Solvent Stabilization and Hydrogenation Catalysis of Trimethylphosphine-Substituted Carbonyl Rhenium Cations

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A series of cationic complexes were designed as catalysts for imine hydrogenation processes, and it was anticipated that for this purpose naked 16e$^-$ cations or relatively labile solvent-coordinated ones possessing noncoordinating counterions would suffice. Solvento complexes $[Re(CO)_3(PMe_3)_2(S)][BAr^F]$ (**4(PhCl)** and **4(THF)**) and [*mer*-$Re(CO)_2(PMe_3)_3(S)][BAr^F]$ (**5-(PhCl)** and **5(THF)**) ($BAr^F = [B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$; S = PhCl)) were obtained from their corresponding hydride complexes **1** and **2** after treatment with $[Ph_3C][BAr^F]$ in chlorobenzene. The five-coordinated cationic complex $[Re(CO)(PMe_3)_4][BAr^F]$ (**6**) ($BAr^F = [B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$) was obtained by the reaction of $ReH(CO)(PMe_3)_4$ (**3**) with 1 equiv of $[Ph_3C][BAr^F]$ in chlorobenzene. Hydride abstraction also occurred except for **1** from **2** and **3** with $B(C_6F_5)_3$, producing $[Re(CO)_2(PMe_3)_3(S)][BH(C_6F_5)_3]$ and $[Re(CO)(PMe_3)_4][BH(C_6F_5)]$ (S = PhCl, THF). Treatment of $ReH(CO)_3(PMe_3)_2$ (**1**) and $ReH(CO)_2(PMe_3)_3$ (**2**) with 1 equiv of [isopropyliso-propylideneiminium][BAr^F] in chlorobenzene at room temperature produced a mixture of **4(PhCl)** and $[Re(CO)_3(PMe_3)_2(HN^iPr_2)][BAr^F]$ (**8**) or in the case of **2** a mixture of **5(PhCl)** and $[Re(CO)_2(PMe_3)_3(HN^iPr_2)][BAr^F]$ (**9**) within a few minutes. After 4 h both mixtures were completely converted to **8** and **9**, respectively. **8** and **9** could also be obtained reacting **4-(PhCl)** and **5(PhCl)** with excess diisopropylamine. Under mild conditions several imines underwent hydrogenation with H_2 in the presence of **4(PhCl)** and **5(PhCl)** as catalysts. **6**, however, showed only poor catalysis. Further studies revealed details of the mechanism of the catalytic process. X-ray diffraction studies were carried out on the molecular structures of **4(PhCl)**, **5(PhCl)**, **6**, and **5(THF)**.

Introduction

Homogeneous hydrogenation of organic substrates is the most widely studied class of catalyzed organometallic reactions.[1−24] The key step of these processes is the activation of H_2 by transition-metal species. Experimental and theoretical studies on the interaction of the H_2 molecule with a metal center have provided valuable insight into how the activation of the H−H bond might occur.[25] The H_2 ligand possesses the binding capacities of both σ-donation and π-back-donation. Depending on the balance of these parts either homolytic or heterolytic cleavage of the H_2 molecule is preferred. Thus, at an electron-rich metal complex which is dominated by d(M)−$\sigma^*(H_2)$ back-donation, homolytic cleavage of the H−H bond is favored.[14,26,27] In contrast, at an electron-deficient metal center $\sigma(H_2)$−d(M) donation is expected to dominate, which should preferentially lead to heterolytic cleavage of the H−H bond (Scheme 1). Here the dihydrogen ligand acts as a Bronsted acid.[28−31] The pK_a of several H_2 ligands in the complexes have been

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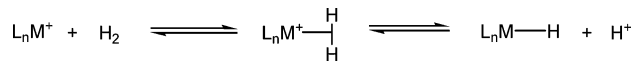
Scheme 1



determined, and the increase in acidity indeed goes along with a decrease in electron density at the metal center.[32−34] Norton and co-workers have previously reported the ionic hydrogenation of iminium cations.[33]

Thus, the pathway for the heterolytic activation of dihydrogen via deprotonation of H_2 complexes is highly dependent on the ratio of σ-donation/π-acceptor and may be adjusted by the ancillary ligand sphere. For example, [*cis*-$Re(CO)_4(PR_3)(\eta\text{-}H_2)]^+$ is much more acidic than [*mer*-$Re(CO)_3(PR_3)_2(\eta\text{-}H_2)]^+$, the earlier bearing more of the π-acceptors CO, allowing its deprotonation by moderately strong bases. It was also demonstrated by Kubas and Heinekey that the solvento complexes $[Re(CO)_4(PR_3)(S)]^+$ and $[Re(CO)_3(PR_3)_2(S)]^+$ (S = CH_2Cl_2, Et_2O) do react with dihydrogen.[22,24,35−39] Recently, our group has studied the formation and reactivity of such dihydrogen complexes.[40−46] It was found that rhenium hydrides $[Re(CO)_{5-n}(PMe_3)_nH]$ (n = 4, 3, and 2)[47,48] react with strong acids to give dihydrogen complexes $[Re(CO)_{5-n}(PMe_3)_n(\eta\text{-}H_2)]^+$ (n = 3 and 2) at low temperature and in the case of $[Re(CO)_{5-n}(PMe_3)_nH_2]^+$ (n = 4) the dihydride complex.[44,45] The hydrides react with acidic alcohols to give equilibrium mixtures of the hydrides and the dihydrogen complexes. The dihydrogen species $[Re(CO)_{5-n}(PMe_3)_n(\eta\text{-}H_2)]^+$ (n = 4 and 3) derived from the corresponding hydrides and acidic alcohols allow stoichiometric hydrogenations of simple imines, aldehydes, and ketones. We note that although heterolytic activation of molecular hydrogen is thought to play a role in homogeneous hydrogenation reactions, conclusive experimental evidence is still rare. We paid special attention to the hydrogenation of imines, as they may be basic enough to induce heterolytic cleavage of the H−H bond in the dihydrogen complexes. Therefore, we decided to further systematically explore the possibility of a heterolytic activation of dihydrogen by unsaturated $[Re(CO)_{5-n}(PMe_3)_n]^+$ cations (n = 2, 3, and 4) or their solvent-stabilized analogues. These compounds are formally derived from the corresponding hydrides by hydride abstraction. It was the first aim of this work to test whether such cations can be produced by such a route, and furthermore it was sought to test their catalytic potential with regard to hydrogenations of imines.

Results and Discussion

Reactions of $ReH(CO)_3(PMe_3)_2$ (1), $ReH(CO)_2(PMe_3)_3$ (2), and $ReH(CO)(PMe_3)_4$ (3) with $[Ph_3C][BAr^F]$ in Chlorobenzene. Both $ReH(CO)_3(PMe_3)_2$ (**1**) and $ReH(CO)_2(PMe_3)_3$ (**2**) react with 1 equiv of $[Ph_3C][BAr^F]$ in chlorobenzene to give the solvent-coordinated complexes $[Re(CO)_3(PMe_3)_2(S)][BAr^F]$, **4(PhCl)**, and [*mer*-$Re(CO)_2(PMe_3)_3(S)][BAr^F]$, **5(PhCl)** ($BAr^F$ = $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$; S = PhCl) (Scheme 2).

The complexes were isolated by crystallization from PhCl at low temperatures and obtained as yellow crystalline compounds in high yields. The coordination of chlorobenzene was confirmed by single-crystal X-ray diffraction. This contrasts the observation of Heinekey on a related bisphosphine complex, which was isolated as a 16e$^-$ unsaturated compound after crystallization from CH_2Cl_2. Solvent coordination did not occur in this case. Kubas et al. have reported that related monophosphine-substituted cations revealed CH_2Cl_2 attachment, suggesting a more electron-deficient and even sterically less crowded cationic Re center.[23,24,35−37] This all shows that there is a subtle balance of stereoelectronic factors, which govern solvent coordination. The coordination of PhCl in **4(PhCl)** and **5(PhCl)** was nevertheless quite unexpected, since the PhCl molecule is a weaker donor ligand than CH_2Cl_2, which was used in the Kubas and Heinekey experiments. PhCl as a solvent should therefore show a higher propensity to produce the "naked" cations, and furthermore there should be a higher tendency to yield the naked 16e$^-$ species with increasing amounts of phosphine substituents. Therefore, at least in the case of the reaction of **2** with $[Ph_3C][BAr^F]$ one would expect the formation of **5** rather than that of **5(PhCl)**. There are some literature reports on only a few examples of η^1-PhCl coordination to a metal center,[49,50] the structures of which were however not confirmed by X-ray diffraction studies. The structures of **4(PhCl)** and **5(PhCl)** are shown in Figures 1 and 2. Selected bond lengths and angles of **4(PhCl)** and **5(PhCl)** are given in Tables 1 and 2. The coordination geometries of **4(PhCl)** and **5(PhCl)** are similar to those of the corresponding hydrides.[47] In both complexes PhCl occupies the original positions of the hydride. The Re−Cl−C units reveal bending at the chlorine atom, which is about 113° in both compounds. The Re−Cl distances in **4(PhCl)** and **5(PhCl)** are 2.5613(11) and 2.560(3) Å,

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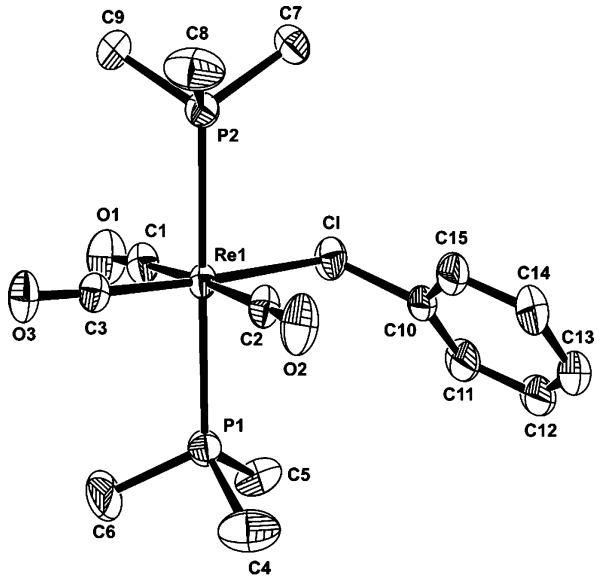


Figure 1. Molecular structure of **4(PhCl)** (30% probability displacement ellipsoids). Hydrogen atoms, chlorobenzene, and the BAr^F anion are omitted for clarity.

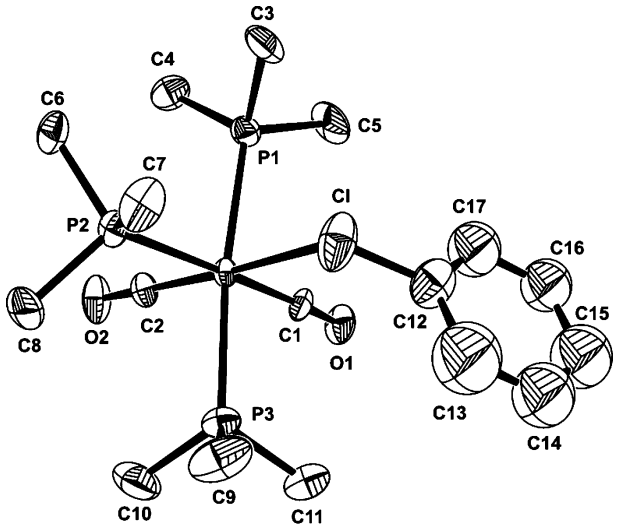


Figure 2. Molecular structure of **5(PhCl)** (30% probability displacement ellipsoids). Hydrogen atoms and the BAr^F anion are omitted for clarity.

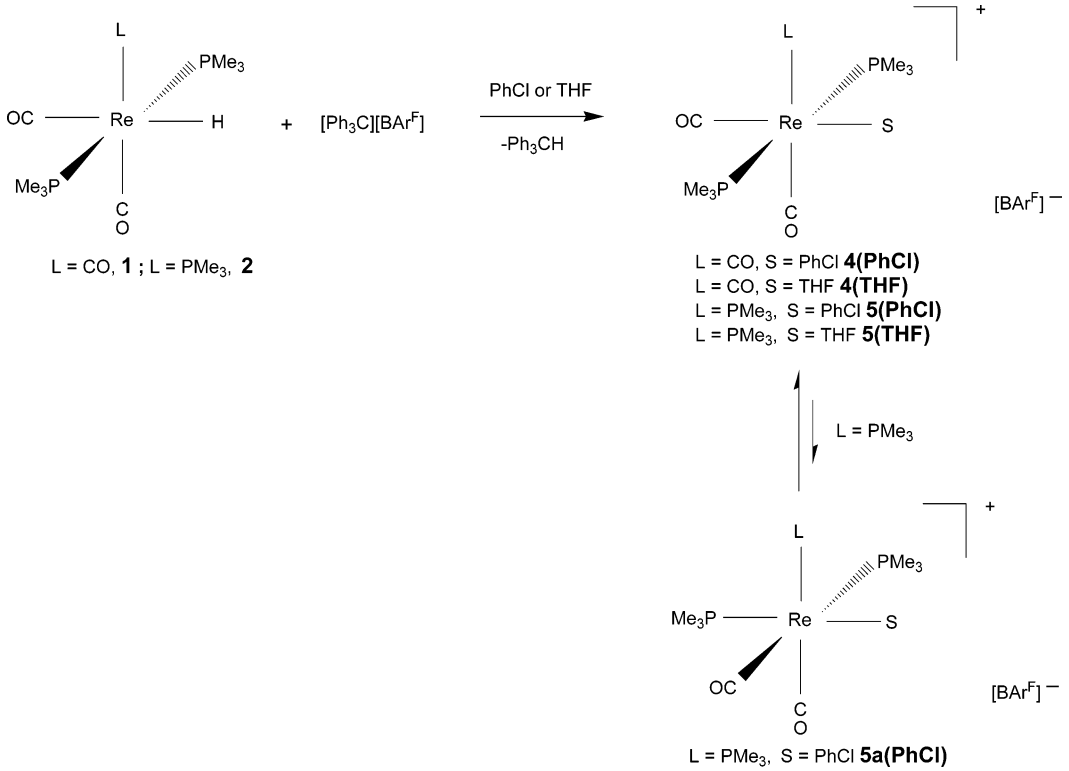
respectively, which are comparable to those found for CH_2Cl_2 coordination in $[Re(CO)_4(P^iPr_3)(CH_2Cl_2)][BAr^F]$, 2.554(2) Å, and $[Re(CO)_4(PPh_3)(CH_2Cl_2)][BAr^F]$, 2.546(2) Å.[35−37] As expected, the Re−Cl distances of **4(PhCl)** and **5(PhCl)** are significantly longer than the corresponding neutral L_nRe−Cl compounds (2.478 Å in $Re(CO)_3(PEt_3)_2Cl$[51] and 2.511 Å in *fac*-$Re(CO)_2(Ph_2PCH_2C(CH_3)CH_2PPh_2CH_2PPh_2)Cl$).[52] The Re−C distances for the CO group trans to PhCl (1.884(4) Å in **4(PhCl)** and 1.896(2) Å in **5(PhCl)**) are definitely shorter than those for the CO groups trans to a CO or PMe_3 ligand (1.975 Å average in **4(PhCl)**) or CO trans to PMe_3 (1.946 Å in **5(PhCl)**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 4(PhCl)

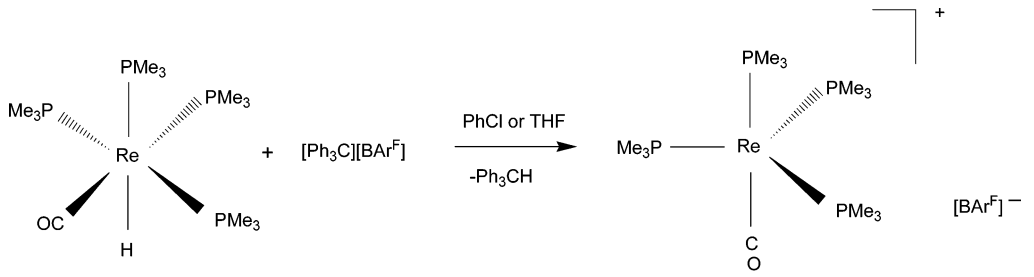
Re(1)−Cl(1)	2.5613(11)	Re(1)−C(1)	1.967(4)
Re(1)−C(2)	1.982(4)	Re(1)−C(3)	1.884(4)
Re(1)−P(1)	2.4236(12)	Re(1)−P(2)	2.4221(11)
C(1)−O(1)	1.145(5)	C(2)−O(2)	1.135(5)
C(3)−O(3)	1.148(5)	Cl(1)−C(10)	1.763(4)
P(1)−Re(1)−P(2)	178.57(4)	C(1)−Re(1)−C(2)	176.47(18)
Cl(1)−Re(1)−C(3)	173.98(12)	Cl(1)−Re(1)−C(1)	87.22(13)
Cl(1)−Re(1)−C(2)	95.89(12)	Cl(1)−Re(1)−P(1)	91.23(4)
Cl(1)−Re(1)−P(2)	88.96(4)	Re(1)−Cl(1)−C(10)	113.18(16)

The spectroscopic data of complexes **4(PhCl)** and **5(PhCl)** in solution are consistent with their solid state structures. The ^{31}P NMR spectrum of **4(PhCl)** shows a singlet at −32 ppm, and the ^1H NMR spectrum exhibits

Scheme 2



Scheme 3



3 **6**

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 5(PhCl)

Re(1)−Cl	2.560(3)	Re(1)−C(1)	1.947(8)
Re(1)−C(2)	1.896(8)	Re(1)−P(1)	2.436(2)
Re(1)−P(2)	2.4638(19)	Re(1)−P(3)	2.428(2)
C(1)−O(1)	1.128(9)	C(2)−O(2)	1.153(10)
Cl −C(12)	1.690(9)		
P(1)−Re(1)−P(3)	173.36(8)	C(1)−Re(1)−P(2)	177.0(2)
Cl−Re(1)−C(2)	175.5(2)	Cl−Re(1)−C(1)	94.0(2)
Cl−Re(1)−P(2)	88.98(8)	Cl−Re(1)−P(1)	86.91(12)
Cl−Re(1)−P(3)	89.31(12)	Re(1)−Cl−C(12)	114.2(4)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 6

Re(1)−C (1)	1.83(4)	Re(1)−P(11^i)	2.453(6)
Re(1)−P(21)	2.457(8)	Re(1)−P(12)	2.407(6)
Re(1)−P(22)	2.377(7)	C(1)−O(1)	1.12(4)
P(11^i)−Re(1)−P(12)	106.4(3)	P(11^i)−Re(1)−P(22)	113.2(3)
P(12)−Re(1)−P(22)	139.1(3)	C(1)−Re(1)−P(21)	177.5(12)
C(1)−Re(1)−P(11^i)	86.9(12)	C(1)−Re(1)−P(12)	88.1(12)
C(1)−Re(1)−P(22)	84.4(12)	P(21)−Re(1)−P(11^i)	94.5(3)
P(21)−Re(1)−P(12)	93.5(3)	P(21)−Re(1)−P(22)	93.2(3)

a broad singlet at 1.21 ppm for the methyl groups. The phosphorus resonances of the complex **5(PhCl)** in PhCl are interpreted in terms of a higher order AB_2 spectrum with very close chemical shifts at −35.7 ppm (1P) and −34.9 ppm (2P). Complex **5(PhCl)** appears to transform in PhCl in a quite strongly temperature-dependent equilibrium to other isomers. At temperatures below 0 °C signals for this second species **5a(PhCl)** are observed, which are almost not visible above room temperature. It also exhibits an AB_2 pattern in the ^{31}P NMR with resonances at −43.3 and −44.0 ppm. It is assumed that its structure corresponds to a *fac*-phosphine-substituted cation. The rearrangement process is assumed to involve PhCl dissociation and subsequent rearrangement of the coordination sphere. Further support for the structure of **5a(PhCl)** comes from the fact that there is a great similarity of the ^{31}P NMR spectra with those of the *fac*−*mer* isomerization of the related hydrides in polar solvents.[53]

Interestingly, *cis*-ReH(CO)$(PMe_3)_4$ (**3**) reacts with 1 equiv of $[Ph_3C][BAr^F]$ in chlorobenzene to give the "naked" 16e$^-$ complex $[Re(CO)(PMe_3)_4][BAr^F]$ (**6**) (BAr^F = $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$) (Scheme 3). The complex was isolated as yellow crystals in high yield by crystallization from PhCl at low temperature.

The structure of **6** was also confirmed by an X-ray diffraction study, which revealed a five-coordinate rhenium center (Figure 3). Selected bond lengths and angles are given in Table 3. The coordination geometry around the rhenium atom can be best described as a highly distorted trigonal bipyramid. The P11^i, P12, and P22 atoms occupy the equatorial plane, in which the main distortion from the ideal geometry is found. Their arrangement deviates from a triangle in the following way: while the angle P11^i−Re1−P12 is close to 120°,

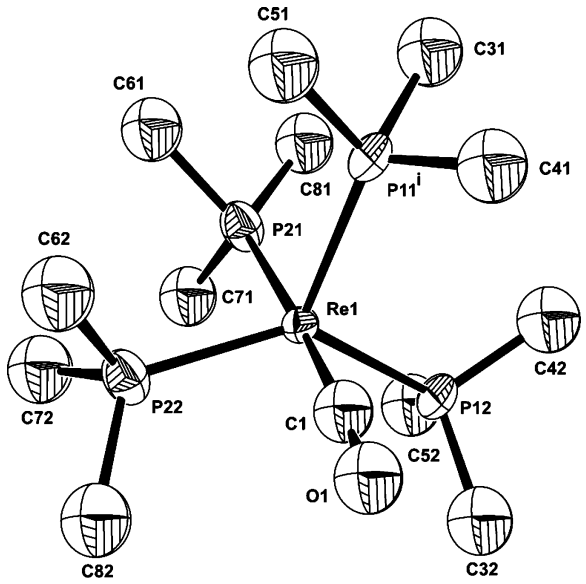


Figure 3. Molecular structure of **6** (30% probability displacement ellipsoids). Hydrogen atoms and the BAr^F anion are omitted for clarity. i = 1.5−x, y, 1.5−z. 2-axis symmetry is removed.

the angles P11^i−Re1−P22 and P12−Re1−P22 are 106.4(3)° versus 139.1(3)°. Thus, a leaning over of P22 toward P11^i with respect to its ideal position of P22 has occurred, which can be interpreted in terms of a pseudo-Jahn−Teller distortion.[54,55] This change in geometry affects the doubly degenerate d-orbital set of an ideal trigonal bipyramid occupied by six electrons having a triplet ground state. The degeneracies of the d-orbital sets are lifted, which consequently induces a singlet ground state with energetic stabilization of the system. The angles between the axial phosphine ligand (P21) and the equatorial ones are close to 90° and show therefore only little distortion with respect to the

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geometry of an ideal trigonal bipyramid. Presumably the solvent-deficient five-coordinate structure gains stabilization not only from the described electronic effect but also from the fact that a high degree of donor substitution causes accumulation of electron density on the metal center, which leads to electronic repulsion of entering ligands. Furthermore there is steric congestion of the four phosphine ligands, which apparently do not leave enough room for the attachment of a just weakly coordinating ligand. The average of the four Re−P distances of **6** is 2.424 Å, which is close to the values of the complexes **4(PhCl)** (2.423 Å) and **5(PhCl)** (2.443 Å). The Re−CO distance in **6** is 1.83(4) Å, which is shorter than the related average distance in complex **4(PhCl)**.

The ^{31}P NMR and ^{1}H NMR spectra of complex **6** in PhCl display qualitatively a signal pattern similar to that of the parent *cis*-hydride **3**. Two doublets of triplets are observed in the ^{31}P NMR appearing at −42.7 and −47.9 ppm, respectively, together with a doublet of doublets at −49.1 ppm. Furthermore in the ^{1}H NMR spectrum a triplet at 1.18 ppm, a doublet at 1.05 ppm, and another doublet at 0.98 ppm were observed. This is indicative of a dynamic process moving one of the equatorial PMe_3 groups (P22 in the solid state structure of **6**). It shifts place from one side to the other rapidly on the NMR time scale, thereby simulating a more symmetric environment with averaging of the other two equatorial P nuclei (P11^{i} and P12 in the solid state structure of **6**). An averaging of all three equatorial P atoms apparently does not take place. It would indeed require another geometric rearrangement pathway, which however could be of higher energy.

Reactions of $ReH(CO)_3(PMe_3)_2$ (1), $ReH(CO)_2(PMe_3)_3$ (2), and *cis*-$ReH(CO)(PMe_3)_4$ (3) with $[Ph_3C][BAr^F]$ in THF. Complexes **1**, **2**, and **3** react with 1 equiv of $[Ph_3C][BAr^F]$ in THF to afford the corresponding solvent-coordinated complexes $[Re(CO)_3(PMe_3)_2(THF)][BAr^F]$, **4(THF)**, $[mer\text{-}Re(CO)_2(PMe_3)_3(THF)][BAr^F]$, **5(THF)**, and the "naked" species **6**. The reactions in THF are instantaneous and much faster than in PhCl. The characterization of the new species is based on their spectroscopic data in comparison with their analogous complexes **4(PhCl)** and **5(PhCl)**. The ^{31}P NMR spectrum of $[Re(CO)_3(PMe_3)_2(THF)][BAr^F]$, **4(THF)**, in THF-$d_8$ appears as a singlet at −28 ppm. The ^{1}H NMR spectrum consists of a singlet at 1.30 ppm for the methyl groups. Similarly, the NMR spectra of $[Re(CO)_2(PMe_3)_3(THF)][BAr^F]$, **5(THF)**, are very close to those of complex **5(PhCl)**; however, from the NMR spectra there was no indication for a *mer*−*fac* rearrangement. For instance the ^{31}P NMR spectrum shows a very related splitting pattern with a triplet at −39.2 ppm and a doublet at −29.5 ppm. The meridional structure of **5(THF)** was confirmed by an X-ray diffraction study and is shown in Figure 4. Selected bond lengths and angles of **5(THF)** are given in Table 4. The Re−O3 distance in **5(THF)** is 2.266(4) Å. The Re−C distance for the ReCO group trans to THF is 1.886 Å, significantly shorter than for the CO group trans to PMe_3 (1.918 Å), reflecting the larger trans-influence of a PMe_3 versus a THF ligand. Therefore, it is reasonable to assume that these new THF ligating species **4(THF)** and **5(THF)** are structurally related to their chlorobenzene congeners **4(PhCl)** and **5(PhCl)**. It is interesting to note that **6** does not even coordinate THF despite the fact that the electron-donating capacity of this molecule is significantly higher than that of PhCl. This indicates that the steric repulsion is indeed a major factor for the existence of **6**, which presumably prevents access of many types of solvent molecules to its rhenium center.

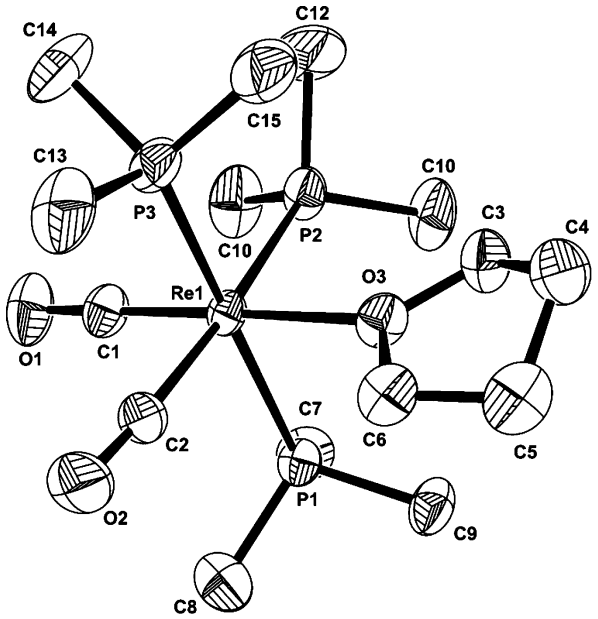

Figure 4. Molecular structure of **5(THF)** (30% probability displacement ellipsoids). Hydrogen atoms and the BAr^F anion are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 5(THF)

Re(1)−C(1)	1.886(6)	Re(1)−P(1)	2.4430(15)
Re(1)−P(3)	2.4161(17)	Re(1)−O(3)	2.266(4)
Re(1)−P(2)	2.4918(17)	C(1)−O(1)	1.164(7)
P(3)−Re(1)−P(1)	171.33(6)	O(3)−Re(1)−P(1)	87.06(12)
P(3)−Re(1)−P(2)	95.59(7)	O(3)−Re(1)−P(2)	95.06(12)
P(1)−Re(1)−P(2)	90.93(6)	C(1)−Re(1)−O(3)	177.9(2)
C(1)−Re(1)−C(2)	84.5(3)	C(2)−Re(1)−O(3)	93.4(2)
O(3)−Re(1)−P(3)	86.68(12)	C(1)−Re(1)−P(3)	93.2(2)

Reactions of $ReH(CO)_2(PMe_3)_3$ (2) and $ReH(CO)(PMe_3)_4$ (3) with $B(C_6F_5)_3$ in Chlorobenzene and THF. While complex **1** does not react with $B(C_6F_5)_3$, complexes **2** and **3** are transformed with 1 equiv of $B(C_6F_5)_3$ in both chlorobenzene and THF to give the corresponding hydride-abstracted solvento species $[Re(CO)_2(PMe_3)_3(S)][BH(C_6F_5)_3]$ (S = chlorobezene and THF) and the complex $[Re(CO)(PMe_3)_4][BH(C_6F_5)_3]$, respectively. All the complexes of the type $[Re(CO)_2(PMe_3)_3(S)][BH(C_6F_5)_3]$ and $[Re(CO)(PMe_3)_4][BH(C_6F_5)]$ are noncrystalline oily substances, which made their isolation in pure form difficult. The assignments of their structures therefore had to be based on spectroscopic grounds in solution, but could nevertheless safely be assigned in comparison with the data for complexes **5(PhCl,THF)** and **6**. The spectroscopic data of the cationic parts of these compounds were thus very similar to those with the $[BAr^F]^-$ counterion and are therefore not discussed here. The anions however gave rise to some changes in the ^{1}H NMR spectra. The most important is the appearance of an additional broad quartet type signal at about 4 ppm, which was attributed to the hydrogen atom of the $[BH(C_6F_5)_3]^-$ anion,

which has also been identified in [Zr][$BH(C_6F_5)_3$] complexes by Marks et al.[56−61] Due to the noncrystalline nature of the [$BH(C_6F_5)_3$]$^-$ salts, satisfactory elemental analysis could not be obtained.

Precatalytic Investigations of the Solvent-Stabilized Cations 4 and 5. (1) Solvent Exchange Reactions of the Complexes 4(solvent) and 5(solvent). Previously in this paper it has been demonstrated that the cations **4** and **5** can be stabilized with different solvent donors and different counterions, while the 16e$^-$ cation **6** is stable by itself. Because of the fact that these complexes were designed as catalysts for hydrogenation processes, it was anticipated that solvent lability of **4(PhCl)** and **5(PhCl)** in combination with the presence of a noncoordinating counterion would even be a basic prerequisite for their catalytic activity. We found that THF coordinates much stronger to the rhenium center than chlorobenzene. For example, the NMR spectra of **4(THF)** and **5(THF)** dissolved in PhCl-d_5 stay unchanged over several hours. In contrast to this the PhCl ligand in **4(PhCl)** and **5(PhCl)** is readily substituted by THF. However, it should be mentioned at this point that catalysis experiments given in the later context indicate that the type of coordinated solvent molecules has no crucial effect on the reactivity of the Re cations. Nevertheless, solvent stabilization is principally a suitable form to deliver the cations **4** and **5** as catalyst precursors for reactions with H_2.

(2) Reaction of 4(PhCl), 5(PhCl), and 6 with H_2. A [$Re(CO)_n(PMe_3)_{5-n}H_2$]$^+$ series of complexes bearing nonclassical H_2 or dihydride ligands have been described earlier by us.[45] These compounds were however obtained by protonation of the corresponding hydride with CF_3-COOH. Thus, the access to these H_2 or dihydride complexes starting from the corresponding cations or their solvent-stabilized precursors has yet to be verified. It should furthermore be recognized that the counteranions of the earlier and the present experiments are different, which principally could influence the physical and chemical behavior of the target molecules. In a ^{1}H NMR experiment in C_6D_5Cl **4(PhCl)** was placed under 1 bar of H_2. A signal for a dihydrogen complex developed at −5.70 ppm. This resonance for the H_2 ligand possesses a T_1 relaxation time of 13 ms at this temperature, suggesting its nonclassical type of binding. Related to this reaction of **4(PhCl)** with H_2 is that of a bisphosphine rhenium carbonyl cation, which even gives rise to a thermally stable dihydrogen complex.[17,22,23] Complex **5(PhCl)** dissolved in C_6D_5Cl at −30 °C was also put under 1 bar of H_2, which, somewhat in contrast to the earlier experiment of protonation of **2**,[45] afforded an equilibrium mixture of the dihydrogen complex **7a** and the dihydride complex **7b**.

In the ^{1}H NMR spectrum of a PhCl-d_5 solution, **7a** was identified by a broad resonance at about −5.76 ppm, with no recognizable phosphorus coupling, and **7b** by a multiplet resonance at about −5.83 ppm split by phosphorus coupling.[45] Determination of the T_1 relaxation time for the signal of **7a** resulted in a value of 12.7 ms at −30 °C; due to its shortness, it confirms the presence of a H_2 ligand. For the dihydride species **7b** the resonance at −5.83 ppm shows a T_1 value of >100 ms, which is a low value for isolated terminal hydride ligands, but too large a value for a H_2 ligand. [17,20,30] Attempts to isolate either the hydride or the dihydrogen complex led to other yet unidentified species apparently with loss of the dihydrogen or the hydride moieties.

In a fashion similar to **4(PhCl)** and **5(PhCl)** complex **6** was subjected to 1 bar of H_2 in C_6D_5Cl at −30 °C. It was found that it reacts with dihydrogen to result in a complicated mixture of complexes. Among the components in the mixture one finds the known dihydride complex indicated by a multiplet resonance at −6.23 ppm. In this experiment, we could not find a resonance for the dihydrogen complex, which was expected as a broad resonance between −6 and −7 ppm.[45] This presumably is due to a stronger preference for the dihydride species based on the presence of the noncoordination counterion in comparison with the earlier studies. The dihydride was observed as a characteristic multiplet at −7.0 ppm with a T_1 time of 259.2 ms. The ^{31}P NMR studies revealed a splitting pattern with multiplets at −26.2, −36.9, and −41.2 ppm. Due to the coupling pattern of ^{31}P nuclei, we suggest that the second species is a pentagonal bipyramidal cis dihydride with the hydride ligands in the equatorial plane. This presumably is the kinetic product, which appears first and transforms to the other hydride species. The existence or coexistence of dihydrogen or dihydride complexes derived from solvent-stabilized **4** and **5** was taken as a major indication for their potential to act as precatalysts in hydrogenations of imines. However, the detection of merely the dihydride complex was taken as an indication for the poor catalytic performance of **6** because the hydrogenation catalysis obviously requires the presence of a dihydrogen complex.

(3) Reaction of $ReH(CO)_3(PMe_3)_2$ (1), $ReH(CO)_2(PMe_3)_3$ (2), and *cis*-$ReH(CO)(PMe_3)_4$ (3) with [Isopropylisopropylideneiminium][BAr^F]. The compounds $ReH(CO)_3(PMe_3)_2$ (**1**) and $ReH(CO)_2(PMe_3)_3$ (**2**) react readily with 1 equiv of [isopropylisopropylideneiminium][BAr^F] in chlorobenzene at room temperature to give a mixture of **4(PhCl)** and [$Re(CO)_3(PMe_3)_2(HN^iPr_2)$][$BAr^F$] (**8**) or in the case of **2** to yield **5(PhCl)** and [$Re(CO)_2(PMe_3)_3(HN^iPr_2)$][$BAr^F$] (**9**) within a few minutes. These insertions of the iminium salts into the Re−H bond were monitored by ^{1}H and ^{13}C NMR spectroscopy, which indicated complete conversion to the amine complexes **8** and **9** after 4 h. After the hydride transfer step competition between the faster coordination of chlorobenzene and slower coordination of the diisopropylamine ligand was noticed. This was further pursued in separate ligand exchange experiments using ^{31}P NMR spectroscopy. These demonstrated that the transformations of **4(PhCl)** and of **5(PhCl)** with excess diisopropylamine to yield **8** and **9**, respectively, go to completion at room temperature. The reaction of *cis*-$ReH(CO)(PMe_3)_4$ (**3**) with [Isopropylisopropylideneiminium][BAr^F] is instantaneous and affords at room temperature the known dihydride complex [$ReH_2(CO)$-

(56) Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10358.
(57) Li, L. T.; Stern, C. L.; Marks, T. J. *Organometallics* **2000**, *19*, 3332.
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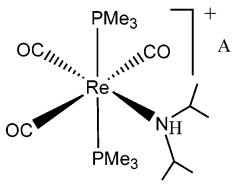
(60) Lanza, G.; Fragala, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 8257.
(61) Chen, Y. X.; Metz, M. V.; Li, L. T.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287.

Table 5. NMR Pursuit of Catalytic Hydrogenations of Imines under H_2 Atmosphere (1−2 bar) Using 5(PhCl) and 6 as Catalysts at Various Temperatures

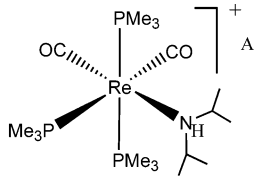
cat.	imine	cat./imine (mol %)	solvent	temp (°C)	time (h)	TOF (h^{-1})	yield of amine (%)
5(PhCl)	$PhCH{=}NCH_2Ph$	4.0	C_6D_5Cl	r.t.	22	0.23	20
				50	22	0.32	28
				90	70	0.36	100
5(PhCl)	$Me_2C{=}NPr^i$	5.6	THF/Tol (1:1)	70	2	1.70	19
				70	85	0.12	57
				90	85	0.20	93
6	$PhCH{=}NCH_2Ph$	2	C_6D_5Cl	90	2	3.5	14
				90	20	0.5	20
				90	150	0.1	30

$(PMe_3)_4][BAr^F]$ by simple proton transfer in quantitative yield.[45] Concomitantly, isopropylazaisopropylidene was identified in the reaction mixture by ^{13}C NMR spectroscopy.

Complexes **8** and **9** possess spectroscopic data very similar to those of **4(PhCl)** and **5(PhCl)**. The presence of coordinated diisopropylamine could be verified through ^1H NMR and ^{13}C NMR spectroscopy. Their structures are thus consistent with the sketches below.



8



9

$A = [B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$

These experiments established at least for **4(PhCl)** and **5(PhCl)** the existence of essential species and elementary steps needed for a catalytic ionic hydrogenation occurring with heterolytic fission of H_2. It is important to note that even in the case of **6**, where the reaction with the [isopropylideneiminium] reagent brought about full proton transfer to **6**, the acidity of the formed dihydride $[ReH_2]^+$ species could still be in a suitable range to allow a remaining protolysis equilibrium between the hydride and the iminium salt. These exploratory iminium experiments provided further indication that the given species **4**, **5**, and **6** could act as precatalysts for the sought hydrogenations of imines.

3. Catalytic Hydrogenation of Imines with the Complexes 4(PhCl), 5(PhCl), and 6. (1) Low-Pressure (1−2 bar) Catalytic Hydrogenation of Imines by 5 and 6 in the Presence of H_2 Pursued by NMR. Hydrogenations of **5(PhCl)** and **6(PhCl)** were explored applying several simple imines in NMR experiments at various temperatures starting from 1 bar of H_2 at room temperature to test the catalytic potential and to obtain further mechanistic details. A mixture of THF/toluene or PhCl was used as solvent. The results and conditions are summarized in Table 5.

On the basis of the resulting amounts of the amine products it is clear that all the hydrogenations of Table 5 were catalytic, differing, however, in the efficiency. The results for complex **5(PhCl)** were most promising. As the hydrogenation proceeded, signals of complex **9** became progressively observable; that is, the amine-coordinated compound was appearing. The latter was indeed thermally stable for a long period of time at 90 °C and is even the prevailing species under the given reaction conditions. The reactions are quite temperature dependent. While the hydrogenations of $PhCH{=}NCH_2Ph$ and $Me_2C{=}N^iPr$ with **5(PhCl)** could practically be brought to completion at about 90 °C, that of $PhCH{=}NCH_2Ph$ with **6** resulted in lower yields and long reaction times. ^1H NMR and ^{31}P NMR monitoring of these reactions also revealed that with the progressing reaction not only does the amine complex accumulate but also more slowly the free amine appears. This indicates that the reaction is catalytic and replacement of the amine ligand by H_2 is rate determining. Accordingly, imines with product amines possessing low coordination abilities are even expected to be favorable substrates in the hydrogenations. This could in particular be the case for the catalysis of complex **6**, which appears sterically more demanding than the corresponding cationic $Re(CO)_2(PMe)_3$ fragment **5**. However, presumably due to its less appropriate acid/base properties complex **6** was not found to be a very efficient catalyst, furnishing low amine yields (Table 5) and catalyst decomposition was noticed by ^{31}P NMR monitoring. The slow replacement of the amine ligands by H_2 points to the possibility that these catalyses with $Re(CO)_n(PMe_3)_{5-n}$ cations could greatly be improved by applying H_2 under pressure.

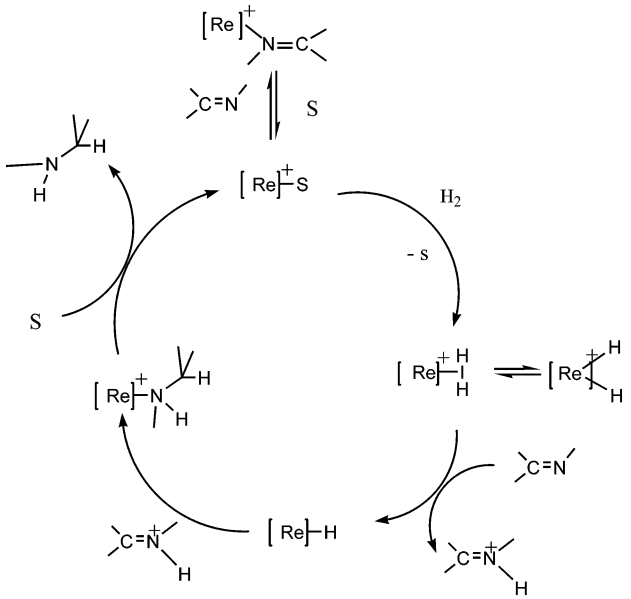
(2) Catalytic Hydrogenation of Imines by 4(PhCl) and 5(PhCl) with H_2 under Pressure. In Table 6 the conditions for several autoclave hydrogenations using **4(PhCl)** and **5(PhCl)** as catalyst precursors are reported, showing that especially with **5(PhCl)** quite high yields of the amines can be obtained and also shorter reaction times are required, even shorter than those in the NMR tube experiments. It should additionally be mentioned that the catalyst loading could be reduced. Solvents of these reactions were not varied greatly (Table 6), since no drastic effects were seen in exploratory reactions. The most effective catalysis was accomplished with the catalyst precursor **5(PhCl)** in the hydrogenation of PhCH=NPh, where at a pressure of 65 bar of H_2 and at 35 °C the imine conversion was almost 100% within just 2 h. Some experiments carried out with **6** under H_2 pressure did not show greatly improved activities and yields in comparison with those of Table 5. This led us to assume that this catalyst system has principal deficiencies (see below), which could not easily be mended by further tuning efforts.

Scheme 4 displays the anticipated mechanism of the catalytic transformations. As described before, the crucial uptake of H_2 is assumed to occur via formation of nonclassical H_2 complexes, which can appear in experiments under pressure in substantially higher

Table 6. Results of Catalytic Hydrogenation of Imines under H_2 Pressure Using 4(PhCl) and 5(PhCl) as Catalysts

cat.	imine	cat./imine (mol %)	solvent	temp (°C)	H_2 (bar)	time (h)	TOF (h^{-1})	yield (%) of amine
4(PhCl)	$PhCH{=}NCH_2Ph$	0.39	C_6D_5Cl	70	100	63	1.79	43.9
				90	100	23	5.50	49.3
5(PhCl)	$Me_2C{=}NPr^i$	2.5	THF/Tol (1:1)	90	55	20	2	100
5(PhCl)		1.18	THF/Tol (1:1)	70	14	22	0.85	22
				90	14	20	2.64	95
5(PhCl)		0.44	C_6D_5Cl	70	100	44	1.34	26
				90	100	41	5.54	100
5(PhCl)	$PhCH{=}NCH_2Ph$	0.51	C_6D_5Cl	75	40	43	0.20	14.3
			C_6D_5Cl	90	40	43	2.00	43.9
5(PhCl)	$PhCH{=}NCH_2Ph$	0.47	C_6D_5Cl	75	100	43	1.34	27
				90	100	65	2.45	75
5(PhCl)	PhCH=NPh	0.575	C_6D_5Cl	75	40	18	9.66	100
5(PhCl)	PhCH=NPh	0.587	C_6D_5Cl	20	35	29.5	2.96	51.2
				65	35	2	81.78	96

Scheme 4



concentrations. In the presence of imines the neutral hydrides and the iminium salts might then be formed by proton transfer. Subsequently this step could be followed by imine insertions to generate the amine complexes of type **8** or **9**. In a last step the catalytic cycle of the "ionic hydrogenation" closes up by replacement of the amine ligand with H_2.

We believe that the irreversible formation of a dihydride compound from the H_2 complex reduces catalytic activity in hydrogenations with heterolytic splitting of H_2, since the proton transfer ability is expected to be reduced. The high catalytic activity of **5(PhCl)** apparently correlates with the ability to form a relatively stable and acidic H_2 complex as prerequisites for effective H_2 heterolysis. While insertions of the iminium cations into the Re−H bond to generate amine complexes are anticipated to be "easygoing" for all the investigated systems, the subsequent and presumably even rate-determining replacement of the amine by a solvent molecule and/or a H_2 molecule to regenerate the starting species could lead to retardation of the whole catalysis depending on the type of amine (or imine).

Conclusions

In the series of the cationic complexes $[Re(CO)_n(PMe_3)_{5-n}]^+$ the solvent-coordinated compounds $[Re(CO)_3(PMe_3)_2(PhCl,THF)]^+$ and $[Re(CO)_2(PMe_3)_3(PhCl,THF)]^+$ were synthesized and structurally characterized. A related $[Re(CO)(PMe_3)_4]^+$ compound stayed "naked" as a $16e^-$ species. Testing catalytic hydrogenation reactions of different imine substrates with the $[Re(CO)_n(PMe_3)_{5-n}]^+$ series of complexes, it could be demonstrated for the first time that the solvent-stabilized $[Re(CO)_n(PMe_3)_{5-n}(solvent)]^+$ cations are suitable for such catalyses. The best catalyst turned out to be the $[Re(CO)_2(PMe_3)_3(solvent)]^+$ system. The $[Re(CO)(PMe_3)_4]^+$ species showed low catalytic activity. All these observations were explained on the basis of an "ionic hydrogenation" pathway occurring with heterolytic cleavage of H_2. For optimum catalysis a subtle balance between the counteracting effects of the strength of back-bonding of the H_2 ligand and its acidity is required, which apparently is satisfied best by the phosphine-trisubstituted system $[Re(CO)_2(PMe_3)_3(solvent)]^+$.

Experimental Section

The preparative work was carried out under nitrogen by standard Schlenk techniques or in a glovebox. All solvents were dried over appropriate drying reagents and distilled under nitrogen before use. Reagent-grade chemicals were used as purchased from Aldrich or Fluka. $[Ph_3C][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$, $B(C_6F_5)_3$, isopropylisopropylideneimine, $ReH(CO)_3(PMe_3)_2$, $ReH(CO)_2(PMe_3)_3$, and *cis*-$ReH(CO)(PMe_3)_4$ were prepared as described in the literature. NMR spectra were obtained on a Varian Gemini-300 spectrometer, measured at 300.23 MHz for ^1H NMR and 121.474 MHz for ^{31}P NMR spectroscopy. Chemical shifts are given in ppm, relative to partially deuterated solvents peaks (^1H) or external 85% H_3PO_4 aqueous solution (^{31}P NMR), with downfield shifts considered positive. T_{1min} measurements were performed on a Bruker WM-500 spectrometer, using a standard 180°−τ−90° inversion−recovery pulse sequence. IR spectra were recorded on a Bio-Rad FTS-45 spectrometer. Hydrogenations under pressure were performed in a stainless steel autoclave (20 mL total volume) with internal stirring. The conversion progress was checked by ^1H NMR analysis.

Synthesis of $[Re(CO)_3(PMe_3)_2(S)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ {S = PhCl, 4(PhCl); S = THF, 4(THF)}. A solution of 17 mg (0.04 mmol) of $ReH(CO)_3(PMe_3)_2$ in 1 mL of PhCl or THF and a solution of 44.5 mg (0.04 mmol) of $[Ph_3C][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ in 5 mL of PhCl or THF were mixed at room temperature. The solution first turned colorless immediately, then dark yellow after several minutes. The solvent was removed in vacuo, and the resulting pale yellow residue was washed with pentane to give off-white solids of **4(PhCl)** or **4(THF)**. Crystals of **4(PhCl)** suitable for the X-ray structure determination were

recrystallized from a minimum amount of PhCl at −30 °C. **4-(PhCl)** gave poor results in the elemental analyses presumably due to solvent losses during processing.

4(PhCl): Yield 42.5 mg (76%). ^{1}H NMR (300.23 MHz, PhCl-d_5, 293 K): δ 1.21 (s, br, Me, 18H). ^{31}P NMR (121.474 MHz, PhCl-d_5, 293 K): δ −33.1 (s, PMe_3). ^{13}C NMR (125.783 MHz, PhCl-d_5, 243 K): δ 192.1 (t, J_{PC} = 8.5 Hz, 2CO), 187.6 (t, J_{PC} = 6 Hz, 1CO), 18.1 (t, J_{PC} = 17 Hz, PMe_3). IR (Nujol): 2066w, 1967s, 1941s. Anal. Calcd for $C_{47}H_{35}ReBClF_{24}O_3P_2$: C, 40.37; H, 2.52. Found: C, 37.44; H, 6.49.

4(THF): Yield 31.4 mg (58%). ^{1}H NMR (300.23 MHz, THF-d_8, 293 K): δ 1.30 (s, br, Me, 18H). ^{31}P NMR (121.474 MHz, THF-d_8, 293 K): δ −26.8.0 (s, PMe_3). ^{13}C NMR (125.783 MHz, THF-d_8, 223 K): δ 195.1 (t, J_{PC} = 9 Hz, 2CO), 193.2 (t, J_{PC} = 5 Hz, 1CO), 18.5 (t, J_{PC} = 17 Hz, PMe_3). Anal. Calcd for $C_{45}H_{38}ReBF_{24}O_4P_2$: C, 39.81; H, 2.82. Found: C, 39.37; H, 2.93.

Synthesis of [Re(CO)$_2$(PMe$_3$)$_3$(S)][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (S = PhCl, 5(PhCl); S = THF, 5(THF)). A solution of 16 mg (0.034 mmol) of ReH(CO)$_2$(PMe$_3$)$_3$ in 1 mL of PhCl or THF and a solution of 37.6 mg (0.034 mmol) of [Ph$_3$C][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] in 5 mL of PhCl or THF were mixed at room temperature. The solution first turned colorless and then dark yellow after several minutes. The solvent was removed in vacuo, and the resulting pale yellow residue was washed with pentane to give off-white solids of **5(PhCl)** or **5(THF)**. Crystals of **5(PhCl)** suitable for X-ray structure determination were recrystallized with a minimum amount of PhCl at −30 °C.

[Re(CO)$_2$(PMe$_3$)$_3$(PhCl)][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (5): Yield 33.6 mg (68%). ^{1}H NMR (300.23 MHz, PhCl-d_5, 293 K): δ 1.17 (t, J_{PH} = 3.6 Hz, Me, 18H), 1.13 (d, J_{PH} = 7.5 Hz, Me, 9H). ^{31}P NMR (121.474 MHz, PhCl-d_5, 293 K): AB_2 system, δ −34.9, −35.7 (J_{AB} = 24 Hz, PMe_3). Anal. Calcd for $C_{49}H_{44}ReBClF_{24}O_2P_3$: C, 40.69; H, 3.07. Found: C, 40.12; H, 2.93.

[Re(CO)$_2$(PMe$_3$)$_3$(THF)][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]: Yield 37.4 mg (76%). ^{1}H NMR (300.23 MHz, THF-d_8, 293 K): δ 1.30 (t, J_{PH} = 3.5 Hz, Me, 18H), 1.25 (d, J_{PH} = 7.2 Hz, Me, 9H). ^{31}P NMR (121.474 MHz, THF-d_8, 293 K): δ −30.4 (d, J_{PP} = 25 Hz, PMe_3), −40.2 (t, J_{PP} = 25 Hz, PMe_3). Anal. Calcd for $C_{47}H_{47}ReBF_{24}O_3P_3$: C, 40.15; H, 3.37. Found: C, 40.34; H, 3.15.

Synthesis of [Re(CO)$_2$(PMe$_3$)$_3$(S)][BH(C$_6$F$_5$)$_3$] (S = PhCl; S = THF). A solution of 16 mg (0.034 mmol) of ReH(CO)$_3$(PMe$_3$)$_2$ in 1 mL of PhCl or THF and a solution of 17.5 mg (0.034 mmol) of B(C$_6$F$_5$)$_3$ in 5 mL of PhCl or THF were mixed at room temperature. The solution immediately turned dark yellow. The solvent was removed in vacuo, and the resulting dark yellow oily residue was washed with pentane to result in dark yellow oils. Satisfactory elemental analyses could not be obtained.

[Re(CO)$_2$(PMe$_3$)$_3$(PhCl)][BH(C$_6$F$_5$)$_3$]: Yield 22 mg (58%). ^{1}H NMR (300.23 MHz, PhCl-d_5, 293 K): δ 1.25 (t, J_{PH} = 3.4 Hz, PMe_3, 18H), 1.18 (d, J_{PH} = 7.2 Hz, PMe_3, 9H). ^{31}P NMR (121.474 MHz, PhCl-d_5, 293 K): ABX system, δ −35.36(A), −35.35(B), −36.38(X) (J_{AB} = 0.4 Hz, J_{AX} = 23.6 Hz, J_{BX} = 24.0 Hz).

[Re(CO)$_2$(PMe$_3$)$_3$(THF)][BH(C$_6$F$_5$)$_3$]: Yield 23 mg (64%). ^{1}H NMR (300.23 MHz, THF-d_8/C$_6$D$_6$, 293 K): δ 1.71 (t, J_{PH} = 3 Hz, PMe_3, 18H), 1.15 (d, J_{PH} = 7 Hz, PMe_3, 9H). ^{31}P NMR (121.474 MHz, THF-d_8/C$_6$D$_6$, 293 K): δ −29.8 (d, J_{PP} = 24 Hz, PMe_3, 1P), −39.8 (t, J_{PP} = 24 Hz, PMe_3, 2P).

Synthesis of [Re(CO)(PMe$_3$)$_4$][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] (6). A solution of 20 mg (0.0385 mmol) of ReH(CO)(PMe$_3$)$_4$ in 1 mL of PhCl or THF and a solution of 42.6 mg (0.0385 mmol) of [Ph$_3$C][B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] in 5 mL of PhCl or THF were mixed at room temperature. The solution immediately turned colorless, then dark yellow after several minutes. The solvent was removed in vacuo, and the resulting pale yellow residue was washed with pentane to give an off-white solid. Yield: 44 mg (82%). Complex **6** can be recrystallized from a minimum amount of PhCl at −30 °C. ^{1}H NMR (300.23 MHz, PhCl-d_5, 293 K): δ 1.18 (t, J_{PH} = 3 Hz, Me, 18H), 1.05 (d, J_{PH} = 7.8 Hz, Me, 9H), 0.98 (d, J_{PH} = 6.9 Hz, Me, 9H). ^{31}P NMR (121.474 MHz, PhCl-d_5, 293 K): δ −42.6 (dt, J_{PP} = 25, 17 Hz, 1P), −47.9 (dt, J_{PP} = 25, 23 Hz, 1P), −49.2 (dd, J_{PP} = 23, 17 Hz, 2P). Anal. Calcd for $C_{45}H_{48}ReBF_{24}OP_4$: C, 39.11; H, 3.50. Found: C, 38.81; H, 3.39.

Synthesis of [Re(CO)(PMe$_3$)$_4$][BH(C$_6$F$_5$)$_3$]. A solution of 20 mg (0.0385 mmol) of ReH(CO)(PMe$_3$)$_4$ in 1 mL of PhCl or THF and a solution of 19.7 mg (0.0385 mmol) of B(C$_6$F$_5$)$_3$ in 5 mL of PhCl or THF were mixed at room temperature. The solution immediately turned dark yellow. The solvent was removed in vacuo, and the resulting dark yellow oily residue was washed with pentane to give a dark yellow oil. Yield: 28 mg (71%). A satisfactory elemental analysis could not be obtained. ^{1}H NMR (300.23 MHz, PhCl-d_5, 293 K): δ 4.25 (q, br, HB, 1H), 1.07 (t, J_{PH} = 3 Hz, Me, 18H), 0.95 (d, J_{PH} = 7.8 Hz, Me, 9H), 0.90 (d, J_{PH} = 6.9 Hz, Me, 9H). ^{1}H NMR (300.23 MHz, THF-d_8, 293 K): δ 3.80 (partial overlap with THF, q, br, HB, 1H), 1.70 (t, J_{PH} = 3.3 Hz, Me, 18H), 1.59 (d, J_{PH} = 4.5 Hz, Me, 9H), 1.57 (d, J_{PH} = 3.3 Hz, Me, 9H). ^{31}P NMR (121.474 MHz, PhCl-d_5, 243 K): δ −42.0 (dt, J_{PP} = 25, 17 Hz, 1P), −48.3 (dt, J_{PP} = 25, 23 Hz, 1P), −49.3 (dd, J_{PP} = 23, 17 Hz, 2P). ^{31}P NMR (121.474 MHz, PhCl-d_5, 293 K): δ −42.9 (dt, J_{PP} = 25, 17 Hz, 1P), −48.0 (dt, J_{PP} = 25, 23 Hz, 1P), −49.0 (dd, J_{PP} = 23, 17 Hz, 2P).

Reactions of 4(PhCl), 5(PhCl), and 6 with 1 bar of H$_2$: Formation of Dihydrogen and Dihydride Complexes. A solution of the cation **4(PhCl)** (12.9 mg, 0.01 mmol), **5(PhCl)** (13.3 mg, 0.01 mmol), or **6** (13.8 mg, 0.01 mmol) in 0.6 mL of C$_6$D$_5$Cl was transferred to a Young NMR tube and was frozen in liquid N_2. The N_2 atmosphere was substituted by H_2. The mixture was allowed to warm to −30 °C. The ^{1}H NMR spectra were recorded at −30 and −10 °C, respectively.

4(PhCl)/H$_2$. ^{1}H NMR (500.23 MHz, PhCl-d_5, 243 K): δ −5.70 (s, br, Re(H_2), 2H, T_1 = 13 ms). ^{31}P NMR (202.49 MHz, PhCl-d_5, 243 K): δ −44.8 (s, PMe_3, 2P).

5(PhCl)/H$_2$. ^{1}H NMR (500.23 MHz, PhCl-d_5, 243 K): δ −5.76 (s, br, Re(H_2), 2H, T_1 = 12.7 ms), − 5.83 (dd, br, J_{PH} = 52, 44 Hz, ReH_2, 2H, T_1 = 358.8 ms). ^{31}P NMR (202.49 MHz, PhCl-d_5, 243 K): AB_2 system, δ −45, −46 (J_{AB} = 24 Hz, Re(H_2)PMe_3), AB_2 system, δ −28.5, −30.8. (J_{AB} = 24 Hz, ReH_2-PMe_3).

6/H$_2$. ^{1}H NMR (300.23 MHz, PhCl-d_5, 243 K): δ − 6.23 (m, ReH_2, 2H, T_1 = 342.14 ms), −7.00 (m, ReH_2, 2H, T_1 = 259.2 ms). ^{31}P NMR (121.474 MHz, PhCl-d_5, 243 K): δ −21.9 (td, $^2J_{PP}$ = 19.4, 16.5 Hz, PMe_3, 1P), −26.2 (td, $^2J_{PP}$ = 188.5, 28.4 Hz, PMe_3, 1P), −36.9 (dd, $^2J_{PP}$ = 188.5, 29.9, 48.9, PMe_3, 1P), −41.2 (td, 2JPP = 27.4, 14.0 Hz, PMe_3, 2P), −45.2 (dd, $^2J_{PP}$ = 27 Hz, 22.4 Hz, PMe_3, 2P), −51.4 (td, $^2J_{PP}$ = 25.4, 15.5 Hz, PMe_3, 2P).

Reactions of ReH(CO)$_3$(PMe$_3$)$_2$, ReH(CO)$_2$(PMe$_3$)$_3$, and ReH(CO)(PMe$_3$)$_4$ with [Isopropylisopropylideneiminium][BAr^F]. A solution of hydride **1** (15 mg, 0.0355 mmol), **2** (16.7 mg, 0.0355 mmol), or **3** (18.4 mg, 0.0355 mmol) in 1 mL of C$_6$H$_5$Cl was transferred to a screw-cap NMR tube containing 34.2 mg (0.0355 mmol) of [isopropylisopropylideneiminium][BAr^F]. The solutions turned yellow. The reactions were monitored by ^{31}P NMR. After 4 h the solvent was removed in vacuo and the resulting yellow residue was washed with pentane to give complex **8**, **9**, or [ReH_2(CO)(PMe$_3$)$_4$][BAr^F] as off-white solids in quantitative yields.

[Re(CO)$_3$(PMe$_3$)$_2$(HN^{i}Pr$_2$)][BAr^F] (8). ^{1}H NMR (300.23 MHz, PhCl-d_5, 293 K): δ 2.80 (sept, J_{HH} = 6.6 Hz HC, 2H), 1.46 (t, J_{PH} = 3.3 Hz, Me, 18H), 0.90 (d, J_{HH} = 6.6 Hz, ^{i}Pr, 12H). ^{31}P NMR (121.474 MHz, PhCl-d_5, 293 K): δ −34.2 (s, PMe_3, 2P). ^{13}C NMR (125.783 MHz, PhCl-d_5, 293 K): δ 47.4 (s, $HNC(Me)_2$, 1C), 21.4 (s, Me(CNH), 4Me), 18.4 (t, J_{PC} = 27 Hz, PMe_3, 6Me). Anal. Calcd for $C_{47}H_{45}ReBF_{24}NO_3P_2$: C, 40.73; H, 3.27. Found: C, 40.32; H, 3.38.

[Re(CO)$_2$(PMe$_3$)$_3$(HN^{i}Pr$_2$)][BAr^F] (9). ^{1}H NMR (300.23 MHz, PhCl-d_5, 293 K): δ 2.69 (sept, J_{HH} = 6.6 Hz HC, 2H), 1.42 (t, J_{PH} = 3.3 Hz, Me, 18H), 1.21 (d, J_{PH} = 7.5 Hz, Me, 9H), 0.96 (d, J_{HH} = 6.6 Hz, ^{i}Pr, 12H). ^{31}P NMR (121.474 MHz,

Table 7. Crystallograhic Details of 4(PhCl), 5(PhCl), 6, and 5(THF)'

	4(PhCl)	5(PhCl)	6	5(THF)
empirical formula	$C_{53}H_{40}BCl_2F_{24}O_3P_2Re$	$C_{49}H_{44}BClF_{24}O_2P_3Re$	$C_{45}H_{48}BF_{24}OP_4Re$	$C_{43}H_{63}BO_4P_3Re$
color	yellow	yellow	brown-yellow	yellow
M_r	1510.70	1446.21	1381.72	933.85
cryst size (mm)	0.72× 0.76 × 0.79	0.12× 0.26 × 0.46	0.24× 0.26 × 0.41	0.07× 0.39 × 0.42
T (K)	183(2)	193(2)	183(2)	193(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2/n$	$P2_1/c$
a (Å)	12.8032(11)	32.678(2)	12.4387(10)	19.4056(14)
b (Å)	14.2668(12)	13.4212(7)	12.6647(6)	9.7996(14)
c (Å)	18.0643(14)	26.6501(12)	19.0231(15)	25.2294(18)
α (deg)	111.148(9)	90	90	90
β (deg)	93.531(10)	99.015(7)	109.176(9)	112.109(8)
γ (deg)	102.851(10)	90	90	90
V (Å^3)	2963.6(4)	11547.1(11)	2830.5(3)	4445.0(5)
Z	2	8	2	4
ρ_{calcd} (g·cm^{-3})	1.693	1.664	1.621	1.395
μ (mm^{-1})	2.311	2.349	2.372	2.880
F(000)	1484	5696	1364	1912
transmn range	0.2874−0.2398	0.8542−0.6610	0.6680−0.5438	0.8239−0.3776
θ range	4.9° < 2θ > 56.88°	4.6° < 2θ < 55.9°	4.72° < 2θ < 56.10°	5.34° < 2θ < 60.64°
no. of measd reflns	29 713	31 278	23 289	45 126
no. of unique reflns	13 723	9069	6621	12 823
$I > 2\sigma(I)$ reflns	10 399	6366	4595	8306
no. of params	788	684	320	478
GOF (for F^2)	1.030	1.073	1.081	1.014
$R_1[I > 2\sigma(I)]$, R_1 all data	0.0451, 0.0613	0.0527, 0.0736	0.0765, 0.1025	0.0545, 0.0795
$wR_2[I > 2\sigma(I)]$, wR_2 all data	0.1042, 0.1093	0.1291, 0.1377	0.2215, 0.2314	0.1264, 0.1311
$\Delta\rho_{max/min}$	1.528, −1.443	0.967, −0.781	1.102, −1.730	3.497, −2.301

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $I > 2\sigma(I)$; $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

PhCl-d_5, 293 K): δ −35.4 (d, J_{PP} = 27 Hz, PMe_3, 2P), −37.8 (t, J_{PP} = 27 Hz, PMe_3, 1P). ^{13}C NMR (125.783 MHz, PhCl-d_5, 293 K): δ 47.3 (s, $HNC(Me)_2$, 1C), 21.1 (s, Me(CNH), 4Me), 19.2 (t, J_{PC} = 25 Hz, PMe_3, 6Me), 17.8 (d, J_{PC} = 25 Hz, PMe_3, 3Me). Anal. Calcd for $C_{49}H_{54}ReBF_{24}NO_2P_3$: C, 41.01; H, 3.79. Found: C, 40.87; H, 3.61.

[$ReH_2(CO)(PMe_3)_4$][BAr^F]. ^{1}H NMR (300.23 MHz, PhCl-d_5, 233 K): δ 1.39 (2, J_{HH} = 9.9 Hz, Me, 9H), 1.21 (d, J_{PH} = 6.3 Hz, Me, 18H), 0.96 (d, J_{PH} = 7.2 Hz, Me, 9H), −6.38 (m, ReH_2, 2H). ^{31}P NMR (121.474 MHz, PhCl-d_5, 233 K): δ −22.8 (dt, J_{PP} = 21, 15 Hz, PMe_3, 1P), −46.1 (dd, J_{PP} = 27, 21 Hz, PMe_3, 2P), −52.3 (dt, J_{PP} = 27, 15 Hz, PMe_3, 1P). ^{13}C NMR (125.783 MHz, PhCl-d_5, 233 K): δ 26.9 (d, J_{PC} = 32 Hz, PMe_3, 1P), 23.6 (t, J_{PC} = 19 Hz, PMe_3, 2P), 23.1 (d, J_{PC} = 29 Hz, PMe_3, 1P). Anal. Calcd for $C_{45}H_{50}ReBF_{24}OP_4$: C, 39.06; H, 3.64. Found: C, 39.51; H, 3.89.

Catalytic Hydrogenation of Imines by 5(PhCl) and 6 under 1−2 bar of H_2 Atmosphere. Complex **5(PhCl)** or **6** was mixed with imines in 0.6 mL of a mixture of THF-d_8/Tol-d_8 or pure C_6D_5Cl. 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 requested temperature, and the NMR spectrum was recorded. The conversions were determined by the integration of the imine and the amine ^{1}H NMR signals.

Catalytic Hydrogenation of Imines with 4(PhCl) and 5(PhCl) under H_2 Pressure. These reactions were carried out as following: complex **4** or **5** was dissolved in 1 mL of a mixture of THF-d_8/Tol-d_8 or pure C_6D_5Cl in a steel autoclave (20 mL), and the imine was added. The reaction vessel was then pressurized with H_2 with pressures according to Table 6. The contents were heated and stirred for given periods of times. The mixtures were then transferred to NMR tubes, and ^{1}H NMR spectra were recorded. The conversions were determined by the integration of the imine and the amine signals. The procedures were repeated until the reactions had stopped.

X-ray Structure Determinations. Crystallographic data for compounds **4(PhCl)**, **5(PhCl)**, **6**, and **5(THF)** are collected in Table 7. The crystals were embedded in polybutene oil and mounted on glass fibers, and they were fixed by a cold N_2-gas stream of an Oxford cryogenic system at the diffractometer. Measurement temperatures of 183(2), 193(2), 183(2), and 193-(2) K were used for these structures. An imaging plate detector system (Stoe IPDS) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used for the exposure of 154, 250, 164, and 225 images at constant times of 1.0, 5.0, 4.0, and 9.0 min per image. The crystal-to-image distances were set to 58, 60, 60, and 50 mm (θ_{max} = 28.44°, 27.95°, 28.05°, and 30.32°). ϕ-rotation for **4(PhCl)** and ϕ-oscillation modes for **5(PhCl)**, **6**, and **5(THF)** were necessary for the increments of 1.3°, 0.8°, 1.1°, and 0.8° per exposure in each case. For the cell parameter refinements 4998 [**5(PhCl)**] and 5000 **5(THF)**[62] and 8000[63] reflections for compounds **4(PhCl)** and **6** were selected out of the whole limiting spheres with intensities $I > 6\sigma(I)$. A total of 29 713, 31 278, 23 289, and 45 126 reflections were collected, of which 13 723, 9069, 6621, and 12 823 were unique after performing absorption corrections and data reductions (R_{int} = 4.02%, 7.95%, 5.01%, and 14.99%). Nineteen, 16, 16, and 10 indexed crystal faces were used for the numerical absorption corrections.[64]

For crystals of **4(PhCl)** including a chlorobenzene solvate molecule, Patterson and direct methods failed to solve the structure in space group $P\bar{1}$, but direct methods allowed the structure solution in space group $P1$. A center of symmetry between independent molecules and shifts of 0.112x, 0.140y, and 0.069z along the unit cell directions allowed final refinement in space group $P\bar{1}$.

The structure of **5(PhCl)** was solved in space group $C2/c$. Due to technical reasons we were not able to obtain the full data set (completeness 62.6%). One of the CF_3 groups showed very large split atomic positions. Fourteen distance restraints (C−C, C−F, and F−F) were necessary for the isotropic refinement of this disordered CF_3 group using EADP and PART options in the refinement program SHELXL-97. The

(62) *STOE-IPDS Software package*, Version 2.87 5/1998; STOE & Cie, GmbH: Darmstadt, Germany, 1998.

(63) *STOE-IPDS Software package*, Version 2.92 5/1999; STOE & Cie, GmbH: Darmstadt, Germany, 1999.

(64) Coopens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *A18*, 1035.

phenyl group of the chlorobenzene ligand had to be refined with isotropic displacement parameters.

The structure of **6** crystallizes in monoclinic space group *P*2/*n*. In space group *P*2/*n*, the 2-fold axes of the molecules coincide with crystallographic 2-axes. The BAr^F anion shows now only one rotational disorder of one (×2) CF_3 group; however, every phosphine group and also the CO group were found on symmetry-related positions, leading to a 10-coordinated disordered Re complex. The refinement was performed with PART and EADP instructions for the disordered trimethyl phosphine groups. All methyl carbon atoms were isotropically refined. The disordered ratio was finally 0.51:0.49. The observed disorder for the refined structure **6** in space group *P*2/*n* may be the result of an unresolved merohedric twinning problem. Four different distance restraints (P−C, C−C) were applied in the refinement. Compound **5(THF)** crystallized as THF solvate in extremely thin plates. Low crystal quality may be the reason for the relatively high R_{int} value of 15% after absorption correction and data reduction.

All structures were solved with SHELXS-97.[66] The structure refinements were performed with SHELXL-97.[67] Programs PLATON[65] and PLUTON[68] were used to check structures for higher symmetry, and they were helpful to complete the structure by interpreting the difference electron density results.

Crystallographic data (excluding structure factors) for **4-(PhCl)**, **5(PhCl)**, **6**, and **5(THF)** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 219386, 219387, 219388, and 219389. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax:(+44) 1223−336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Details of crystal structure determination for compounds **4(PhCl)**, **5(PhCl)**, **6**, and **5(THF).** This material is available free of charge via the Internet at http://pubs.acs.org.

OM034196Y

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(68) Spek, A. L. *PLUTON, A computer program for the graphical representation of crystalographic models;* University of Utrecht: The Netherlands, 1991−1997.