_B). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, ppm): 36.8 (s). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, ppm): 29.2 (t, *J*(PC) = 13.1 Hz, $(CH_3)_2CHP$), 23.1 (br, H_2C=), 21.0 and 19.3 (2s,$(CH_3)_2CHP$). The complex was a viscous liquid, and due to this, a satisfactory elemental analysis could not be obtained.

Preparation of [Re(H)$_2$(η^2-C$_2$H$_4$)(NO)(Pcy$_3$)$_2$] (4b). Similar to the synthesis of **4a**, compound **4b** (0.051 g, 0.06 mmol, 84%) was obtained by the reaction of **3b** (0.06 g, 0.08 mmol) and C_2H_4. IR (KBr, cm^{-1}): 2929, 2848 (s, ν(C−H)), 1858 (w, ν(Re−H)),1614 (vs, ν(NO)). ^1H NMR (300.1 MHz, toluene-d_8, ppm): 2.28−0.88 (m, 70H, H_2C=CH_2 and P$(C_6H_{11})_3$), −0.68(dt, 1H, ^2J(HH) = 7.9 Hz, ^2J(PH) = 36.3 Hz, Re−H_A), −5.51 (dt, 1H, ^2J(HH) = 7.7 Hz), ^2J(PH) = 25.7 Hz, Re−H_B). $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8, ppm): 27.5 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, ppm): 39.7 (t, *J*(PC) = 12.8 Hz, P$(C_6H_{11})_3$), 31.6 and 31.2 (2s, H_2C=CH_2), 30.5, 29.5, 28.3, and 27.3 (4s, P$(C_6H_{11})_3$). Anal. Calcd for $C_{38}H_{72}NOP_2Re$ (807.138)·$^1/_3$pentane: C, 57.32; H, 9.22; N, 1.68. Found: C, 57.70; H, 9.34; N, 1.79.

Preparation of [Re(H)(η^2-C$_2$H$_4$)(NO)(P*i*Pr$_3$)$_2$][BF$_4$] (5a). A cooled, dilute solution of HBF_4·ether (54% in ether, 0.016 g, 0.054 mmol) in 1 mL of ether was added dropwise to a solution of **4a** (0.031 g, 0.054 mmol) in 8 mL of ether at −30 °C. The mixture was allowed to stir at room temperature for 15 h, then filtered over Celite. The solvent was removed *in vacuo*, and the residue was washed with pentane, extracted with toluene, and recrystallized from toluene/pentane at −30 °C to afford the oily yellow complex **5a** (0.023 g, 0.04 mmol, 65%). IR (ATR, cm^{-1}): 2969, 2936, 2878 (s, ν(C−H)), 2025 (w, ν(Re−H)), 1684 (vs, ν(NO)). ^1H NMR (200.0 MHz, toluene-d_8, ppm): 6.38 (dt, 1H, ^2J(HF) = 5.8 Hz, ^2J(PH) = 34.8 Hz), 2.85 (br, 4H, H_2C=CH_2), 2.58−2.37 (m, 6H, $(CH_3)_2CHP$), 1.24−1.12 (m, 18H, $(CH_3)_2CHP$). $^{31}P\{^1H\}$ NMR (80.9 MHz, toluene-d_8, ppm): 32.5 (d, ^2J(PF) = 16.5 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, toluene-d_8, ppm): 35.7 (br, H_2C=), 26.6 (t, *J*(PC) = 12.3 Hz, $(CH_3)_2CHP$), 19.6 and 19.5 (2s,$(CH_3)_2CHP$). Anal. Calcd for $C_{20}H_{47}BF_4NOP_2Re$ (652.55): C, 36.81; H, 7.26; N, 2.14. Found: C, 36.93; H, 7.45; N, 2.29.

Preparation of [Re(H)(η^2-C$_2$H$_4$)(NO)(Pcy$_3$)$_2$][BF$_4$] (5b). 5b was prepared by the reaction of HBF_4·ether (54% in ether, 0.022 g, 0.07 mmol) diluted with 1 mL of ether with **4b** (0.060 g, 0.07 mmol) in a mixture of 10 mL ether/toluene (4:1) at −30 °C. The mixture was allowed to stir at room temperature for 17 h and then filtered over Celite. The solvents were removed *in vacuo*, and the residue was washed with pentane and dried *in vacuo* to afford **5b** as a yellow powder. Yield: 0.047 g, 0.05 mmol, 71%. Crystals suitable for X-ray diffraction were obtained from a concentrated solution of **5b** in toluene by slow evaporation and were dried *in vacuo*. IR (ATR, cm^{-1}): 2925, 2851 (s, ν(C−H)), 1963 (w, ν(Re−H)), 1687 (vs, ν(NO)). ^1H NMR (200.0 MHz, toluene-d_8, ppm): 6.58 (dt, 1H, ^2J(HF) = 4.4 Hz, ^2J(PH) = 34.3 Hz), 2.82−0.89 (m, 70H, H_2C=CH_2 and P$(C_6H_{11})_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, toluene-d_8, ppm): 26.2 (d, ^2J(PF) = 17.5 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, toluene-d_8, ppm): 37.3 (t, *J*(PC) = 11.4 Hz, P$(C_6H_{11})_3$), 36.2 (br, H_2C=), 31.58 and 31.20, 29.85 and 29.57, 28.28 and 28.21, 26.85 and 26.54 (4 × 2 s, P$(C_6H_{11})_3$). Anal. Calcd for $C_{38}H_{71}BF_4NOP_2Re$ (893.94). C, 51.11; H, 8.01; N, 1.57. Found: C, 51.40; H, 8.21; N, 1.53.

Catalytic Hydrogenation Using Complexes 4a,b under 68−75 bar of H$_2$. The reactions were carried out in a steel autoclave. An appropriate amount of the catalyst (see ratios in Table 4) was dissolved in toluene-d_8, and 1 mmol of 1-hexene, cyclohexene, acetophenone, *N*-benzylidenemethylamine, or phenyl acetylene was added by a microsyringe. The autoclave was pressurized with different H_2 pressures (Table 4), and the reaction mixture was stirred and heated to around 70−80 °C for several hours. The reaction mixture was analyzed by NMR spectroscopy at given reaction times. ^1H NMR spectroscopy of the products: Hexane (199.97 MHz, C_6D_6, 25 °C, ppm): 0.82 (m, *J*(H,H) = 6.9 Hz, Me), 1.17 (br, CH_2). Cyclohexane (199.97 MHz, C_6D_6, 25 °C, ppm): 1.40 (s). *N*-Methylbenzylamine (199.97 MHz, C_6D_6, 25 °C, ppm): 7.06 (m, br, CH Ph), 3.43 (br, CH_2), 2.15 (br, Me), 2.04 (m, br, NH). α-Methylbenzyl alcohol (199.97 MHz, C_6D_6, 25 °C, ppm): 1.30 (d, *J*(H,H) = 6.5 Hz, CH_3), 2.98 (br, OH), 4.62 (q, *J*(H,H) = 6.5 Hz, CH), 7.22 (m, CH Ph). Styrene (199.97 MHz, C_6D_6, 25 °C, ppm): 5.26 (d, *J*(H,H) = 10.8 Hz, 1H CH_2), 5.78 (d, *J*(H,H) = 17.4 Hz, 1H CH_2), 6.75 (dd, *J*(H,H) = 10.9 Hz, CH), 7.18−7.60 (m, CH Ph).

Catalytic Hydrosilylation with 4a,b. Complexes **4a**,**b** were mixed with the substances in a 1:1 ratio in C_6D_6 or toluene-d_8. The solution was transferred to a Young NMR tube and was frozen. The N_2 atmosphere was substituted by H_2. The mixture was warmed to the required temperature, and the NMR spectrum was recorded. The conversions were determined by the integration of the olefin and the alkane ^1H NMR signals. Characteristic ^1H NMR resonances of the products: $C_6H_{11}SiMe_3$ (199.97 MHz, toluene-d_8, 80 °C, ppm): 1.39 (s, 16 H, Me, cy). PhCH(OSiEt$_3$)Me (199.97 MHz, toluene-d_8, 80 °C, ppm): 1.38 (d, 3H, *J*(H,H) = 6.3 Hz, Me), 4.75 (q, 1H, *J*(H,H) = 6.3 Hz, CH). PhCH(OSiPh$_3$)Me (199.97 MHz, toluene-

Table 6. Summary of Crystallographic Data for Complexes 1a, 2b, 2c, and 5b

	1a	2b	2c	5b
empirical formula	$C_6H_9Br_2N_4ORe$, C_2H_3N	$2(C_{38}H_{69}Br_2N_2OP_2Re)$, $3(C_4H_8O)$	$C_{44}H_{45}Br_2N_2OP_2Re$	$2(C_{38}H_{71}BF_4NOP_2Re)$, C_7H_8
molecular weight	540.25	2172.12	1025.78	1877.95
color	orange	orange	light orange	pale yellow
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	*P*1	$P\bar{1}$	$P\bar{1}$	*C* 2/*c*
a (Å)	8.1046(13)	9.9073(12)	10.8340(13)	35.9176(15)
b (Å)	9.4847(15)	14.117(2)	12.4513(15)	12.8715(6)
c (Å)	10.0314(17)	17.523(2)	15.6724(18)	18.6666(7)
α (deg)	86.04(2)	106.501(16)	79.551(14)	90
β (deg)	82.60(2)	93.603(15)	86.688(14)	99.542(5)
γ (deg)	85.370(19)	96.888(16)	76.017(14)	90
V (Å^3)	761.6(2)	2320.8(5)	2031.9(4)	8510.4(6)
Z	2	1	2	4
calcd density (g cm^{-3})	2.356	1.554	1.677	1.466
μ (mm^{-1})	13.126	4.447	5.072	2.981
transmn range	0.778−0.925	0.752−0.909	0.320−0.813	0.714−0.805
cryst size (mm)	0.31 × 0.17 × 0.14	0.02 × 0.05 × 0.21	0.04 × 0.14 × 0.18	0.07 × 0.08 × 0.12
hkl limiting indices	−11/11, −13/13, −14/14	−11/12, −18/17, −23/23	−15/15, −17/17, −22/22	−44/43, −15/15, −22/22
F(000)	496	1108	1012	3880
θ limits (deg)	2.89−30.52	2.71−28.04	2.77−30.43	1.96−25.93
no. of measd reflns	12 842	25 597	32 318	32 427
no. of unique reflns	4210	10 310	11 163	8207
no. of params	159	462	476	450
$R_1[I > 2\,(I)]$, R_1 all data	0.0449, 0.0600	0.0409, 0.0932	0.0314, 0.0577	0.0299, 0.0489
$wR_2[I > 2\,(I)]$, wR_2 all data	0.1200, 0.1350	0.0771, 0.0850	0.0618, 0.0663	0.0697, 0.0709
GOF (for F^2)	1.086	0.688	0.817	0.729
max./min.	−4.19, 3.06	−1.55, 1.13	−1.93, 1.11	−0.58, 1.64

d_8, 80 °C, ppm): 1.44 (d, 3H, *J*(H,H) = 6.2 Hz, Me), 5.17 (q, 1H, *J*(H,H) = 6.2 Hz, CH).

Catalytic H_2/D_2 Scrambling. Complexes **4a**,**b** were dissolved in C_6D_6 and transferred to a Young tap NMR tube, and the solution was frozen. The N_2 atmosphere was removed and substituted by 1200 mbar of a 1:1 mixture of H_2 and D_2. The ^{1}H NMR spectrum showed that the equilibration was instantaneous at room temperature. ^{1}H NMR (300.0 MHz, toluene-d_8, ppm): 4.41 (t, ^1J(HD) = 43 Hz).

X-ray Structure Analyses of Compounds 1a, 2b, 2c, and 5b. All four crystals were protected in hydrocarbon oil and prepared for the X-ray experiment by using a polarizing microscope. Selected crystals of **1a**·MeCN, 2 **2b**·3 THF, **2c**, and **5b**·C_6H_5Me were crystallized from MeCN saturated at 60 °C, THF/pentane, THF/pentane, and toluene, respectively. They were mounted on the tip of a glass fiber and immediately transferred to the goniometer of an imaging plate detector system (Stoe IPDS diffractometer). The crystals were cooled to 183(2) K in an Oxford Cryogenic System. The crystal-to-image distances were set to 50, 60, 50, and 70 mm, resulting in θ_{max} values given in Table 4. For compounds **2b** and **5b** oscillation and for **1a** and **2c** rotation scan modes were applied. A total of 8000 reflections with $I > 6\sigma(I)$ were selected for the cell parameter refinements of all four structures. A total of 12 842 (**1a**), 25 597 (**2b**), 32 318 (**2c**), and 32 427 (**5b**) diffraction intensities were collected, of which 4210, 10 310, 11 163, and 8207 were unique (R_{int} = 8.70, 9.08, 5.98, and 5.35%) after data reduction. Numerical absorption corrections[37] based on 11, 6, 9, and 6 crystal faces were applied with FACEitVIDEO and XRED.[38] The four structures were solved by the Patterson methods using the SHELXS-97 program.[39] Interpretation of the difference electron density maps, preliminary plot generation, and checking for higher symmetry were done with PLATON[40] and with the LEPAGE program.[41] All heavy atoms were refined with the program SHELXL-97[42] using anisotropic displacement parameters; more crystallographic details are given in Table 6 and in the exptl_special_details of the CIF files (see CCDC deposition numbers). Positions of H atoms were calculated after each refinement cycle (riding model). Structural plots were generated using ORTEP.[43]

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond distances, and angles for **1a**, **2b**, **2c**, and **5b**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org. This material has also been deposited in.cif format with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 664340 (**1a**), CCDC 664341 (**2b**), CCDC 664342 (**2c**), and CCDC 664343 (**5b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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