Rhenium Complexes with Weakly Coordinating Solvent Ligands, *cis*-[Re(PR_3)$(CO)_4$(L)][BAr_F], L = CH_2Cl_2, Et_2O, NC_5F_5: Decomposition to Chloride-Bridged Dimers in CH_2Cl_2 Solution

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The solvent-coordinated complexes [*cis*-Re$(CO)_4(PR_3)(S)$][BAr_F] (R = Ph, ^{i}Pr, Cy, BAr_F = [B(3,5-$(CF_3)_2C_6H_3)_4$]$^-$) for S = Et_2O, CH_2Cl_2, and NC_5F_5 have been prepared from reaction of the neutral methyl precursors, *cis*-Re$(CO)_4(PR_3)$(Me), with either [$H(OEt_2)_2$][BAr_F] or [Ph_3C][BAr_F] in the appropriate solvent. A crystal structure of the complex [*cis*-Re$(CO)_4(P^iPr_3)(ClCH_2Cl)$][$BAr_F$] shows that the dichloromethane ligand is coordinated through one chlorine, with an Re−Cl distance of 2.554(2) Å. The first example of a structurally characterized pentafluoropyridine complex of rhenium was also determined, [*cis*-Re$(CO)_4(P^iPr_3)(NC_5F_5)$][BAr_F], with an Re−N distance of 2.319(5) Å. Activation of C−Cl bonds in the dichloromethane complexes result in the formation of the chloride-bridged dimers, {[*cis*-Re$(CO)_4(PR_3)]_2(\mu$-Cl)}{BAr_F}, and the X-ray structures of the Ph and Cy derivatives were determined.

Introduction

There has recently been a great deal of interest in cationic transition metal complexes [L_nM(S)][A] which possess a noncoordinating anion (A), such as PF_6^- or BAr_F^- (BAr_F = [B(3,5-$(CF_3)_2C_6H_3)_4$]), and a weakly coordinated solvent molecule (S). Due to the lability of the solvent ligand, these complexes act as a source of the corresponding 16e organometallic Lewis acid [L_nM][A] and are therefore highly reactive toward σ donors (eq 1).[1]

$$[L_nM(S)][A] \underset{+S}{\overset{-S}{\rightleftharpoons}} [L_nM][A] \xrightarrow{+L'} [L_nM(L')][A] \qquad (1)$$

For example, Gladysz's chiral Re complex [$Cp^*Re(PPh_3)(NO)(ClCH_2Cl)$][$BF_4$] binds ligands by loss of methylene chloride;[2] we have previously demonstrated that the weak solvent ligand in *trans*-[$PtH(P^iPr_3)_2$(S)][BAr_f] (S = Et_2O, CH_2Cl_2) can be easily substituted by PhI or H_2,[3] and Bergman's [$Cp^*Ir(PMe_3)$(Me)(ClCH$_2$Cl)][BAr_F][4] system and Bercaw's [Pt(Me)(tmeda)(NC_5F_5)][BAr_F][5] complexes activate C−H bonds of alkanes and other functionalized organic compounds.

Part of the success of these systems stems from the ability to have the appropriate solvent (S): one which is polar enough to provide adequate solubility of the ionic complex, but does not itself react or bind irreversibly with the metal center. An illustration of this balance is evident in Bercaw's Pt(NC_5F_5) system, where if either Et_2O or CH_2Cl_2 are used as the solvent instead of NC_5F_5, products resulting from C−H activation (Et_2O) or C−Cl activation (CH_2Cl_2) are isolated.[5] Keeping these points in mind, we have generated a simple organometallic Lewis acid system with a noncoordinating anion [*cis*-Re$(CO)_4(PR_3)]^+$ and examined its reactivity toward the solvents commonly present in [L_nM(S)][A] systems: Et_2O, CH_2Cl_2, and NC_5F_5. The preparation of the anion coordinated complexes [*cis*-Re$(CO)_4$-(PPh_3)(A)] have previously been reported by Hope[6] (A = $OTeF_5^-$) and Beck[7] (A = FBF_3^-). However, we are interested in systems with *noncoordinating* anions, such as BAr_F^-, which are much more likely to show reactivity toward substrates since there are no interactions with the anion to stabilize the electrophilic metal center.

This paper describes the preparation of solvent coordinated complexes [*cis*-Re$(CO)_4(PR_3)$(S)][BAr_F] (R = Ph, ^{i}Pr, Cy) for diethyl ether, dichloromethane, and pentafluoropyridine, and the first crystal structure of a Re complex with a bound NC_5F_5 is presented. We also observe the irreversible C−Cl bond activation of coordinated CH_2Cl_2, which is proposed to be formed from nucleophilic attack of the weak base Et_2O on the methylene carbon. A brief report of the isolation of [*cis*-Re$(CO)_4(PR_3)$-(S)][BAr_F] (R = Ph, Cy; S = OEt_2, $ClCH_2Cl$) and their activation of H_2 has been recently communicated.[8]

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Table 1. IR and ^{31}P Spectral Data for Complexes **1**−**6**

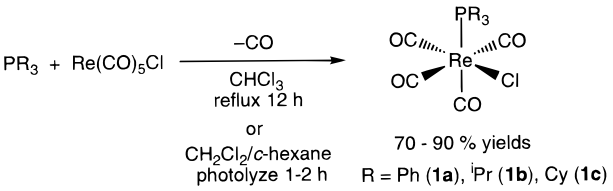
complex	IR (Nujol, ν_{CO}, cm^{-1})	^{31}P (CD_2Cl_2, RT)
1a	2106(m), 2018(s), 2002(vs), 1945(s)[a]	4.8
1b	2101(m), 2010(s), 1995(vs), 1934(s)	27.5
1c	2098(m), 2008(s), 1992(vs), 1932(s)	18.5
2a	2077(m), 1992(s), 1973(vs), 1935(s)[b]	10.1
2b	2072(m), 1980(s), 1964(vs), 1927(s)	22.4
2c	2070(m), 1976(s), 1969(vs), 1924(s)	13.1
3a	2118(m), 2035(s), 2010(s), 1988(s)	15.5[c]
3b	2118(m), 2034(s), 2015(s), 1979(s)	36.3
3c	2111(m), 2032(s), 1999(s), 1974(s)	27.9
4a	2122(m), 2051(s), 2041(s), 2033(s), 2019(vs), 2008(vs), 1987 (s)	11.1
4b	2124(m), 2044(s), 2026(s), 1996(s)	33.6
4c	2119(m), 2040(s), 2017(s), 1990(s)	25.5
5a	2122(m), 2116(m), 2034(s), 2011(vs), 1982(s), 1973(s)	10.0
5b	2118(m), 2110(w), 2025(s), 2015(s), 1965(s)	31.7
5c	2113(m), 2104(m), 2025(s), 2003(s), 1992(s), 1984(s), 1967(s)	23.3
6	2124(m), 2042(s), 2030(s), 1988(s)	30.4[d]

[a] Solvent was CCl_4, ref 10. [b] Reference 12. [c] ^{31}P{^{1}H} NMR (CD_2Cl_2, −73 °C) 16.2. [d] Solvent was NC_5F_5.

Results and Discussion

Preparation of *cis*-Re(CO)$_4$(PR$_3$)Cl (1a−c) and Reaction with NaBAr$_F$. Neutral metal halide complexes MX are often a convenient precursor to solvent or anion coordinated cationic systems, i.e., organometallic Lewis acid sources. For instance, our [*trans*-PtH(P^{i}Pr$_3$)$_2$(S)][BAr$_f$] (S = Et_2O, CH_2Cl_2) solvent complexes were prepared from metathesis of the PtCl precursor with NaBAr$_F$.[3] A similar route has been used by Beck to prepare the anion coordinated [*cis*-Re(CO)$_4$(PPh$_3$)(A)] (A = FBF_3, OSO_2CF_3) from the neutral ReBr precursor and Ag(A).[7]

Reaction of 1 equiv of phosphine (PPh_3, P^iPr_3, PCy_3) with $Re(CO)_5Cl$ in refluxing chloroform proceeded with the elimination of CO and cleanly provided the monophosphine complexes **1a**−**c** in high yields after 12 h. Similarly, **1a** could be obtained at shorter reaction times under photolytic conditions in a 1/1 mixture of dichloromethane/cyclohexane (eq 2). In both routes,



(2)

a slight excess of $Re(CO)_5Cl$ (5%) was used to ensure that none of the bis-phosphine complex *trans*-Re(CO)$_3$(PR$_3$)$_2$Cl would be generated. The progress of the reaction was monitored by measuring an IR spectrum of the reaction mixture periodically, and was judged complete when bands attributed to the carbonyl groups of $Re(CO)_5Cl$ (2056, 1987 cm^{-1})[9] were approximately less than 10% of the total intensity. Evaporation of solvents gave a crude product, which was dissolved in hot cyclohexane, and unreacted $Re(CO)_5Cl$ was removed by filtration. The monophosphine complexes were isolated as air stable white solids by crystallization from cyclohexane/hexane solutions. Complex **1a** has been prepared previously from $[Re(CO)_4Cl]_2$ and PPh_3 in CCl_4,[10] and the thermal route shown in eq 2 is similar to that used to prepare *cis*-Re(CO)$_4$(PPh)$_3$Br from Re(CO)$_5$Br and PPh_3.[11] The ^{31}P{^{1}H} NMR spectra for **1a**−**c** show

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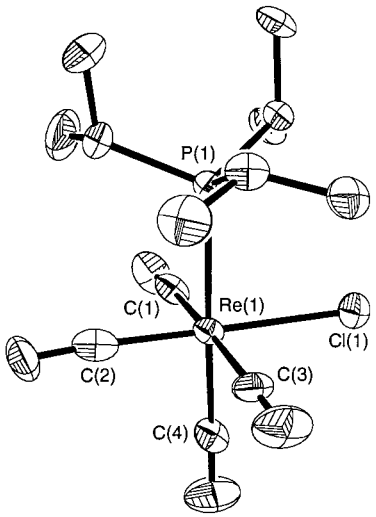


Figure 1. ORTEP diagram for *cis*-Re(CO)$_4$(P^{i}Pr$_3$)Cl, **1b** (50% probability ellipsoids).

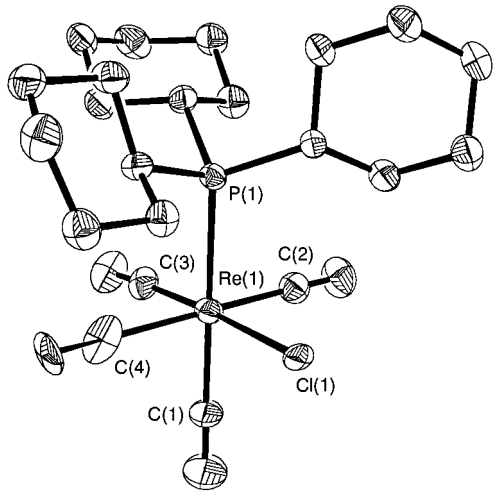


Figure 2. ORTEP diagram for *cis*-Re(CO)$_4$(PCy$_3$)Cl, **1c** (50% probability ellipsoids).

a singlet for each complex, and the ^{13}C{^{1}H} NMR spectrum of the carbonyl region shows three doublets from coupling to the phosphine, consistent with a cis arrangement of the phosphine and chloride ligands. The carbonyl region in the IR spectra each show one weak band around 2100 cm^{-1}, and three strong bands between 1930 and 2010 cm^{-1}, also consistent with a cis configuration. Table 1 lists the IR and ^{31}P spectral data for all compounds described in this paper.

The reaction of **1** with an excess (up to 5 equiv) of NaBAr$_F$ in CH_2Cl_2 was very slow and did not lead to the isolation of the cationic chloride-free complex. Instead, the chloride-bridged Re dimers {[*cis*-Re(CO)$_4$(PR$_3$)]$_2$(μ-Cl)}{BAr$_F$} (**5**) were present after 12 h in solution and were identified as the major products after 1 week in solution. The dimers were not isolated but were assigned on the basis of their ^{31}P chemical shift that was identical to that found for authentic samples of **5** as described later in this paper. The formation of the dimers must occur from the incomplete metathesis of **1** with NaBAr$_F$ to generate [*cis*-Re(CO)$_4$(PR$_3$)(ClCH$_2$Cl)][BAr$_F$] (**4**, not observed), followed by quick reaction with remaining chloride complex **1** to form the dimer.

Structure of *cis*-Re(CO)$_4$(PR$_3$)Cl (1b, 1c). The structures of **1b** and **1c** were solved by X-ray diffraction for the purpose of comparing neutral Re−Cl complexes with the cationic solvent

Table 2. Crystal Data and Structure Refinement[a]

complex	**1b**[b]	**1c**[c]	**4b**[d]	**5a**[e]	**5c**[f]	**6**[g]
empirical formula	$C_{13}H_{21}ClO_4PRe$	$C_{22}H_{30}ClO_4PRe$	$C_{46}H_{35}BCl_2F_{24}O_4PRe$	$C_{76}H_{46}BClF_{24}O_{10}P_2Re_2$	$C_{76}H_{72}BClF_{24}O_8P_2Re_2$	$C_{50}H_{33}BF_{29}NO_4PRe$
fw	493.92	611.01	1406.62	2055.73	2049.94	1490.75
space group	*C*2/*c*	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
temp (°C)	−80	−80	−70	−75	−70	−70
a (Å)	25.803(2)	9.1150(10)	11.4222(5)	13.048(2)	13.4105(2)	14.1056(8)
b (Å)	8.6720(10)	11.2030(10)	16.7303(8)	16.348(2)	18.0091(3)	14.2860(8)
c (Å)	15.578(2)	23.195(2)	27.772(1)	19.496(4)	18.9398(3)	14.7448(7)
α (deg)	90	90	90	92.52(1)	91.776(1)	94.555(1)
β (deg)	92.254(7)	93.589(6)	97.325(1)	96.58(1)	108.642(1)	109.249(1)
γ (deg)	90	90	90	100.24(1)	103.470(1)	100.458(1)
volume (Å^3)	3483.1(7)	2363.9(4)	5263.7(4)	4056.7(12)	4187.27(11)	2727.3(3)
Z	8	4	4	2	2	2
ρ_{calc} (g cm^{-1})	1.884	1.717	1.775	1.683	1.626	1.815
μ (cm^{-1})	0.7230	0.5345	0.2568	0.3164	0.3063	0.2402
final *R* indices	R1 = 0.0429	R1 = 0.0348	R1 = 0.0441	R1 = 0.0665	R1 = 0.0525	R1 = 0.0476
	$R2_w$ = 0.1045	$R2_w$ = 0.0829	$R2_w$ = 0.1105	$R2_w$ = 0.1483	$R2_w$ = 0.1441	$R2_w$ = 0.1199

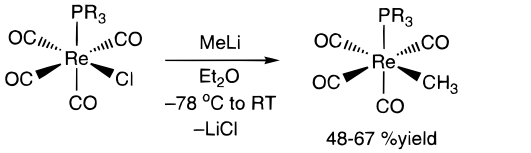
[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R2_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [b] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0744P)^2]$. [c] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 14.9032P]$. [d] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$. [e] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0758P)^2]$. [f] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0622P)^2]$. [g] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0759P)^2]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **1b** and **1c**

	distances			angles	
	1b	**1c**		**1b**	**1c**
Re(1)−P(1)	2.507(2)	2.521(2)	P(1)−Re(1)−Cl(1)	88.38(7)	86.39(14)
Re(1)−Cl(1)	2.483(2)	2.489(7)	P(1)−Re(1)−C(1)	90.9(2)	175.2(2)
Re(1)−C(1)	1.986(9)	1.959(6)	P(1)−Re(1)−C(4)	176.6(2)	91.6(12)
Re(1)−C(2)	1.879(9)	1.955(7)	Cl(1)−Re(1)−C(2)	177.2(2)	92.7(2)
Re(1)−C(3)	1.993(9)	1.961(8)	Cl(1)−Re(1)−C(3)	86.1(3)	176.9(2)
Re(1)−C(4)	1.956(8)	2.10(5)			

analogues $[Re-(S)]^+$. Table 2 lists a summary of crystallographic data for all of the structures presented in this paper. ORTEP diagrams of **1b** and **1c** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles can be found in Table 3. The ORTEP diagrams show the expected octahedral cis arrangement of the ligands about the metal, with Re−Cl distances of 2.483(2) Å (**1b**) and 2.489(7) Å (**1c**).

Preparation of *cis*-Re(Me)(CO)$_4$(PR$_3$) (2a−c). Neutral methyl or hydride species are often useful precursors to coordinately unsaturated cationic transition metal complexes. The chloride complexes **1a**−**c** are converted to the methyl complexes **2a-c** by treatment with one equiv of MeLi at low temperature in ether solution (eq 3). Removal of the solvent

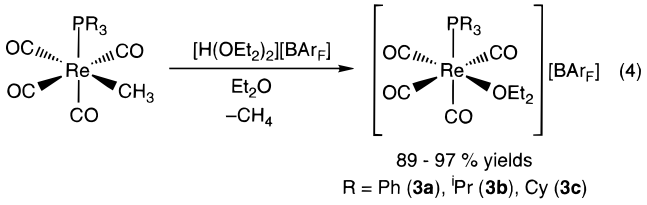


(3)

under vacuum provided a mixture of LiCl and the crude product as a yellow paste or foam. The product was purified by eluting the crude product through an SiO_2 column with hexanes or benzene/hexanes, which removed the yellow color and LiCl. Complexes **2a**−**c** were isolated as air stable white solids in moderate yields. Similar preparation of **2a** from MeLi and *cis*-Re(CO)$_4$(PPh$_3$)Br has been previously reported.[12]

The ^{1}H NMR spectra for **2** each show an upfield doublet for the rhenium methyl ligand due to coupling to the phosphine, and the ^{31}P{^{1}H} NMR spectra show a single phosphorus signal for each complex. The ^{13}C{^{1}H} NMR spectra exhibit three carbonyl resonances which are all doublets (confirming the cis geometry), and an upfield doublet for the rhenium methyl ligand. A carbonyl band pattern similar to that observed in the IR spectra for the chloride complexes **1** was obtained for the methyl complexes **2**. However, the CO bands are shifted to slightly lower frequencies due to the increased electron donation of methyl versus chloride to the Re and therefore increased back-donation from the Re to the CO antibonding orbitals.

Reaction of *cis*-Re(Me)(CO)$_4$(PR$_3$) with [H(OEt$_2$)$_2$][BAr$_F$]. Protonation of the methyl complexes **2** with 1 equiv of [H(OEt$_2$)$_2$][BAr$_F$] in diethyl ether provided the solvent-coordinated complexes [*cis*-Re(CO)$_4$(PR$_3$)(OEt$_2$)][BAr$_F$] (**3a**−**c**) (eq 4). The complexes were isolated by addition of hexanes



(4)

to the reaction mixture and were obtained in excellent yields as colorless crystals. These cationic complexes are insoluble in aromatic and aliphatic hydrocarbon solvents but soluble in Et$_2$O and CH$_2$Cl$_2$. The presence of 1 equiv of Et$_2$O in **3** was confirmed by elemental analysis. The coordinated Et$_2$O could not be removed by exposing the crystals to a vacuum for 12 h but was easily replaced by more basic ligands such as water and THF. Complexes **3a**−**c** are air stable for hours in crystalline form but slowly form water complexes in Et$_2$O solutions in air.

The IR spectra for these complexes show four bands in the carbonyl region similar to those for **1** and **2**, but at slightly higher frequencies due to the decreased electron donation of Et$_2$O versus CH_3^- or Cl^- and the positive charge on the complex. The X-ray crystal structure of **3a** was determined to confirm coordination of the ether to the metal center (Re−O = 2.254(11) Å) and has been recently communicated.[8] The ^{13}C and ^{1}H NMR spectra for **3a** were measured at −73 °C and confirmed the coordination of one Et$_2$O molecule in CD$_2$Cl$_2$ solution. The resonances assigned to the bound Et$_2$O appear in the ^{1}H NMR

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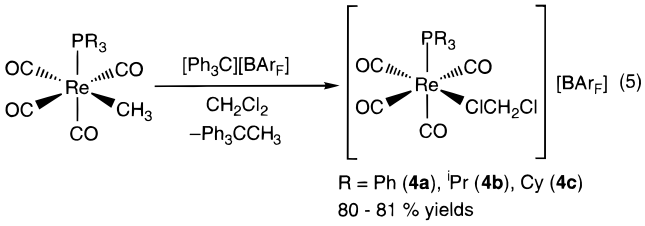
spectrum at δ 3.54 (q) and 0.98 (t), and at 77.13 (br) and 12.82 (br) in $^{13}C\{^1H\}$ NMR spectrum. These are shifted from those of free Et_2O at this temperature in CD_2Cl_2 solution at δ 3.34 (q) and 1.02 (t), and at δ 65.79 (s) and 14.98 (s) in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. The ^{31}P NMR spectrum for **3a** at −73 °C showed one phosphorus environment. The room temperature ^1H NMR spectra of **3a**−**c** after 5 min in CD_2Cl_2 solution confirmed the persistence of coordinated Et_2O, identified by resonances shifted downfield from that of free Et_2O, as well as peaks due to reaction of **3** with dichloromethane (discussed below).

The strong coordination of diethyl ether to the Re center is quite surprising when considering that Heinekey's analogous bis-phosphine complexes [*mer*-$Re(CO)_3(PR_3)_2][BAr_F]$ are isolated as the *agostic* compounds from protonation of [*mer*-$(PR_3)_2Re(CO)_3Me]$ with $[H(OEt_2)_2][BAr_F]$.[13] An agostic complex is one in which the sixth coordination site is taken up by interaction between the metal center and a C−H bond of one of the phosphine ligands. These complexes are usually deeply colored, and the agostic interaction is readily displaced by other substrates. This preference for the [*cis*-$Re(CO)_4(PR_3)]^+$ fragment to form solvent complexes instead of an agostic compound is due to the high electrophilicity of the metal center and the lack of steric hindrance at the open coordination site. There are a number of examples of isolated diethyl ether complexes reported in the literature,[3,14] including one other complex of rhenium, $[CpRe(NO)(PPh_3)(OEt_2)][BF_4]$.[2d]

Preparation of [*cis*-$Re(CO)_4(PR_3)(ClCH_2Cl)][BAr_F]$ (4a−c). Reaction of the methyl complexes **2** with 1 equiv of $[Ph_3C][BAr_F]$ in methylene chloride provided the solvent-coordinated complexes [*cis*-$Re(CO)_4(PR_3)(ClCH_2Cl)][BAr_F]$ (**4a**−**c**) (eq 5).



The complexes were isolated from the Ph_3CCH_3 by addition of hexanes to the reaction mixture and were obtained in good yields as pale yellow or colorless crystals. The presence of 1 equiv of CH_2Cl_2 in **4** was confirmed by elemental analysis. Complexes **4a**−**c** are stable in methylene chloride solution for 1 day; however, they will form the chloride-bridged dimers **5a**−**c** after days in CD_2Cl_2 solution or in the presence of water or other bases. These dichloromethane complexes are much more stable than Gladysz's $[Cp'Re(NO)(PPh_3)(ClCH_2Cl)][BF_4]$ (Cp′ = C_5H_5, C_5Me_5), which decomposes to a chloride-bridged dimer in CH_2Cl_2 solution above −20 °C.[2a,e,g]

The IR spectra for **4b** and **4c** in Nujol mulls each show one weak band around 2120 cm^{-1} and three strong bands between 1980 and 2050 cm^{-1}. The spectrum for **4a** is a bit more complicated with one weak band at 2122 cm^{-1} and six overlapping bands between 1980 and 2050 cm^{-1}, presumably because of band splitting. The bound CH_2Cl_2 in **4** exchanges

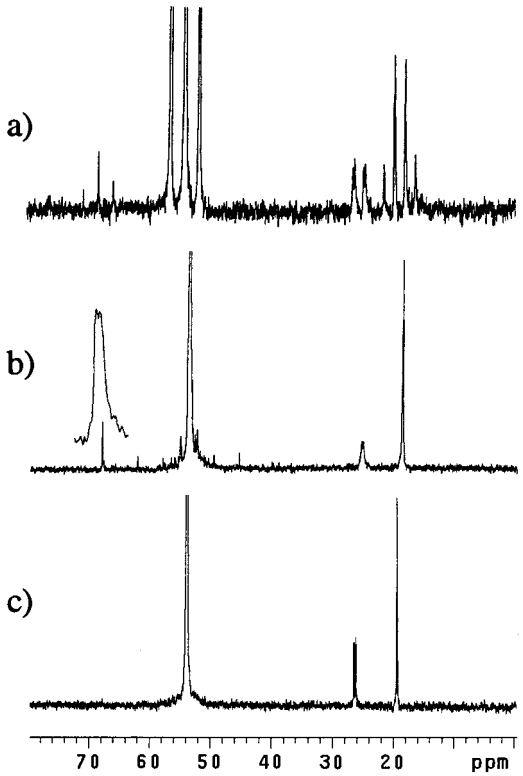


Figure 3. ^{13}C NMR spectra for [*cis*-$Re(CO)_4(P^iPr_3)(ClCH_2Cl)][BAr_F]$, **4b**, in CH_2Cl_2 solution. (a) ^{13}C, −80 °C; (b) $^{13}C\{^1H\}$, −80 °C; (c) $^{13}C\{^1H\}$, 20 °C.

rapidly on the NMR time scale in CH_2Cl_2 solution at room temperature, and is not distinguishable from free CH_2Cl_2 in the ^1H or ^{13}C NMR spectra. However, when CH_2Cl_2 solutions of **4** are cooled to −80 °C, signals assigned to bound CH_2Cl_2 at 66.36 (**4a**), 68.05 (**4b**), and 67.62 (**4c**) ppm are observed in the $^{13}C\{^1H\}$ NMR spectra. The peak assigned to bound CH_2Cl_2 in **4b** is a doublet (J_{CP} = 2.1 Hz), while those for **4a** and **4c** are slightly broadened singlets. These peaks are split into triplets J_{CH} = 184.3 (**4a**), 184.8 (**4b**), and 186.5 (**4c**) Hz in the ^1H-coupled experiment, as shown in Figure 3. The signals are shifted downfield from that of free CH_2Cl_2 at −80 °C (54.00 ppm, J_{CH} = 179.9 Hz), and are not present in the analogous NMR experiments performed in CD_2Cl_2 due to peak broadening from deuterium coupling. These observations in the low temperature ^{13}C spectra are very similar to those observed by Gladysz with $[Cp'Re(NO)(PPh_3)(ClCH_2Cl)][BF_4]$ in CH_2Cl_2 at −85 °C (78.3 ppm, J_{CH} = 185.5 Hz, J_{CP} = 3.8 Hz).

There have recently been a number of examples of isolated complexes with coordinated dichloromethane, most of which are derived from extremely electron deficient cationic metal centers with low-interacting anions.[2a,3,4b,15] In the complexes characterized by X-ray crystallography, dichloromethane has

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(14) For example: (a) Yi, C. S.; Wodka, D.; Rhingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 2−4. (b) Rix, R. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436−21448. (c) Solari, E.; Musso, F.; Gallo, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 2265−2276. (d) Kolodziej, R. M.; Schrock, R. R.; Dewan, J. C. *Inorg. Chem.* **1989**, *28*, 1243−1248.

(15) For example: (a) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398−7399. (b) Forniés, J.; Martínez, F.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 1813−1819. (c) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349−2362. (d) Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762−3764. (e) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1983**, 187−194. (f) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33*, 1214−1222. (g) For a review on the coordination chemistry of halocarbons, see: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89−115.

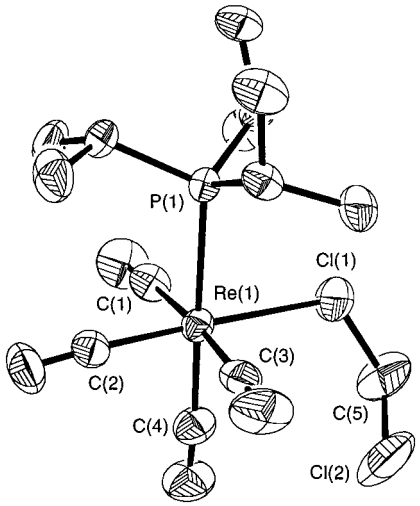


Figure 4. ORTEP diagram for [*cis*-Re(CO)$_4$(P^{i}Pr$_3$)(ClCH$_2$Cl)][BAr$_F$], **4b**; BAr$_F$ not shown (50% probability ellipsoids).

Table 4. Selected Bond Distances (Å) and Angles (deg) for Methylene Chloride Complex **4b**

distances (Å)		angles (deg)	
Re(1)−Cl(1)	2.554(2)	P(1)−Re(1)−Cl(1)	86.59(5)
Cl(1)−C(5)	1.765(13)	P(1)−Re(1)−C(4)	177.2(2)
Cl(1)−C(5)′	1.86(2)	C(1)−Re(1)−C(3)	174.9(9)
C(5)−Cl(2)	1.78(2)	Cl(1)−Re(1)−C(2)	178.3(2)
C(5)′−Cl(2)′	1.55(2)	Re(1)−Cl(1)−C(5)	117.8(6)
Re(1)−P(1)	2.5354(13)	Re(1)−Cl(1)−C(5)′	112.6(6)
Re(1)−C(1)	2.006(6)	Cl(1)−C(5)−Cl(2)	109.8(9)
Re(1)−C(2)	1.914(6)	Cl(1)−C(5)′−Cl(2)′	116.6(11)
Re(1)−C(3)	1.998(6)		
Re(1)−C(4)	1.973(6)		

been found to coordinate *bidentate* through the chloride atoms in Ag$_2$(CH$_2$Cl$_2$)$_4$Pd(OTeF$_5$)$_2$[15d] and [RuH(CO)(CH$_2$Cl$_2$)(P^{t}Bu$_2$Me)$_2$][BAr$_F$],[15a] and *monodentate* through one of the chloride atoms in [PtAg(CH$_2$Cl$_2$)(C$_6$F$_5$)$_2$(acac)]$_2$,[15b] [Cp*Ir(Me)(PMe$_3$)(ClCH$_2$Cl)][BAr$_F$],[4b] and [*trans*-PtH(P^{i}Pr$_3$)$_2$(ClCH$_2$Cl)][BAr$_F$].[3] The coordinated dichloromethane in [CpMo(CO)$_3$(ClCH$_2$Cl)][PF$_6$][15f] and [Cp′Re(NO)(PPh$_3$)(ClCH$_2$Cl)][BF$_4$][2a] has been assigned on the basis of IR spectral data and low-temperature ^{13}C NMR spectral data, respectively.

Structure of [*cis*-Re(CO)$_4$(P^{i}Pr$_3$)(CH$_2$Cl$_2$)][BAr$_F$] (4b). The X-ray crystal structure of **4a** was recently communicated and confirmed the retention of cis geometry and η^1-coordination of the CH$_2$Cl$_2$ ligand through one chloride.[8] In the current study, we determined the structure of the ^{i}Pr complex **4b** for the purpose of comparison to that of the Ph analogue. An ORTEP diagram of **4b** is shown in Figure 4, and selected bond lengths and angles are listed in Table 4. As in the case of **4a**, the coordinated CH$_2$Cl$_2$ is η^1-bound to the Re through one chloride. The CH$_2$Cl$_2$ ligand is disordered at the methylene carbon C(5) and the unbound chloride Cl(2), and these were refined as two one-half occupancy atom positions.

The Re−Cl distance in **4b** is 2.554(2) Å, which is comparable to that found for the PPh$_3$ derivative **4a**, 2.546(2) Å,[8] and those reported for the related η^1-coordinated dichloromethane complexes [Cp*Ir(Me)(PMe$_3$)(ClCH$_2$Cl)][BAr$_F$] (2.462(3) Å)[4b] and [*trans*-PtH(P^{i}Pr$_3$)$_2$(ClCH$_2$Cl)][BAr$_F$] (2.489(4), 2.60(1) Å), which was disordered at the bound chloride and methylene carbon.[3] As expected, the Re−Cl distance in **4b** is longer than the Re−Cl distance (2.554(3) Å) in the corresponding neutral chloride compound **1b** (2.483(2) Å). The C−Cl(bound) distances in **4b** are 1.765(13) and 1.86(2) Å for C(5) and C(5)′, respectively.

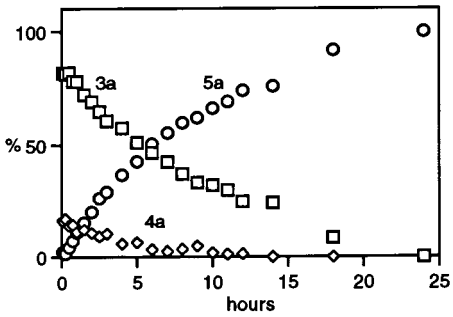


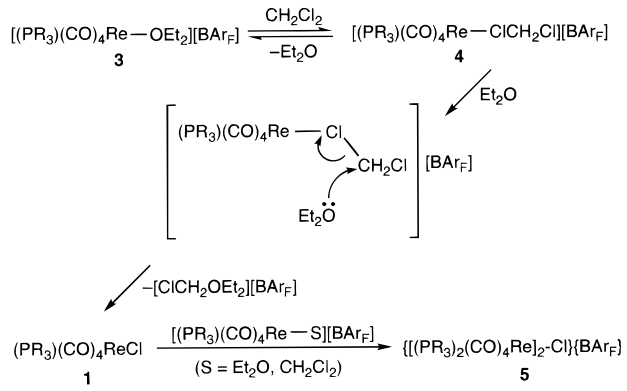
Figure 5. Decomposition of **3a** in CD$_2$Cl$_2$ solution, 20 °C, monitored by integration of ^{31}P{^{1}H} signals.

These distances are similar to those found for **4a** (1.817(6) Å), the Ir complex (1.820(15) Å), and the Pt complex (1.79(2), 1.80(4) Å). The C−Cl(unbound) distances were refined as 1.78(2) and 1.55(2) Å for **4b**, 1.716(6) Å for **4a**, 1.730(15) Å for Ir, and 1.70(2) and 1.69(4) Å for Pt. Finally, the Cl−C−Cl angles for **4b** are 109.8(9) and 116.6(11)°, compared to 112.0(3)° for **4a**, 110.7(8)° for the Ir complex, and 111.6(13) and 103(2)° for the Pt complex. The orientation of the dichlromethane ligand in **4a** and **4b** differs somewhat. In **4a**, the two chlorine atoms of the CH$_2$Cl$_2$ molecule are essentially in the plane defined by the Re and three equatorial CO carbon atoms, with the methylene C atom pointed down away from the phosphine: Cl(bound) +0.19 Å, C(methylene) −0.82 Å, and Cl(unbound) −0.11 Å out of the equatorial plane. In contrast to this, the whole dichloromethane ligand in **4b** is pointed down away from the phosphine, with Cl(1) 0.0 Å, C(5) −1.57 Å, C(5)′ −1.15 Å, Cl(2) −2.31 Å, and Cl(2)′ −2.63 Å out of the equatorial plane.

Decomposition of [*cis*-Re(CO)$_4$(PR$_3$)(S)][BAr$_F$]. The ether complexes **3** are not stable in methylene chloride solution at room temperature, and after 24 h **3a**−**c** convert entirely to the chloride-bridged dimers {[*cis*-Re(CO)$_4$(PR$_3$)]$_2$(μ-Cl)}{BAr$_F$} (**5a**−**c**). The decomposition of the **3** in CD$_2$Cl$_2$ solution was monitored by ^{31}P{^{1}H} NMR spectroscopy. The rate of formation of the chloride-bridged dimers was found to vary with the nature of the phosphine, with the P^{i}Pr$_3$ and PCy$_3$ derivatives completely converting to the dimers within 7 h, while the PPh$_3$ analogue required 24 h to completely convert to the dimer. The dichloromethane complexes [*cis*-Re(CO)$_4$(PR$_3$)(ClCD$_2$Cl)][BAr$_F$], identified by comparison of ^{31}P shift to authentic samples of **4**, were observed as intermediates in the decomposition of **3** to **5**. A graph illustrating the conversion of **3a** to **5a** over 24 h is shown in Figure 5. Similar plots were obtained for **3b** and **3c**, and are provided in the supplementary data.

Changes were also apparent in the ether and BAr$_F$ regions of the ^{1}H NMR spectra as **3** converted to **5** in CD$_2$Cl$_2$ solution. The resonances due to coordinated Et$_2$O in **3** decreased in intensity as two sets of peaks at δ 4.63 (q, J_{HH} = 7.1 Hz) and 1.63 (t, J_{HH} = 7.1 Hz), and 3.5 (br) and 1.2 (br t) grew in, and no peaks due to coordinated Et$_2$O in **3** were observed in the ^{1}H NMR spectra after 24 h in CD$_2$Cl$_2$ solution. These two new sets of ethyl resonances were at virtually identical chemical shifts for all three phosphine derivatives, whereas the original resonances due to bound Re−OEt$_2$ varried slightly for each derivative of **3**. This observation suggests that the two new sets of resonances are due to ether which is not associated with a Re center. When the reaction mixture was placed under a vacuum after 24 h in CD$_2$Cl$_2$ solution, free ether was observed in the trapped volatiles. Subsequent dissolution of the residue in CD$_2$Cl$_2$ resulted in the same two sets of ether resonances in the ^{1}H NMR spectra (δ 4.63, 1.63 and 3.5, 1.2), with an overall

Scheme 1. Proposed Mechanism for Conversion of **3** to **5**



integration of phosphine protons versus ethyl protons consistent with 1 equiv of Et_2O per Re dimer.

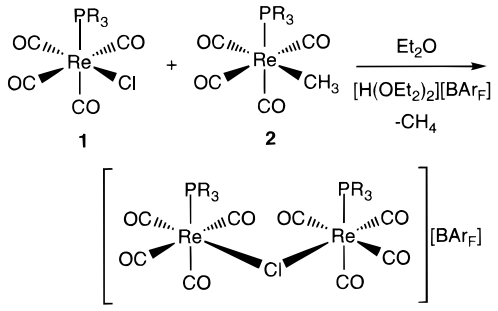
The chemical shifts in the ^1H NMR spectra of the downfield set of Et_2O resonances at δ 4.63 (q, J_{HH} = 7.1 Hz) and 1.63 (t, J_{HH} = 7.1 Hz) are consistent with the existence of an ethyloxonium ion. For comparison, $[Et_3O][BF_4]$ (Acros Organics) in CD_2Cl_2 solution exhibits resonances at δ 4.78 (q, J_{HH} = 7.1 Hz) and 1.63 (t, J_{HH} = 7.1 Hz). The second set of resonances at δ 3.5 and 1.2 ppm increase in intensity when free ether is added and thus have been assigned as a solvate of the oxonium ion. To support this assignment, similar broad resonances at δ 3.6 and 1.2 ppm in the ^1H NMR spectrum of $[Et_3O][BF_4]$ in CD_2Cl_2 increased in intensity upon addition of free ether.

Formation of an oxonium ion in this system could result from nucleophilic attack of the weak base Et_2O on the methylene carbon of $[Re{-}ClCH_2Cl]^+$ (**4**), generating the neutral chloride, **1**, and $[Et_2OCH_2Cl]^+$. The dichloromethane complex **4** would be formed by dissociation of the Et_2O from the Re center in solution, and should be faster for the P^{i}Pr and PCy_3 complexes **3b** and **3c** than for the PPh_3 complex **3a** since the more electron donating and bulkier phosphines should not bind Et_2O as strongly. This is consistent with the observed slower rate for conversion of **3** to **5** for the PPh_3 derivative versus the P^{i}Pr$_3$ and PCy_3 analogues. In a separate experiment, 1 μL of Et_2O was added to a CD_2Cl_2 solution of **4a** (10 mg/0.5 mL) and conversion to **5a** was complete within 24 h. The proposed mechanism for conversion of **3** to **5** is shown in Scheme 1.

In an attempt to determine the fate of the methylene chloride molecule which must give up a Cl^- to form the chloride-bridged Re dimer **5**, a CH_2Cl_2 solution of **3a** was allowed to stand for 24 h, the volatiles removed under vacuum, and the residue redissolved in CD_2Cl_2. The resulting ^1H NMR spectrum was identical to that obtained from the reaction in CD_2Cl_2, as described in the previous paragraph. Unfortunately, no new peaks were observed in the ^1H NMR spectrum that could be assigned to $[ClCH_2OEt_2][BAr_F]$ products that would result from loss of Cl^- from CH_2Cl_2. GC/MS analysis of the trapped volatiles showed the presence of CH_2Cl_2, Et_2O, $CHCl_3$, and 1,3-$(CF_3)_2C_6H_4$. This would seem to suggest that if $[ClCH_2OEt_2][BAr_F]$ were formed, it is unstable under the reaction conditions and reacts further with the BAr_F to form a new ethyloxonium ion, $[Et_2OX]^+$. Furthermore, small additional peaks appeared in the BAr_F region of the ^1H NMR spectra as **3** converted to **5**, providing more evidence that decomposition of BAr_F occurs. Finally, there was no indication of $[H(OEt_2)_2][BAr_F]$ formation in the ^1H NMR spectra, and no observation of a carbene in the ^{13}C NMR spectra.

The reaction of a base with coordinated methylene chloride has precedence in Gladysz's observation of nucleophilic attack of halide ions X^- upon the methylene carbon in $[Cp'Re(NO)(PPh_3)(ClCH_2Cl)][BF_4]$ to provide the neutral ReCl complex and CH_2ClX.[2g] The decomposition of the corresponding diethyl ether and tetrahydrofuran coordinated complexes $[Cp'Re(NO)(PPh_3)(OR_2)][BF_4]$ were also observed when warmed above −20 °C in CD_2Cl_2 solution, although the decomposition products and pathway were not reported.[2d] It is possible that the conversion of **3** to **5** is catalyzed by trace amounts of adventitious water in solution, even though water was rigorously excluded from these systems. This would require nucleophilic attack of H_2O on the methylene carbon of **4** to generate $[H_2OCH_2Cl]^+$, which would then have to react further with Et_2O to produce an ethyloxoinium ion.

Preparation of {[*cis*-Re(CO)$_4$(PR$_3$)]$_2$(μ-Cl)}{BAr$_F$} (5a−c). To unambiguously assign the decomposition products of the ether complexes **3** in methylene chloride solution, the chloride-bridged Re dimers $\{[cis\text{-}Re(CO)_4(PR_3)]_2(\mu\text{-}Cl)\}\{BAr_F\}$ (**5**) were prepared. Reaction of the chloride complexes **1** with 1 equiv of the corresponding methyl compound **2** in the presence of 1 equiv of $[H(Et_2O)_2][BAr_f]$ in diethyl ether solution cleanly provided **5** as colorless crystals (eq 6). The dimers gave satisfactory



(6)

R = Ph (**5a**), ^{i}Pr (**5b**), Cy (**5c**)
77 - 81 % yields

elemental analysis. The IR spectra for each derivative of **5** showed two weak or medium bands in the region 2100−2122 cm^{-1} and multiple strong overlapping bands between 1965 and 2030 cm^{-1}. The ^1H and ^{31}P NMR spectra corresponded to one phosphine environment, and one BAr_F anion per two phosphine ligands. The complexes were quite stable and did not decompose when exposed to air for 1 day. No reaction was observed from combination of the dimer **5a** with approximately 10 equiv of $NaBAr_F$ in CD_2Cl_2 solution after one week.

The stability of the dimers and ease of formation from $[Re(S)]^+$ and chloride sources is not surprising when considering the high electrophilicity of the rhenium center and the lack of steric restraint from the ligands. This is not the case in the more sterically demanding bis-phosphine complexes which react completely with $NaBAr_F$ in CH_2Cl_2 solution to remove all of the halide: *mer*-$ReCl(CO)_3(PR_3)_2$ forms the $Re(H_2)$ complex under H_2 atmosphere,[13] *mer*-$MnBr(CO)_3(PCy_3)_2$ forms the agostic complex,[16] and *trans*-$PtH(Cl)(P^iPr_3)_2$ forms the Pt-$(ClCH_2Cl)$ solvent complex.[3]

Structures of {[*cis*-Re(CO)$_4$(PR$_3$)]$_2$(μ-Cl)}{BAr$_F$} (5a, 5c). Addition of bulk hexanes (not dried) to a CH_2Cl_2 solution of **4a** and storage for 1 week at room temperature provided approximately a 20% yield of **5a** as colorless crystals with two water molecules in the lattice. Similar conditions produced **5c** as large crystals in approximately 40% yield. The structures of each were determined by X-ray crystallography and ORTEP

(16) Toupadakis, A.; Kubas, G. J.; King, W. A.; Scott, B. L.; Huhmann-Vincent, J. *Organometallics* **1998**, *17*, 5315−5323.

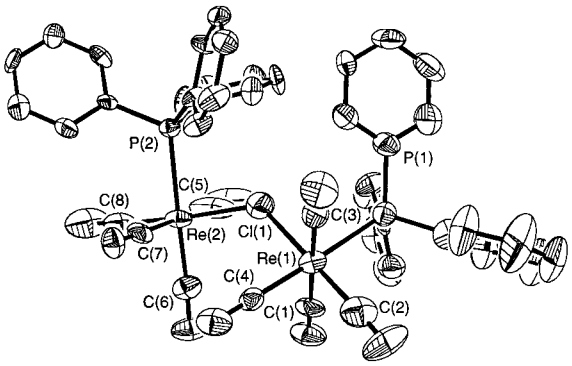


Figure 6. ORTEP diagram for {[*cis*-Re(CO)$_4$(PPh$_3$)]$_2$(μ-Cl)}{BAr$_F$}, **5a**; BAr$_F$ not shown (50% probability ellipsoids).

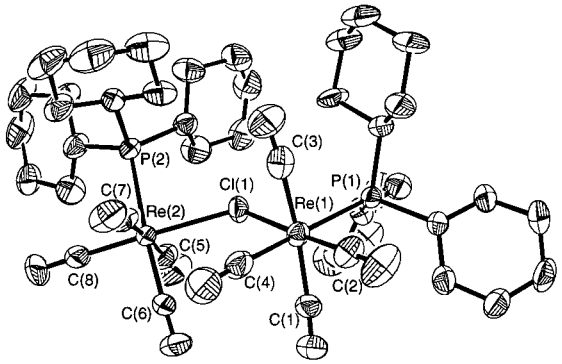


Figure 7. ORTEP diagram for {[*cis*-Re(CO)$_4$(PCy$_3$)]$_2$(μ-Cl)}{BAr$_F$}, **5c**; BAr$_F$ not shown (50% probability ellipsoids).

diagrams of **5a** and **5c** are shown in Figures 6 and 7, and selected interatomic distances and angles can be found in Table 5.

The structures are similar, both retaining the cis orientation of phosphines and chloride, with approximately octahedral geometry about each Re. The Re−Re interatomic distances are 4.333 Å for the Ph derivative **5a** and 4.460 Å for the Cy derivative **5c**. There is no center of symmetry about the bridging chloride thus complex has two inequiv Re−Cl distances, 2.421(4) and 2.397(5) Å for **5a**, and 2.5264(5) and 2.5285(7) Å for **5c**. As expected, the bulkier PCy$_3$ complex has a longer Re−Re distance and longer Re−Cl distances than the PPh$_3$ complex. The Re−Cl distances for **5a** are slightly shorter than the Re−Cl distances found in the dichloromethane complex **4a** (2.546(2) Å), and the Re−Cl bond lengths of **5c** are slightly longer than that of the neutral chloride complex **1c** (2.489(7) Å). The Re−Cl−Re angle is larger for the PPh$_3$ complex **5a** (128.2(2)°) than for the PCy$_3$ complex **5c** (123.85(2)°), due to the shorter Re−Re distance in **5a** versus **5c**.

Preparation of [*cis*-Re(CO)$_4$(P^{i}Pr$_3$)(NC$_5$F$_5$)][BAr$_F$] (6). Reaction of the ^{i}Pr complex **2b** with 1 equiv of [Ph$_3$C][BAr$_F$] in NC$_5$F$_5$ provided the pentafluoropyridine-coordinated complex [*cis*-Re(CO)$_4$(P^{i}Pr$_3$)(NC$_5$F$_5$)][BAr$_F$] (**6**). Complex **6** is isolated from hexanes/NC$_5$F$_5$ as colorless crystals and is stable in NC$_5$F$_5$ solution. The presence of one NC$_5$F$_5$ molecule in the complex was determined by elemental analysis. The IR spectrum for **6** is very similar to that obtained for the methylene chloride complex **4b**, and the ^{1}H and ^{31}P NMR spectra in NC$_5$F$_5$ solution are consistent with one phosphine environment.

Solutions of **6** in CD$_2$Cl$_2$ (5−7 mg/0.5 mL) immediately convert to the ClCD$_2$Cl-coordinated complex **4b** as determined by the ^{31}P NMR chemical shift of 33.6 ppm. However, when an aliquot of 50 μL of NC$_5$F$_5$ was injected to a CD$_2$Cl$_2$ solution of **6** (10 mg/0.5 mL) and the ^{31}P{^{1}H} NMR spectrum measured, one sharp peak was observed at 30.4 ppm, which is at the same chemical shift observed for **6** in NC$_5$F$_5$ solutions (see Experimental Section). This peak in CD$_2$Cl$_2$ solution is therefore assigned to the pentafluoropyridine-coordinated complex **6**. Subsequent addition of 25 μL of Et$_2$O resulted in complete conversion to the diethyl ether complex **3b** (36.3 ppm). These results give the binding order of Et$_2$O > NC$_5$F$_5$ ≫ CH$_2$Cl$_2$. Finally, conversion of **6** to the chloride-bridged dimer **5b** in CD$_2$Cl$_2$ solution is slow, and only 50% conversion was obtained after one week (^{31}P NMR).

Structure of [*cis*-Re(CO)$_4$(P^{i}Pr$_3$)(NC$_5$F$_5$)][BAr$_F$] (6). The X-ray crystal structure of **6** was determined in order to confirm the coordination of pentafluoropyridine to the Re center, instead of just being in the lattice. An ORTEP diagram of **6** is shown in Figure 8, and selected bond lengths and angles are listed in Table 6. The Re−N distance is 2.319(5) Å, which is intermediate in length between the corresponding Re−Cl distances in the methylene chloride complexes **4a** (2.546(2) Å) and **4b** (2.554(2) Å), and the Re−O distance in the ether complex **3a** (2.254(11) Å). The pentafluoropyridine is tilted 27.9° about the Re−N axis from the plane defined by the Re and three equatorial carbonyl C atoms (C(1)−C(3)). There are no short contacts between the Re−NC$_5$F$_5$ cation and the BAr$_F$ anion. Bercaw has recently reported the crystal structure of a Pt−NC$_5$F$_5$ complex, [Pt(Me)(tmede)(NC$_5$F$_5$)][BAr$_F$], with a much shorter Pt−N distance of 2.043(6) Å.[5a]

Conclusions

The solvent coordinated complexes [*cis*-Re(PR$_3$)(CO)$_4$(S)][BAr$_F$] are conveniently prepared from the corresponding neutral ReMe precursors and either [H(OEt$_2$)$_2$][BAr$_F$] (S = Et$_2$O) or [Ph$_3$C][BAr$_F$] (S = CH$_2$Cl$_2$, NC$_5$F$_5$) in the appropriate solvent. The low-temperature ^{13}C NMR data and X-ray structures of the dichloromethane complexes confirm that CH$_2$Cl$_2$ coordination persists in both solution and the solid state. Of the structurally characterized complexes (**3a**, **4a**, **4b**, **6**) for this [*cis*-Re(PR$_3$)(CO)$_4$(S)]$^+$ system, the Re−S distance increases in the order Et$_2$O < NC$_5$F$_5$ < CH$_2$Cl$_2$, and the binding affinities of S to Re$^+$ in methylene chloride solution decreases in the order Et$_2$O > NC$_5$F$_5$ ≫ CH$_2$Cl$_2$. The dichloromethane complexes are not stable in CH$_2$Cl$_2$ solution in the presence of the weak base diethyl ether, and decompose to chloride-bridged Re dimers.

Experimental Section

General Considerations. NMR spectra were measured on a Varian UNITY series 300 MHz spectrometer. FT-IR spectra were obtained either on a Bio-Rad FTS-40 or Nicolet Magna 750 spectrometer. Solvents were dried either by distillation from P$_2$O$_5$ (CH$_2$Cl$_2$, NC$_5$F$_5$), Na/benzophenone (Et$_2$O, hexanes), or by elution from columns of activated alumina and BTS catalyst according to the procedure describe by Grubbs.[17] NMR solvents were dried over either CaH$_2$ or P$_2$O$_5$ and vacuum transferred before use. ^{1}H NMR spectra were referenced to either CHDCl$_2$ or TMS, ^{31}P NMR spectra were referenced to H$_3$PO$_3$, and ^{13}C spectra were referenced to CD$_2$Cl$_2$. The BAr$_F$ peaks are not reported in the ^{13}C NMR data and are virtually identical to those previously reported, regardless of the cationic fragment.[3] All manipulations and reactions with air-sensitive compounds were carried out either in a Vacuum Atmospheres He Drybox or under Ar using standard Schlenk techniques. All reactions were carried out at atmospheric pressure, which is 600 milliTorr at Los Alamos (elevation = 7000 ft) unless otherwise noted. The reagents [H(OEt$_2$)$_2$][BAr$_F$][18] and [Ph$_3$C]-

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Table 5. Selected Interatomic Distances (Å) and Angles (deg) for Chloride-Bridged Complexes **5a** and **5c**

	distances			angles	
	5a	**5c**		**5a**	**5c**
Re(1)−Re(2)	4.333	4.460	Re(1)−Cl−Re(2)	128.2(2)	123.85(2)
Re(1)−Cl	2.421(4)	2.5264(5)	P(1)−Re(1)−Cl	84.8(2)	86.87(2)
Re(1)−P(1)	2.510(4)	2.5371(6)	P(1)−Re(1)−C(4)	176.5(5)	178.62(8)
Re(1)−C(1)	2.03(2)	1.997(2)	C(2)−Re(1)−Cl	177.9(6)	177.31(9)
Re(1)−C(2)	1.95(2)	1.908(3)	C(1)−Re(1)−C(3)	178.8(6)	173.97(10)
Re(1)−C(3)	2.01(2)	1.997(3)	P(2)−Re(2)−Cl	83.93(14)	87.66(2)
Re(1)−C(4)	1.94(2)	1.939(3)	P(2)−Re(2)−C(6)	178.0(5)	176.13(8)
Re(2)−Cl	2.397(5)	2.5285(7)	C(8)−Re(2)−Cl	170.7(5)	178.23(7)
Re(2)−P(2)	2.493(3)	2.5277(6)	C(5)−Re(2)−C(7)	177.6(7)	174.35(12)
Re(2)−C(5)	1.98(2)	2.006(2)			
Re(2)−C(6)	1.92(2)	1.960(3)			
Re(2)−C(7)	1.96(2)	1.990(2)			
Re(2)−C(8)	1.91(2)	1.915(3)			

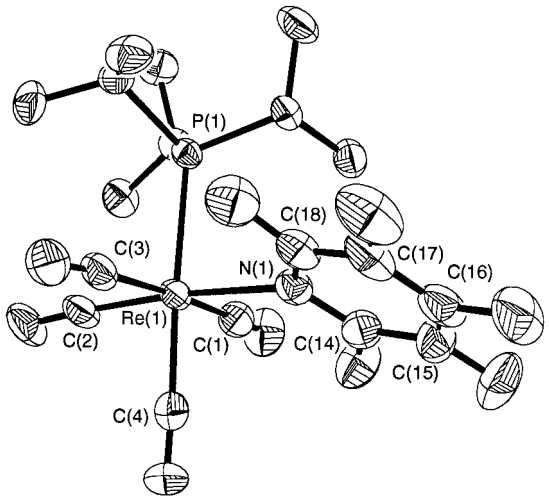

Figure 8. ORTEP diagram for [*cis*-Re(CO)$_4$(P^{i}Pr$_3$)(NC$_5$F$_5$)][BAr$_F$], **6**; BAr$_F$ not shown (50% probability ellipsoids).

Table 6. Selected Bond Distances and Angles for Pentafluoropyridine Complex **6**

Distances (Å)			
Re(1)−(P1)	2.534(1)	N(1)−C(14)	1.327(8)
Re(1)−N(1)	2.319(5)	C(14)−C(15)	1.382(9)
Re(1)−C(1)	2.002(7)	C(15)−C(16)	1.365(11)
Re(1)−C(2)	1.919(6)	C(16)−C(17)	1.365(11)
Re(1)−C(3)	2.004(7)	C(17)−C(18)	1.376(9)
Re(1)−C(4)	1.982(7)	C(18)−N(1)	1.332(8)

Angles (deg)	
P(1)−Re(1)−N(1)	92.79(12)
P(1)−Re(1)−C(4)	176.9(2)
C(3)−Re(1)−C(1)	175.0(2)
N(1)−Re(1)−C(2)	173.5(2)
C(18)−N(1)−C(14)	114.7(5)

[BAr$_F$][19] were prepared according to literature procedures. The Re(CO)$_5$Cl and all phosphines were purchased from Strem Chemicals and used as supplied, MeLi was purchased from Aldrich in Et$_2$O solution (1.4 M). Characterization data for **1a** and **2a** have been reported elsewhere.[10,12]

Preparation of *cis*-Re(CO)$_4$(PR$_3$)Cl for R = Ph (1a), ^{i}Pr (1b), Cy (1c). Re(CO)$_5$Cl (1.00 g, 2.76 mmol) and P^{i}Pr$_3$ (0.449 g, 2.80 mmol) were weighed into a Schlenk flask, and CHCl$_3$ (100 mL) was added. The reaction mixture was gently refluxed for 15 h with stirring, after which time the clear and colorless solution was obtained. The chloroform was removed under vacuo and the resulting white residue was dissolved in hot cyclohexane (30 mL). The solution was filtered hot through a frit under Ar to remove any unreacted Re(CO)$_5$Cl, and then concentrated to a volume of 5 mL. Hexanes (10 mL) were added and the solution concentrated until white crystal began to form. Storage in a freezer (−30 °C) for 10 h afforded white crystals, which were washed once with cold hexane (5 mL) and dried in a vacuum to provide 1.10 g of **1b** (81% yield). Colorless prisms suitable for X-ray diffraction studies were obtained by recrystallization from cyclohexane/hexane (1/5) at −30 °C. Complexes **1a** and **1c** were prepared analogously to **1b** and isolated as white solids in 91% and 83% yields, respectively. Colorless prisms of **1c** suitable for X-ray diffraction studies were obtained by recrystallization from cyclohexane/hexane (1/2) at −30 °C. Data for **1b**. Anal. Calcd for $C_{13}H_{21}O_4ClPRe$: C, 31.61; H, 4.29. Found: C, 32.05; H, 4.31. ^{1}H NMR (CD_2Cl_2) 2.56 (d of septets, J_{HP} = 9.2, J_{HH} = 7.2, 3H, CH), 1.35 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 18H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2) 188.16 (d, J_{HP} = 9.2, CO), 184.93 (d, J_{HP} = 5.0, CO), 183.55 (d, J_{HP} = 53.0, CO), 25.40 (d, J_{CP} = 23.6, ^{i}Pr), 19.85 (s, ^{i}Pr). Data for **1c**. Anal. Calcd for $C_{22}H_{33}ClO_4PRe$: C, 43.03; H, 5.42. Found: C, 42.75; H, 5.26. ^{1}H NMR (CD_2Cl_2) 2.24 (m, 1H, PCy$_3$), 2.00 (m, 2H, PCy$_3$), 1.87 (m, 2H, PCy$_3$), 1.52 (m, 2H, PCy$_3$), 1.74 (m, 1H, PCy$_3$), 1.31 (m, 3H, PCy$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2) 188.49 (d, J_{CP} = 8.8, CO), 185.20 (d, J_{CP} = 6.7, CO), 183.67 (d, J_{CP} = 52.5, CO), 34.91 (d, J_{CP} = 21.7, Cy), 30.03 (s, Cy), 28.02 (d, J_{CP} = 10.4, Cy), 26.72 (s, Cy).

Photochemical Preparation of 1b and 1c. Re(CO)$_5$Cl (1.88 g, 5.20 mmol) and P^{i}Pr$_3$ (0.834 g, 5.20 mmol) were weighed into a Schlenk flask and CH_2Cl_2 (50 mL) and cyclohexane (50 mL) were added. The reaction mixture was placed approximately two inches from a 450 W lamp (which was inserted in a quartz water cooled jacket) and photolized for 1.5 h with stirring, after which time a pale yellow solution was obtained. The volatiles were removed under vacuo, and the resulting white residue was dissolved in hot cyclohexane (50 mL). The solution was filtered hot through a frit under Ar to remove any unreacted Re(CO)$_5$Cl and then concentrated to a volume of 5 mL. Hexanes (10 mL) were added, and the solution was concentrated until crystals began to form. Storage in a freezer (−30 °C) for 10 h afforded white crystals, which were washed once with cold hexane (5 mL) and dried in a vacuum to provide 1.98 g of **1b** (77% yield). Complex **1c** was prepared similarly from phosphine and Re(CO)$_5$Cl, and isolated in 78% yield.

Preparation of *cis*-Re(CO)$_4$(PR$_3$)(CH$_3$) (R = Ph (2a), ^{i}Pr (2b), Cy (2c)). An aliquot of MeLi (0.72 mL, 1.4 M) was added to a stirred and cooled (−78 °C) solution of **1b** (0.500 g, 1.01 mmol) in Et$_2$O (50 mL). The reaction mixture was stirred for 5 min, then slowly warmed to room temperature and stirred for 30 min. To the resulting pale yellow reaction mixture was added CH_2Cl_2 (0.50 mL) to quench any unreacted MeLi. The solvents were removed under vacuum and the residue was chromatographed on SiO_2 (15 g) eluting with hexanes/benzene (10/1). The first fraction was collected, and removal of volatiles provided **2b** as a white solid (0.30 g, 62% yield). Compounds **2a** and **2c** were prepared analogously to **2b** from MeLi and **1a** or **1c** and isolated as white solids in 55% and 48% yields, respectively. Data for **2b**. Anal. Calcd for $C_{14}H_{24}O_4PRe$: C, 35.51; H, 5.11. Found: C, 35.51; H, 4.91. ^{1}H NMR (CD_2Cl_2) 2.33 (d of sept, J_{HP} = 8.8, J_{HH} = 7.2, 3H, ^{i}Pr), 1.27 (dd, J_{HP} = 13.7, J_{HH} 7.2, 18H, ^{i}Pr), −0.45 (d, J_{HP} = 6.3, CH_3, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2) 193.81 (d, J_{CP} = 10.2, CO), 189.37 (d, J_{CP} = 47.0, CO), 188.46 (d, J_{CP} = 7.2, CO), 26.02 (d, J_{CP} = 22.4, ^{i}Pr), 19.78 (s, ^{i}Pr), −34.30 (d, J_{CP} = 8.2, CH_3). Data for **2c**. Anal. Calcd for $C_{23}H_{36}O_4PRe$: C, 46.53; H, 6.11. Found: C, 46.67; H, 5.95. ^{1}H NMR (CD_2Cl_2) 2.01 (m, 3H, Cy), 1.89 (m, 12H, Cy), 1.72 (br s, 3H, Cy),

1.46 (m, 6H, Cy), 1.29 (m, 9H, Cy), −0.49 (d, J_{HP} = 6.4, 3H, CH_3). $^{13}C\{^1H\}$ (CD_2Cl_2) 194.10 (d, J_{CP} = 9.5, CO), 189.59 (d, J_{CP} = 47.3, CO), 188.51 (d, J_{CP} = 9.3, CO), 35.55 (d, J_{CP} = 20.5, Cy), 29.93 (s, Cy), 28.13 (d, J_{CP} = 10.1, Cy), 26.90 (s, Cy), −34.28 (d, J_{CP} = 8.5, CH_3).

Preparation of [*cis*-Re(CO)$_4$(PR$_3$)(OEt$_2$)][BAr$_F$] (R = Ph (3a), ^{i}Pr (3b), Cy (3c)). Compound **2a** (0.200 g, 0.347 mmol) was added to a 20 mL flask and dissolved in Et_2O (7 mL). Subsequent addition of $[H(OEt_2)_2][BAr_F]$ (0.354 g, 0.500 mmol) with stirring resulted in fast evolution of methane. The pale yellow reaction mixture was stirred for 5 min before the addition of hexanes (2 mL). The solution was stored at −30 °C overnight to give colorless crystals of **3a** which were washed twice with hexanes (5 mL) and dried in vacuo (0.502 g, 97% yield). Compounds **3b** and **3c** were prepared in analogous fashion from $[H(OEt_2)_2][BAr_F]$ and **2b** or **2c** and isolated in 91% and 89% yields, respectively. Data for **3a**. Anal. Calcd for $C_{58}H_{37}BF_{24}O_5PRe$: C, 46.51; H, 2.49. Found: C, 46.40; H, 2.36. ^1H NMR (CD_2Cl_2, −73 °C) 7.73 (s, 8H, BAr_F), 7.3−7.6 (m, 19H, Ph, BAr_F), 3.53 (q, 6.9 Hz, 4H Et_2O), 0.98 (t, 6.9 Hz, 6H, Et_2O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −73 °C) 187.0 (d, J_{CP} = 9.3, CO), 183.51 (d, J_{CP} = 5.2, CO), 183.11 (d, J_{CP} = 51.2, CO), 132.9 (br s, Ph), 132.3 (br s, Ph), 129.6 (br s, Ph), 127.6 (d, J_{CP} = 44.6, *i*-Ph), 77.13 (br s, OEt_2), 12.82 (br s, OEt_2). ^1H NMR (CD_2Cl_2) 7.73 (s, 8H, BAr_F), 7.3−7.6 (m, 19H, Ph, BAr_F), 3.71 (q, 7.1 Hz, 4H Re−OEt_2), 1.12 (t, 7.1 Hz, 6H, Re−OEt_2). Data for **3b**. Anal. Calcd for $C_{49}H_{43}BF_{24}O_5PRe$: C, 42.16; H, 3.11. Found: C, 41.80; H, 3.13. ^1H NMR (CD_2Cl_2) 7.73 (s, 8H, BAr_F), 7.56 (s, 4H, BAr_F), 4.10 (br, 4H, Re−OEt_2), 2.46 (m, 3H, ^{i}Pr), 1.30 (m, 24H, ^{i}Pr + Re−OEt_2). Data for **3c**. Anal. Calcd for $C_{58}H_{55}BF_{24}O_5PRe$: C, 45.95; H, 3.66. Found: C, 45.93; H, 3.44. ^1H NMR (CD_2Cl_2) 7.73 (s, 8H, BAr_F), 7.56 (s, 4H, BAr_F), 4.00 (br, 4H, Re−OEt_2), 0.8−2.2 (br m, Cy + Re−OEt_2).

Preparation of [*cis*-Re(CO)$_4$(PR$_3$)(ClCH$_2$Cl)][BAr$_F$] (R = Ph (4a), ^{i}Pr (4b), Cy (4c)). A solution of $[Ph_3C][BAr_F]$ (0.481 g, 0.434 mmol) in CH_2Cl_2 (5 mL) was added dropwise via cannula to a stirred solution of **2a** (0.250 g, 0.434 mmol) in CH_2Cl_2 (15 mL). After 15 min of stirring, the yellow solution was concentrated to ca. 5 mL in vacuo and hexanes (20 mL) were added. The reaction mixture was further concentrated to 10 mL and allowed to stand for 1 h, providing yellow microcrystals. The solution was syringed off, and the product washed with hexanes and dried in vacuo (0.53 g, 81% yield). Complexes **4b** and **4c** were prepared analogously to the PPh_3 analogue in 92% and 80% yields, respectively, from **2b** and **2c**. Data for **4a**. Anal. Calcd for $C_{55}H_{29}BCl_2F_{24}PO_4Re$: C, 43.79; H, 1.94. Found: C, 44.15; H, 1.75. ^1H NMR (CD_2Cl_2) 7.72 (s, 8H, BAr_F), 7.3−7.7 (m, 19H, Ph, BAr_F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 184.86 (d, J_{CP} = 9.0, CO), 182.64 (d, J_{CP} = 44, CO), 181.89 (d, J_{CP} = 6.8, CO), 133.50 (d, J_{CP} = 2.0, Ph), 133.46 (d, J_{CP} = 10.6, Ph), 130.61 (d, J_{CP} = 10.6, Ph), ^{i}Ph not observed. Data for **4b**. Anal. Calcd for $C_{46}H_{35}BCl_2F_{24}O_4PRe$: C, 39.28; H, 2.51. Found: C, 39.27; H, 2.63. ^1H NMR (CD_2Cl_2) 7.72 (s, 8H, BAr_F), 7.57 (s, 4H, BAr_F), 2.45 (m, 3H, ^{i}Pr), 1.34 (dd, J_{HH} = 7.2, J_{HP} = 15.0, 18H, ^{i}Pr). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 185.85 (d, J_{CP} = 8.2, CO), 181.14 (d, J_{CP} = 6.7, CO), 180.93 (d, J_{CP} = 39.4, CO), 26.84 (d, J_{CP} = 24.7, ^{i}Pr), 19.92 (s, ^{i}Pr). Data for **4c**. Anal. Calcd for $C_{55}H_{47}BCl_2F_{24}PO_4Re$: C, 43.27; H, 3.10. Found: C, 43.62; H, 3.53. ^1H NMR (CD_2Cl_2) 7.72 (s, 8H, BAr_F), 7.53 (s, 4H, BAr_F), 1.0−2.1 (m, 33H, PCy_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) 185.95 (d, J_{CP} = 8.9, CO), 181.10 (d, J_{CP} = 6.4, CO), 180.68 (d, J_{CP} = 41, CO), 35.78 (d, J_{CP} = 23, Cy), 30.10 (s, Cy), 27.35 (d, J_{CP} = 11.4, Cy), 25.78 (s, Cy).

Preparation of {[*cis*-Re(CO)$_4$(PR$_3$)]$_2$(μ-Cl)}{BAr$_F$} (R = Ph (5a), ^{i}Pr (5b), Cy (5c)). Diethyl ether (5 mL) was added to a vial containing **1a** (0.052 g, 0.087 mmol), **2a** (0.050 g, 0.087 mmol) and $[H(OEt_2)_2][BAr_F]$ (0.088 g, 0.087 mmol). The colorless solution was stirred for 5 min, and then hexanes (3 mL) were added. The solution was stored at room temperature for 5 h, providing needles of **5a** which were washed with hexanes and dried in vacuo (0.135 g, 77% yield). Complexes **5b** and **5c** were prepared analogously from $[H(OEt_2)_2][BAr_F]$, and the corresponding chloride and methyl compounds and isolated in 62% and 77% yields, respectively. Data for **5a**. Anal. Calcd for $C_{76}H_{42}BClF_{24}O_8P_2Re_2$: C, 45.20; H, 2.10. Found: C, 45.43; H, 2.44. ^1H NMR (CD_2Cl_2) 7.73 (s, 8H, BAr_F), 7.3−7.6 (m, 34H, Ph + BAr_F). $^{31}C\{^1H\}$ NMR (CD_2Cl_2) 186.07 (d, J_{CP} = 9.5, CO), 184.80 (d, J_{CP} = 50.4, CO), 181.26 (d, J_{CP} = 6.5, CO), 133.68 (d, J_{CP} = 10.6, Ph), 132.70 (d, J_{CP} = 2.5, Ph), 130.01 (d, J_{CP} = 10.6, Ph). Data for **5b**. Anal. Calcd for $C_{58}H_{54}BClF_{24}O_8P_2Re_2$: C, 38.37; H, 3.00. Found: C, 38.37; H, 2.98. ^1H NMR (CD_2Cl_2) 7.73 (s, 8H, BAr_F), 7.57 (s, 4H, BAr_F), 2.47 (m, 6H, ^{i}Pr), 1.33 (dd, J_{HH} = 7.5, J_{HP} = 15.0, 36H, ^{i}Pr). $^{31}C\{^1H\}$ NMR (CD_2Cl_2) 187.45 (d, J_{CP} = 8.4, CO), 183.94 (d, J_{CP} = 46.7, CO), 181.95 (d, J_{CP} = 6.8, CO), 26.03 (d, J_{CP} = 24.0, ^{i}Pr), 19.85 (s, ^{i}Pr). Data for **5c**. Anal. Calcd for $C_{76}H_{78}BClF_{24}O_8P_2Re_2$: C, 44.40; H, 3.82. Found: C, 44.76; H, 3.99. ^1H NMR (CD_2Cl_2) 7.73 (s, 8H, BAr_F), 7.57 (s, 4H, BAr_F), 1.1−2.3 (m, 66H, Cy). $^{31}C\{^1H\}$ NMR (CD_2Cl_2) 187.90 (d, J_{CP} = 8.5, CO), 184.36 (d, J_{CP} = 45.8, CO), 182.34 (d, J_{CP} = 6.2, CO), 35.66 (d, J_{CP} = 21.9, Cy), 30.33 (s, Cy), 28.01 (d, J_{CP} = 10.7, Cy), 26.40 (s, Cy).

Preparation of [*cis*-Re(CO)$_4$(P^{i}Pr$_3$)(NC$_5$F$_5$)][BAr$_F$] (6). Solid $[Ph_3C][BAr_F]$ (0.057 g, 0.052 mmol) was added to a solution of **2b** (0.025 g, 0.052 mmol) in 2 mL NC_5F_5 to provide a clear, yellow solution. Hexanes (5 mL) were added, and the solution was stored at room temperature overnight, after which time clear, colorless crystals which were suitable for X-ray crystallographic studies had formed. The solution was pipetted off, and the crystals were washed twice with hexanes and dried in vacuo to provide 0.048 g of **6** (62% yield). Anal. Calcd for $C_{50}H_{33}BF_{29}NO_4PRe$: C, 40.28; H, 2.23; N, 0.94. Found: C, 39.97; H, 2.45; N, 1.14. ^1H NMR (NC_5F_5) 7.68 (s, 8H, BAr_F), 7.27 (s, 4H, BAr_F), 2.50 (m, 3H, ^{i}Pr), 1.34 (dd, J_{HH} = 7.2, J_{HP} = 15.0, 18H, ^{i}Pr).

X-ray Structures of 1b, 1c, and 5a. Crystals of each complex were each mounted from a pool of mineral oil under argon gas flow on a thin glass fiber with silicon grease, and placed under a liquid nitrogen stream on a Siemens P4/PC diffractometer. The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 0.82° (**1b**), 0.86° (**1c**), and 1.24° (**5a**) scan range. Three check reflections monitored every 97 reflections shoed no systematic variation of intensities. Lattice determination and data collection for **1a** and **1c** were performed using the SHELXTL PC Version 4.2/360 software. Lattice determination and data collection for **5a** was carried out using XSCANS Version 210b software. All data reduction, including Lorentz and poarization corrections and structure solution and graphics were performed using SHELXTL PC Version 4.2/360 software. The structure refinements were performed using SHELX 93 software.[20] All data were corrected for absorption using either the ellipsoidal (**1a**, **1c**) or laminar (**5a**) options in the XEMP facility of SHELXTL PC.

The structures were solved using Patterson and difference Fourier techniques. These solutions yielded the rheneium atoms and the majority of all other non-hydrogen atom positions. Subsequent Fourier synthesis gave all remaining non-hydrogen atom positions. An occupational disorder in **1c** between Cl(1) and the C(4)−O(4) carbonyl group was modeled, with each site at one-half occupancy for chlorine and one-half occupancy for carbonyl. The phenyl rings of the triphenylphosphine ligands **5a** were refined as rigid bodies with the C−C distances fixed at 1.39 Å. All hydrogen atoms were fixed in positions of ideal geometry, with a C−H distances of 0.97 Å (sp^3) or 0.93 Å (sp^2) and refined using the riding model in the HFIX facility in SHELX 93. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 times (**1c**, **5a** and methylene of **1b**) or 1.5 times (**1b** methyl) the equiv isotropic *U* of the carbon atom they were bonded to.

X-ray Structure of 4b, 5c, and 6. Crystals of **4b**, **5c**, and **6** were mounted from a pool of mineral oil under argon gas flow on a thin glass fiber with silicon grease, and placed under a liquid nitrogen stream on a Bruker P4/CCD/PC diffractometer. The lattice parameters were determined using 185 (**4b**), 66 (**5c**), and 75 (**6**) reflections. A hemisphere of data was collected using a combination of φ and ω scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement was performed using SMART[21] softltware. Frame integration and final cell parameter calculation were carried out

(20) XSCANS and SHELXTL PC are products of Siemens Analytical X-ray Instruments, Inc., 6300 Enterprise Lane, Madison, WI 53719. SHELX-93 is a program for crystal structure refinement written by G. M. Sheldrick, University of Göttingen, Germany, 1993.

(21) *SMART*, Version 4.210; Bruker Analytical X-ray Systems, Inc.: 6300 Enterprise Lane, Madison, WI 53719, 1996.

using SAINT[22] software. The final cell parameters were determined using a least-squares fit to 7627 (**4b**), 5670 (**5c**), and 8192 (**6**) reflections. The data were corrected for absorption using the SADABS[23] program. Decay of reflection intesitiy was not observed.

The structure were solved using Patterson and difference Fourier techniques. The initial solutions revealed Re and the majority of all other non-hydrogen atom positions. The remaining atomic positions were determined from subsequent Fourier synthesis. All hydrogen atom positions were fixed in ideal positions. The C−H distances were fixed at 0.93, 0.96, 0.97 and 0.98, and 0.97 Å for aromatic, methyne, methylene, and methyl hydrogen atoms, respectively. The hydrogen atoms were refined using a riding model, with their isotropic temperature factors set to 1.2 (aromatic, methyne, methylene) or 1.5 (methyl) times the equiv isotropic *U* of the carbon atom they were bonding to.

For **4b**, the methylene chloride ligand was disordered. As a result of this disorder, the carbon atom C(5) and nonbonded chlorine atom Cl(2) were each refnined as two one-half occupancy atom positions. For **5c**, several disordered fluoride atoms were refined in two positions, with the sum of their site occupancy factors tied to one. One fluoride atom was refined in three positions, with each atom having its occupancy fixed at one-third. Three disordered cyclohexyl carbon atoms were refined in two positions, with their site ocupancy factors set to one-half. Hydrogen atoms were not placed on disordered cyclohexyl carbon atoms (vide infra) or the carbon atoms they were bonded to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms (except the disordered fluoride and carbon atoms in **5c**). Structure solution and graphics were performed using SHELXTL PC.[24] SHELX-93 was used for structure refinement and creation of publication tables.[20]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes **1b**, **1c**, **4b**, **5a**, **5c**, and **6** are available on the Internet only. Access information is given on any current masthead page.

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(22) *SAINT*, Version 4.05; Bruker Analytical X-ray Systems, Inc.: 6300 Enterprise Lane, Madison, WI 53719, 1996.
(23) First release; Sheldrick, G. M. *SADABS*; University of Göttingen: Germany.
(24) *SHELXTL PC*, Version 5.03; Bruker Analytical X-ray Systems, Inc.: 6300 Enterprise Lane, Madison, WI 53719, 1994.