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Alkyne Reactions with Rhenium(V) Oxo Alkyl Phosphine Complexes—Phosphine Displacement versus Apparent Re–P Insertion

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Reactions of rhenium(V) oxo alkyl phosphine complexes with various alkynes were examined. $Re(O)R_3(PMe_3)$ (R = Me and CH_2SiMe_3) and *cis*-$Re(O)Me_2Cl(PMe_2R)_2$ (R = Me and Ph) react with ethyne to give respectively $Re(O)R_3(CHCH(PMe_3))$ and $[Re(O)Me_2(CHCH(PMe_2R))_2]Cl$, which are products of the formal insertion of ethyne into the Re—P bonds. Substituted alkynes, on the other hand, react with $Re(O)Me_3(PMe_3)$ to give the adducts $Re(O)Me_3(RC{\equiv}CR')$ (R = R′ = Me, Et, or Ph; R = Me or Ph and R′ = H). On the basis of spectroscopic studies and the X-ray crystal structures of $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$ and $[Re(O)Me_2(CHCH(PMe_2Ph))_2]Cl$, the insertion products are best described as anologs of resonance stabilized ylides in which the resonance stabilization involves the high oxidation state organometallic fragment. Valence bond and MO descriptions of the delocalization are presented. The mechanism by which the insertion products are formed is proposed to involve phosphine displacement and subsequent attack on coordinated ethyne by external phosphine. The X-ray crystal structure of $Re(O)Me_3(PhC{\equiv}CPh)$ was also determined. Crystal data for $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$ at −151(1) °C: $C_{17}H_{44}OPSi_3Re$, orthorhombic, $a = 14.097(6)$ Å, $b = 13.242(5)$ Å, $c = 13.807(6)$ Å, $P2_12_12_1$, $Z = 4$. Crystal data for $[Re(O)Me_2(CHCH(PMe_2Ph))_2]Cl{\cdot}CH_3CN$ at −80(1) °C: $C_{24}H_{35}ClNOP_2Re$, monoclinic, $a = 14.026(4)$ Å, $b = 10.691(3)$ Å, $c = 18.388(5)$ Å, $\beta = 99.49(2)°$, $P2_1/n$, $Z = 4$. Crystal data for $Re(O)Me_3(PhC{\equiv}CPh)$ at −83(1) °C: $C_{17}H_{19}ORe$, orthorhombic, $a = 15.537(5)$ Å, $b = 18.181(6)$ Å, $c = 5.402(2)$ Å, *Pnma*, $Z = 4$.

A common reaction in organometallic chemistry is the displacement of phosphine by a good π acceptor ligand such as carbon monoxide, olefin, or alkyne. In the course of examining the reactivity of rhenium(V) oxo alkyl phosphine complexes with alkynes, we have discovered an ostensibly different reaction pathway; namely, formal insertion of alkynes into Re–P bonds to form organometallic analogs of resonance stabilized ylides. We describe here the synthesis, structural characterization, and qualitative MO description of the organometallic ylides, as well as simple phosphine displacement reactions by alkynes that illuminate the mechanism by which the organometallic ylides are formed.[2]

Results

Synthesis of Ylide Analogs. The reaction of square pyramidal $Re(O)(PMe_3)(CH_2SiMe_3)_3$ in toluene with an excess of ethyne gives red $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$ (**1a**) in 46% yield.[3] Similarly, reaction of thermally unstable $Re(O)Me_3(PMe_3)$, prepared in situ,[4] with ethyne produces red-orange $Re(O)Me_3(CHCH(PMe_3))$ (**1b**) (eq 1).

$$Re(O)R_3(PMe_3) + C_2H_2 \rightarrow Re(O)R_3(CHCH(PMe_3)) \quad (1)$$
$$R = CH_2SiMe_3\ (\mathbf{1a}),\ Me\ (\mathbf{1b})$$

The addition of excess ethyne to a toluene solution of *cis*-$Re(O)Me_2Cl(PMe_2R)_2$ (R = Me or Ph)[4] results in the slow formation of a red solution and a dark solid. Filtration, followed by washing with acetonitrile, yields an intensely red filtrate and an insoluble dark residue. Crystallization from the filtrate, after addition of toluene, gives $[Re(O)Me_2(CHCH(PMe_2R))_2]Cl$ (R = Me (**2a**) and Ph (**2b**)) as acetonitrile solvates (eq 2). The dark solid formed in the reaction is not observed when only 2 equiv of ethyne is used. Reaction of $Re(O)Me_2Cl(PMe_2R)_2$ with only 1 equiv of ethyne gives a 1:1 mixture of **2** and unreacted starting material. This suggests that the initial insertion product reacts with the second equivalent of ethyne faster than the starting material or that a comproportionation occurs between two singly inserted complexes.

$$Re(O)Me_2Cl(PMe_2R)_2 + 2C_2H_2 \rightarrow [Re(O)Me_2(CHCH(PMe_2R))_2]Cl \quad (2)$$
$$R = Me\ (\mathbf{2a}),\ Ph\ (\mathbf{2b})$$

Starting with *cis*- or *trans*-$[Re(O)Me_2(PMe_3)_2(CH_3CN)][BF_4]$ as a cation source,[4] reactions with ethyne produce $[Re(O)Me_2(CHCH(PMe_2R))_2][BF_4]$ by ^1H NMR. No reaction is observed between $Re(O)Me_2Cl(PMe_2R)_2$ and propyne, 3-hexyne, or phenylacetylene, indicating that steric factors play an important role in the

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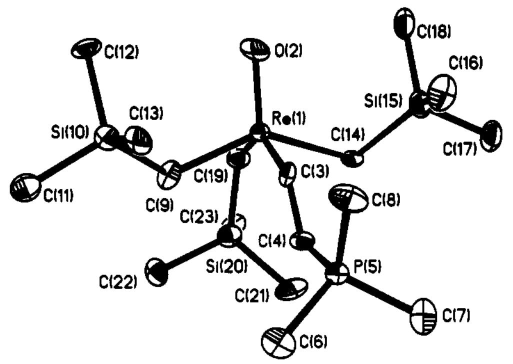

Figure 1. Plot of $\mathrm{Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))}$ (**1a**) showing the atom-numbering scheme (50% probability level ellipsoids).

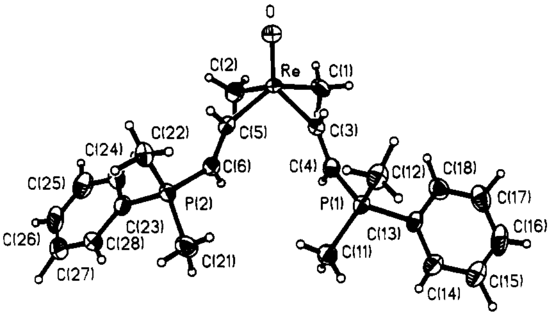

Figure 2. Plot of $\mathrm{[Re(O)Me_2(CHCH(PMe_2Ph))_2]^+}$ (**2b** cation) showing the atom-numbering scheme (50% probability level ellipsoids).

reaction. Reactions of $\mathrm{Re(O)(PMe_3)(CH_2SiMe_3)_3}$ with 2-butyne and phenylacetylene were not clean and did not appear to form inserted products or simple adducts.

The dark solid byproduct of reaction 2 has been studied by cross polarization magic angle spinning ^{13}C NMR.[5] The analysis reveals it to be a mixture of *cis*- and *trans*-polyacetylene (δ 135 (broad)).[6] Although we have not identified the polymerization catalyst, solutions of **2a** which had been isolated by crystallization will produce polyacetylene on exposure to ethyne.

Spectroscopic and X-ray Crystallographic Characterization. Plots of **1a** and **2b** taken from X-ray crystallographic studies are shown in Figures 1 and 2. Crystal data are presented in Table I, and selected bond distances and angles are given in Tables II and III. The structures of **1a** and **2b** display many common structural features. In both cases the geometry about the rhenium atoms is square pyramidal with an apical oxo ligand. In **1a** the basal plane is defined by the carbons of one η^1-CHCH(PMe$_3$) ligand and three (trimethylsilyl)methyl ligands, and in **2b** by the carbons of two η^1-CHCH(PMe$_2$Ph) ligands and two methyl ligands. The rhenium atoms are displaced by 0.73 (**1a**) and 0.78 (**2b**) Å from the basal planes. In both compounds the CHCH(PMe$_2$R) ligands are attached to the rhenium via one carbon atom such that there is an (*E*)-ReCH=CH(PMe$_2$R) arrangement. The Re—CHCH(PMe$_2$R) bond distances are approximately 0.13 Å shorter than the alkyl ligand Re—C(sp^3) distances and are 0.10 Å shorter than the Re—C(sp^2) distance of 2.124(17) Å in the alkenyl cluster $\mathrm{Re_3(\mu\text{-}O\text{-}\mathit{i}\text{-}Pr)_3(\eta^1\text{-}C(Ph)CH_2)(O\text{-}\mathit{i}\text{-}Pr)_5}$, indicating some multiple bond character.[7] The C—C distances in the CHCH(PMe$_2$R) ligands are typical olefin distances, and the P—C=C angles are olefin in nature. In both compounds the P—CHCHRe bond distances, 1.74–6 Å, are within 3σ of the average P—Me distances, and they are much longer than the P—C$_{\mathrm{ylide}}$ bond distance of 1.661(8) Å reported for the unstabilized ylide $\mathrm{Ph_3PCH_2}$.[8] The P—CHCH(PMe$_2$R) distances are similar, however, to the P—C$_{\mathrm{ylide}}$ distances reported for the resonance stabilized ylides triphenylphosphonium cyclopentadienylide, 1.718(2) Å,[9] and triphenylphosphonium dicyanomethylide, 1.753(8) Å.[10]

The Re–O bond distances in **1a** and **2b** are normal for high oxidation rhenium oxo complexes, as are the Re–O stretching frequencies (e.g., for **1a** ν(Re–O) 982 (ν(Re–^{18}O) 921), and for **2b** ν(Re–O) 981 (ν(Re–^{18}O) 945).[11]

The chemical shifts of the ylide carbon resonances (ReCH*C*HP, 85 (**1a**) and 92 (**2b**) ppm) are close to the value reported for C$_{\mathrm{ylide}}$ in resonance-stabilized triphenylphosphonium cyclopentadienylide (78 ppm)[12] and are far downfield of the shifts reported for unstabilized ylides such as $\mathrm{Me_3PCH_2}$ (−2.4 ppm).[12,13] The ^{13}C$_{\mathrm{ylide}}$—H coupling constants, 163 (**1a**) and 165 (**2b**) Hz, are similar to the values reported for other ylides.[13] The coupling constants across the C=C bonds, $^3J_{\mathrm{HH}} \approx 17$ Hz, indicate that the (*E*)-ReCH=CH(PMe$_2$R) configurations observed in the solid state are retained in solution.[14] The ^{13}C and ^{1}H chemical shifts in **1a** for the α carbon (Re—*C*) and hydrogen (Re—C*H*) of the ReCH=CH(PMe$_3$) group are 228 and 12.3 ppm, respectively, and $^1J_{\mathrm{CH}} = 122$ Hz; **2b** gives similar results. The carbon chemical shift is significantly downfield of the C$_\alpha$ resonance of 153 ppm for $\mathrm{Re_3(\mu\text{-}O\text{-}\mathit{i}\text{-}Pr)_3(\eta^1\text{-}C(H){=}C(H)Ph)(O\text{-}\mathit{i}\text{-}Pr)_5}$[7] and is in fact reminiscent of Schrock-type rhenium alkylidenes.[15] Spectroscopic data for **1b** and **2a** indicate they are isostructural with **1a** and **2b**, respectively. Our spectroscopic and structural data are in accord with data reported for low valent analogs of **1a** such as $\mathrm{(OC)_5M(C(OSiMe_3)CH(PMe_3))}$ (M = Cr, Mo, W).[16,17]

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Table I. Crystal Data Summary for $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$ (1a), $[Re(O)Me_2(CHCH(PMe_2Ph))_2]Cl \cdot CH_3CN$ (2b·CH_3CN), and $Re(O)Me_3(PhC{\equiv}CPh)$ (4e)

	1a	2b·CH_3CN	4e
diffractometer	Picker 4-circle	Nicolet R3m/V	Nicolet R3m/V
radiation type	Mo Kα (monochromated)	Mo Kα (monochromated)	Mo Kα (monochromated)
wavelength, Å	0.710 69	0.710 73	0.710 73
color of crystal/habit	red-orange/block	yellow/block	pale yellow/block
empirical formula	$C_{17}H_{44}OPSi_3Re$	$C_{22}H_{32}ClNOP_2Re \cdot C_2H_3N$	$C_{17}H_{19}ORe$
crystal dimens, mm	0.12 × 0.12 × 0.15	0.40 × 0.40 × 0.45	0.20 × 0.25 × 0.25
space group	$P2_12_12_1$	$P2_1/n$	*Pnma*
temp °C	–151(1)	–80(1)	–83(1)
cell dimens			
a, Å	14.097(6)	14.026(4)	15.537(5)
b, Å	13.242(5)	10.691(3)	18.181(6)
c, Å	13.807(6)	18.388(5)	5.402(2)
β, deg		99.49(2)	
Z (molecules/cell)	4	4	4
vol, Å^3	2577.3	2719.5(1)	1526(1)
d_{calcd}, g cm^{-3}	1.46	1.56	1.85
abs coeff, cm^{-1}	49.8	47.6	80.6
scan type	θ–2θ	θ–2θ	θ–2θ
2θ range, deg	6–45	4–50	4–50
data collcd	*hkl*	$\pm h, \pm k, l$	*hkl*
no. of refns collcd	6032	10576	2430
no. of unique reflns	3322	4791	1806
no. with $F_o > n\sigma(F_o)$	2905 ($n = 3$)	3941 ($n = 6$)	1480 ($n = 6$)
structure soln	direct methods (Multan78)	direct methods (SHELXTL+)	direct methods (SHELXTL+)
R_{merg}[a]		0.0353	0.026
$R(F)$[b]	0.0434	0.0275	0.0394
$R_w(F)$[c]	0.0436	0.0339	0.0424
"goodness of fit"[d]	0.874	1.41	1.05
largest Δ/σ for last cycle	0.05	0.01	0.001

[a] $R_{merg} = [(\sum N \sum w(F_o(\text{mean}) - F_o)^2)/(\sum(N-1)\sum w F_o^2)]^{1/2}$, where the inner summations are over the N equivalent reflections averaged to give F(mean), and the outer summations are over all unique observed reflections. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F) + gF^2]^{-1}$. [d] GOF $= [\sum w(||F_o| - |F_c||)^2/(n_{obs} - n_{params})]^{1/2}$.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$ (1a)

	Distances		
Re(1)–O(2)	1.700(6)	Re(1)–C(3)	1.996(9)
C(3)–C(4)	1.355(13)	Re(1)–C(14)	2.153(12)
P(5)–C(4)	1.737(10)	Re(1)–C(9)	2.100(13)
Si(10)–C(9)	1.857(13)	Re(1)–C(19)	2.136(10)
Si(15)–C(14)	1.859(13)	Si(20)–C(19)	1.882(11)
	Angles		
Re(1)–C(3)–C(4)	132.6(8)	P(5)–C(4)–C(3)	124.4(8)
Re(1)–C(9)–Si(10)	109.5(8)	Re(1)–C(14)–Si(15)	115.0(6)
Re(1)–C(19)–Si(20)	125.1(5)	Re(1)–C(3)–H(1)	99.0(6)
C(4)–C(3)–H(1)	123.0(6)	P(5)–C(4)–H(2)	116.0(7)
C(3)–C(4)–H(2)	113.0(7)	O(2)–Re(1)–C(9)	110.3(5)
O(2)–Re(1)–C(3)	110.5(4)	O(2)–Re(1)–C(14)	110.3(5)
O(2)–Re(1)–C(19)	110.3(4)	C(3)–Re(1)–C(9)	83.6(5)
C(3)–Re(1)–C(14)	85.6(6)	C(3)–Re(1)–C(19)	139.1(4)
C(9)–Re(1)–C(14)	139.2(4)	C(9)–Re(1)–C(19)	82.5(6)
C(14)–Re(1)–C(19)	80.4(6)		

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Re(O)Me_2(CHCH(PMe_2Ph))_2]Cl \cdot CH_3CN$ (2b·CH_3CN)

	Distances		
Re–O	1.678(4)	P(1)–C(12)	1.793(6)
Re–C(1)	2.138(5)	P(1)–C(13)	1.801(5)
Re–C(2)	2.121(6)	P(2)–C(6)	1.763(5)
Re–C(3)	2.024(5)	P(2)–C(21)	1.801(7)
Re–C(5)	2.025(5)	P(2)–C(22)	1.795(6)
P(1)–C(4)	1.755(5)	P(2)–C(23)	1.795(5)
P(1)–C(11)	1.779(6)	C(3)–C(4)	1.349(7)
P(1)–C(12)	1.793(6)	C(5)–C(6)	1.342(7)
	Angles		
O–Re–C(1)	109.6(2)	C(11)–P(1)–C(13)	109.4(3)
O–Re–C(2)	112.9(2)	C(12)–P(1)–C(13)	105.2(2)
C(1)–Re–C(2)	80.0(2)	C(6)–P(2)–C(21)	112.0(3)
O–Re–C(3)	112.8(2)	C(6)–P(2)–C(22)	110.9(3)
C(1)–Re–C(3)	84.0(2)	C(21)–P(2)–C(22)	108.0(3)
C(2)–Re–C(3)	134.3(2)	C(6)–P(2)–C(23)	109.8(2)
O–Re–C(5)	110.2(2)	C(21)–P(2)–C(23)	107.9(3)
C(1)–Re–C(5)	140.2(2)	C(22)–P(2)–C(23)	108.1(3)
C(2)–Re–C(5)	83.3(2)	Re–C(3)–C(4)	131.8(4)
C(3)–Re–C(5)	82.4(2)	P(1)–C(4)–C(3)	122.6(4)
C(4)–P(1)–C(11)	109.7(3)	Re–C(5)–C(6)	137.0(4)
C(11)–P(1)–C(12)	108.8(3)	P(2)–C(6)–C(5)	122.5(4)
C(4)–P(1)–C(13)	112.6(2)		

Bonding in 1 and 2. The structural and spectroscopic data suggest that the resonance composites [**Ia** ↔ **Ib**] and [**IIa** ↔ **IIb** ↔ **IIc**] best describe the bonding in **1** and **2**. Structures **Ia** and **IIa** are the most important contributors, as the P^+—C^- interactions suggested by the others would be inconsistent with the long P—CHCHRe bonds. In principle, resonance structures in which the Re≡O bonds are involved could contribute to the anion delocalization, but these can be excluded because the Re—O bond distances and IR stretching frequencies are normal.

Qualitative molecular orbital descriptions of **1** and **2**, formulated by using symmetry and perturbation theory,[18] are shown in Figure 3. The HOMOs for **1** and **2** are primarily Re d_{xy} in character, but should have a significant contribution from the ylide carbon p orbital. Note that the rhenium d orbital involved in the resonance (d_{xy}) has the wrong symmetry to interact with the oxo ligand. This explains why the Re≡O bonds are unaffected by the resonance. The molecular orbital descriptions are entirely consistent with the valence bond formulations **I** and **II**.

Deuterium Incorporation at the Ylide Carbon. If the assignments of the HOMOs in Figure 3 are correct, frontier orbital considerations would indicate that electrophilic attack will occur at the ylide carbons in **1** and **2**.

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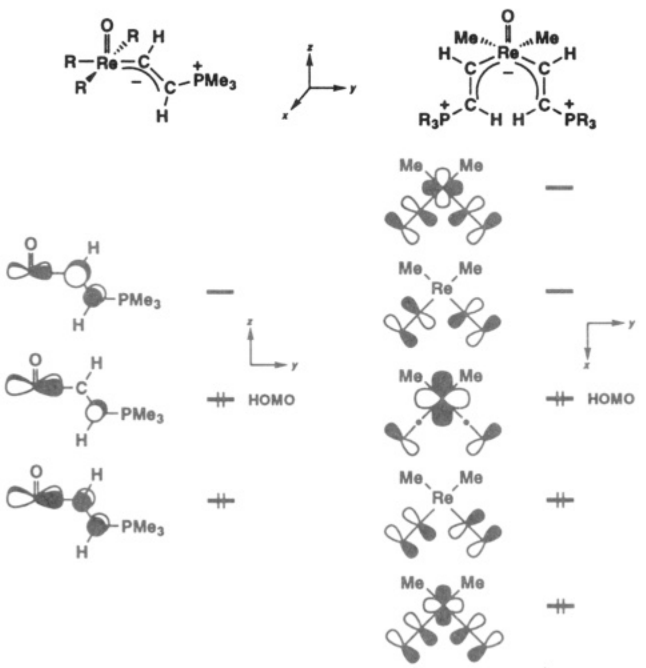
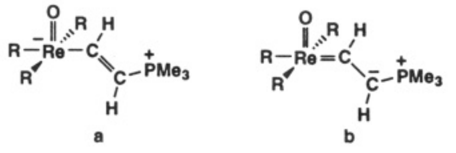
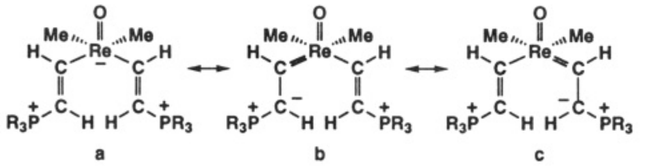


Figure 3. Molecular orbitals involved in the resonance stabilization of $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$ (left) and $[Re(O)Me_2(CHCH(PMe_2Ph))_2]^+$ (right). The view at left is from the side and at right down the O–Re bond vector.



I



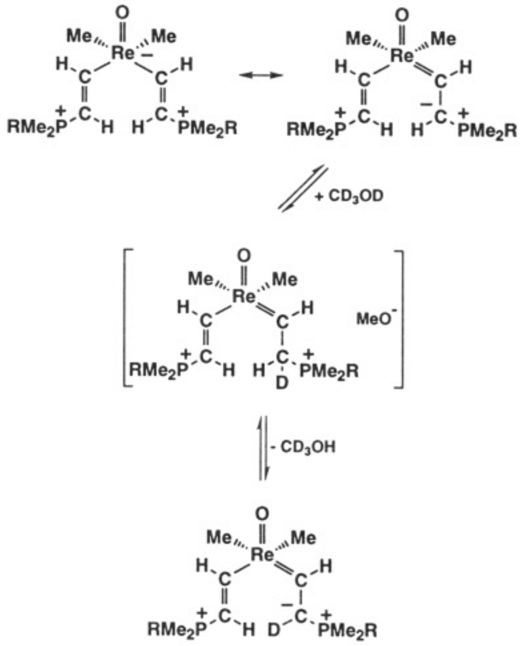
II

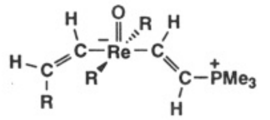
The same conclusion is reached by considering resonance forms **Ib** and **IIb/IIc**.

In order to test this hypothesis, **1a** was reacted with neat methanol-d_4 (i.e., D^+ was used as the electrophile). As judged by ^1H NMR integration, deuterium incorporation into the ylide position, $ReCHC\mathit{H}(PMe_3)$, occurs with a half life of ≈75 min. In contrast, no deuterium is scrambled into the α position, $ReC\mathit{H}CH(PMe_3)$, after 6 h, within the limits of NMR integration. Similarly, when **2a** is dissolved in methanol-d_4, complete incorporation of deuterium into the ylide carbon sites occurs within ≈2.5 h, but no scrambling into the α sites is observed after 48 h. Scheme I shows a mechanism that rationalizes the observed deuterium incorporation in **2a**; an analogous mechanism can be written for **1a**.

In Situ Characterization of $Re(O)(CH_2SiMe_3)_2(CHCH(PMe_3))(CHCH(CH_2SiMe_3))$, 3. Reaction 1 involving $Re(O)(CH_2SiMe_3)_3(PMe_3)$ produces a persistent trace impurity in the isolated crystalline product. The impurity has been tentatively formulated as $Re(O)(CH_2SiMe_3)_2(CHCH(PMe_3))(CHCH(CH_2SiMe_3))$, (**3**), on the basis of ^1H, ^{13}C and ^{31}P NMR data.

Scheme I





R = CH_2SiMe_3

3

The ^1H NMR spectrum of **3** has a broad doublet at 8.3 ppm and a doublet of triplets at 6.4 ppm, arising from the α and β protons of the $ReCH{=}CH(CH_2SiMe_3)$ group. The proton coupling constant across the double bond ($^3J_{HH}$ = 11.6 Hz) is more consistent with a (*Z*)-$ReCH{=}CH(CH_2SiMe_3)$ configuration than *E*; for example, in propene $^3J_{HH}$ is 17 Hz between the trans protons and 10 Hz between the cis.[14] Two doublet of doublet resonances at 12.3 and 3.6 ppm, characteristic of the (*E*)-$ReCHCH(PMe_3)$ fragment, are also observed, along with the phosphine doublet and resonances corresponding to three CH_2SiMe_3 groups. Two of the three CH_2SiMe_3 groups are equivalent, related by a mirror plane, and one is unique, lying on the mirror plane (i.e., the $CHCH(PMe_3)$ and the $CHCH(CH_2SiMe_3)$ ligands are trans).

Carbon-13 NMR spectra for **3** are also consistent with the proposed formulation. There are four resonances corresponding to sp^2 hybridized carbons with one at 230 ppm assigned to $Re\mathit{C}HCH(PMe_3)$ (cf., 228 ppm for **1a**) and one at 87 ppm assigned to $ReCH\mathit{C}H(PMe_3)$ (cf., 85 ppm for **1a**). Resonances at 181 and 120 ppm are assigned to the α and β carbons of $ReCHCH(CH_2SiMe_3)$, respectively, and resonances corresponding to the two equivalent (trimethylsilyl)methyl alkyl ligands are observed at chemical shifts similar to those for $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$. The resonance arising from the methylene carbon of the unique CH_2SiMe_3 group, however, appears at a higher field than those arising from the alkyl ligands of **1a** (25 ppm for $ReCHCH(\mathit{C}H_2SiMe_3)$ vs 37 ppm for $Re\mathit{C}H_2SiMe_3$ in **1a**, an indication that the unique (trimethylsilyl)methyl group is not directly bonded to the rhenium center.

Reaction of a large excess of ethyne with **1a** that had been purified by crystallization does not give **3**. This observation is consistent with initial competitive insertion of ethyne into the Re–C and Re–P bonds of $Re(O)(CH_2SiMe_3)_3(PMe_3)$. When there is insertion into the Re–P

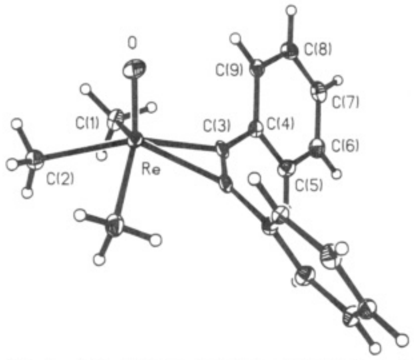


Figure 4. Plot of Re(O)Me$_3$(PhC≡CPh) (**4e**) showing the atom-numbering scheme (50% probability level ellipsoids).

bond to give **1a**, no subsequent reaction occurs, but when insertion into the Re–C bond occurs first, it is apparently always followed by insertion into the R–P bond to yield **3** (eq 3).

$$\mathrm{Re(O)(CH_2SiMe_3)_3(PMe_3) + C_2H_2 \rightarrow [Re(O)(CH_2SiMe_3)_2(PMe_3)(CHCH(CH_2SiMe_3))]} \quad (3a)$$

$$\mathrm{[Re(O)(CH_2SiMe_3)_2(PMe_3)(CHCH(CH_2SiMe_3))] + C_2H_2 \rightarrow \mathbf{3}} \quad (3b)$$

Reactions of Re(O)Me$_3$(PMe$_3$) with Substituted Alkynes. Re(O)Me$_3$(PMe$_3$), generated in situ,[4] reacts with propyne, 2-butyne, 3-hexyne, phenylacetylene, and diphenylacetylene to give simple alkyne adducts and free phosphine (eq 4). Compounds **4a–4c** are oils, whereas **4d** is a waxy solid and **4e** is crystalline. Isolated yields are low (40–65%).

$$\mathrm{Re(O)Me_3(PMe_3) + RC{\equiv}CR' \rightarrow Re(O)Me_3(RC{\equiv}CR') + PMe_3} \quad (4)$$

R = Me, R′ = H (**4a**)
R = R′ = Me (**4b**)
R = R′ = Et (**4c**)
R = Ph, R′ = H (**4d**)
R = R′ = Ph (**4e**)

The alkyne adducts do not react with PMe$_3$ or other alkynes. For example, there is no reaction between excess PMe$_3$ and **4a** or **4e** at room temperature or at 45 °C. Also, reaction of the 3-hexyne adduct **4c** with 2-butyne or ethyne showed no alkyne exchange.

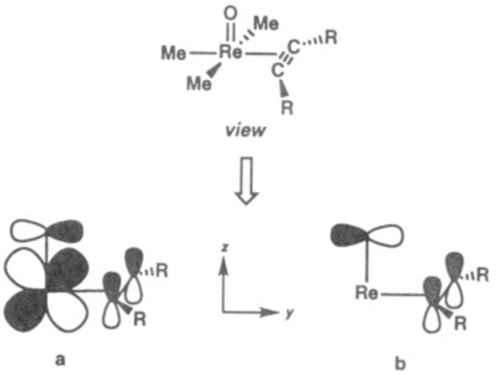
Spectroscopic and X-ray Crystallographic Characterization. The X-ray structure of the diphenylacetylene adduct **4e** has been determined. A plot of the molecule is shown in Figure 4. Crystal data are presented in Table I, and bond distances and angles are given in Table IV.

4e has crystallographically imposed mirror symmetry, with the diphenylacetylene lying perpendicular to the Re–O bond vector. The geometry about the rhenium is square pyramidal, with an apical oxo ligand and a basal plane defined by three methyl ligands and the alkyne ligand centroid. The Re is displaced by 0.68 Å from the basal plane. The Re–C(alkyne) distance of 2.090(7) Å is shorter than the Re–C(methyl) distances (average 2.158(13) Å), but it is close to the distances reported in other rhenium alkyne complexes in which the alkyne is thought to function as more than a two electron donor.[19] The C–C distance for the alkyne ligand (1.290(14) Å) is between a double (1.34 Å) and triple bond (1.20 Å) distance.[20] The alkyne substituents bend away form the metal center by 36°, which is a normal value.[19]

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Re(O)Me$_3$(PhC≡CPh) (4e)

Distances			
Re–O	1.694(8)	C(3)–C(4)	1.468(9)
Re–C(1)	2.161(8)	C(3)–C(3A)	1.290(14)
Re–C(2)	2.155(10)	Re(C≡C)$_{\mathrm{cent}}$	1.998(8)
Re–C(3)	2.090(7)		
Angles			
O–Re–C(1)	110.4(2)	C(3)–Re–C(3A)	35.9(4)
O–Re–C(2)	103.2(4)	Re–C(3)–C(4)	143.7(5)
C(1)–Re–C(2)	74.3(2)	Re–C(3)–C(3A)	72.0(2)
O–Re–C(3)	108.8(3)	C(4)–C(3)–C(3A)	144.1(4)
C(1)–Re–C(3)	77.3(3)	(C≡C)$_{\mathrm{cent}}$–Re–O	109.8(4)
C(2)–Re–C(3)	142.9(3)	(C≡C)$_{\mathrm{cent}}$–Re–C(2)	146.9(4)
C(1)–Re–C(1A)	132.9(4)	(C≡C)$_{\mathrm{cent}}$–Re–C(1)	93.8(4)
C(3)–Re–C(1A)	110.2(3)		

The ^{13}C (and where applicable ^{1}H) data for the alkyne ligands in **4** indicate that they function as three electron donors according to Templeton's NMR criterion.[21] In a crude approximation this can be explained by considering the symmetry adapted linear combinations of the oxo p_y and alkyne $\pi(p_z)$ orbitals (**III**). One of the two combinations (**IIIa**) has a symmetry match with a metal orbital (d_{yz}), while the other does not (**IIIb**). Thus, only two of the four electrons from the two symmetry combinations are contributed to the metal, one electron each from the oxo and alkyne ligands, and the other two electrons remain in the essentially nonbonding symmetry adapted combination **IIIb**. The one electron from the alkyne, plus the two electrons contributed from the alkyne π orbital of σ symmetry with respect to M–alkyne bonding, makes the neutral alkyne effectively a three electron donor.



III

The competition between the alkyne and oxygen for π bonding as described by **III** would be expected to weaken

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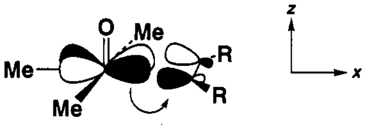
(19) For example, see: Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946; *Angew. Chem.* **1988**, *100*, 975. Spaltenstein, E.; Mayer, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7744 and references therein. Cai, S. Ph.D. Dissertation, Harvard University, 1990.

(20) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley: New York, 1985.

(21) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1. Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W. *Inorg. Chem.* **1981**, *20*, 1248. Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

the metal–oxygen multiple bond. The rhenium–oxo streching frequencies for these compounds are normal, however, when compared, for example, with the frequency of 998 cm^{-1} observed in $Re(O)(CH_2SiMe_3)_3(PMe_3)$.[3] An additional consideration is the back-bonding which occurs from the metal to the alkyne (**IV**). The metal–oxo bonding is oppositely affected by **III** and **IV**: The competition described by **III** serves to weaken the bond, while the π back-bonding **IV** strengthens it by increasing the effective oxidation state of the metal. Because the rhenium–oxo streching frequencies are normal for these compounds, the two effects apparently cancel each other.



IV

For the propyne adduct **4a**, the ^1H spectrum has three methyl proton resonances for the methyl ligands, as well as the expected signals from the alkyne. The alkyne proton couples weakly to the protons of one of the methyl ligands ($^4J_{HH} = 1.5$ Hz). Difference NOE spectra suggest that the coupling arises from the methyl group on the opposite side of the molecule from the alkyne proton.

Variable temperature ^1H NMR studies for **4a** indicate the activation barrier for rotation is at least 18 kcal mol^{-1}.[22] The high barrier is a consequence of the HOMO–LUMO interaction **IV** which orients the alkyne perpendicular to the Re–O vector. Rotation would result in a nearly complete loss of back-bonding and is threfore a high energy process.

Compounds **4a–e** give weak IR bands between 1750 and 1850 cm^{-1}, which are assigned to $\nu(C{\equiv}C)$ of the coordinated alkynes.[19] These frequencies are approximately 550 cm^{-1} lower than in free alkynes, consistent with a substantial weakening of the triple bond on coordination. The stretching frequencies are similar to those reported for other rhenium–oxo alkyne compounds.[19]

Discussion

On the basis of our experimental results and bonding description, **1** and **2** are best described as analogs of resonance stabilized ylides in which the ylide charge delocalization involves a high oxidation state organometallic fragment. Although compounds **2a** and **2b** do not appear to have a structural precedent, organometallic analogs of phosphonium propenylide akin to **1** have been reported.[16,17] All of the previous examples, however, are low valent compounds that have a stabilizing substituent at the M–C_α position, such as $OSiMe_3$ or C(=O)OR.

The (*E*)-ReCH=CH(PMe_2R) configurations in **1** and **2** suggest that the molecules are formed by attack of external PMe_2R on coordinated ethynes in putative $Re(O)(C_2H_2)(CH_2SiMe_3)_3$ and $[Re(O)(C_2H_2)Me_2(PMe_2R)]^+$ intermediates.[23] The fact that **4a** and **4e** do not react with external phosphine suggests that the steric bulk of the alkynes limits the ability of the phosphine to attack. Literature precedent for phosphine attack on coordinated alkynes includes Kolobova and co-workers report of reaction 5,

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2(HC{\equiv}CCO_2Me) + PPh_3 \rightarrow (\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^1\text{-}C(CO_2Me)CH(PPh_3)) \quad (5)$$

which forms a low valent manganese organometallic analog of a phosphonium propenylide.[17,24] It is also conceivable that reaction 1 proceeds via insertion of ethyne into the Re—P bonds to yield (*Z*)-ReCH=CH(PMe_2R) followed by isomerization[23] or that a dipolar intermediate $[RMe_2P^+\text{—}CH{=}CH^-]$, formed from free PMe_2R and ethyne,[25] reacts with the phosphine complexes or phosphine dissociated intermediates to form the products.

Conclusion

$Re(O)R_3(PMe_3)$ (R = Me and CH_2SiMe_3) and *cis*-$Re(O)Me_2Cl(PMe_2R)_2$ (R = Me and Ph) react with ethyne to give, respectively, $Re(O)R_3(CHCH(PMe_3))$ and $[Re(O)Me_2(CHCH(PMe_2R))_2]Cl$, which are products of the formal insertion of ethyne into the Re—P bonds. Substituted alkynes, on the other hand, react with $Re(O)Me_3(PMe_3)$ to give the adducts $Re(O)Me_3(RC{\equiv}CR')$ (R = R′ = Me, Et, or Ph; R = Me or Ph and R′ = H). On the basis of spectroscopic studies and the X-ray crystal structures of $Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$ and $[Re(O)Me_2(CHCH(PMe_2Ph))_2]Cl$, the insertion products are best described as anologs of resonance stabilized ylides in which the resonance stabilization involves a high oxidation state organometallic fragment. The mechanism by which the inserted products are formed is proposed to involve phosphine displacement and subsequent attack on coordinated ethyne by external phosphine, consistent with the (*E*)-ReCH=CH(PMe_2R) configurations of the $Re(O)R_3(CHCH(PMe_3))$ and $[Re(O)Me_2(CHCH(PM_2R))_2]Cl$ compounds.

Experimental Section

All manipulations and reactions were carried out under atmospheres of dry, oxygen-free nitrogen or argon or *in vacuo*, by using standard Schlenk techniques or dryboxes. Solvents were purified by using standard techniques. The compounds $Re(O)(CH_2SiMe_3)_3(PMe_3)$, $Re(O)Me_3(PMe_2R)$, $Re(O)Me_2Cl(PMe_2R)_2$ (R = Me or Ph), and *cis*- and *trans*-$[Re(O)Me_2(PMe_3)_2(CH_3CN)][BF_4]$ were prepared as described previously.[3,4] Proton and ^{13}C NMR spectra were referenced internally to solvent ^1H and ^{13}C resonances, respectively. Infrared spectra were referenced externally to the 1601-cm^{-1} band of polystyrene.

$Re(O)(CH_2SiMe_3)_3(CHCH(PMe_3))$, 1a. In a Schlenk reaction flask, $Re(O)(PMe_3)(CH_2SiMe_3)_3$ (0.140 g, 0.26 mmol) was dissolved in toluene (30 mL). The greenish brown solution was frozen and excess C_2H_2 (2 mmol) was condensed into the flask via a calibrated vacuum manifold. After the mixture was allowed to warm to room temperature, it was stirred for 48 h. The volatile components were then removed under reduced pressure, and the residue was extracted with CH_3CN (5 × 5 mL). The extracts were filtered and the solution was reduced in volume in vacuo. Slowly cooling the solution to −30 °C produced red cubic crystals. The crystals were isolated by removing the supernatant liquid via a cannula (yield 0.068 g, 46%). Anal. Calcd for $RePSi_3OC_{17}H_{44}$: C, 36.08; H, 7.84. Found: C, 36.11; H, 7.73.

^1H NMR (CD_3CN): δ 12.31 (dd, 1, $^3J_{HH} = 17.2$ Hz, $^3J_{PH} = 34.2$ Hz, C*H*CHPMe$_3$), 3.42 (dd, 1, $^3J_{HH} = 17.2$ Hz, $^2J_{PH} = 33.6$ Hz,

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[22] Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic: New York, 1988; pp 291–321.

[23] Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101 and references therein.

[24] Other low valent propenylide analogs are made by addition of a preformed ylide to carbonyl complexes—see ref 16.

[25] Cullen, W. R.; Dawson, D. S. *Can. J. Chem.* **1967**, *45*, 2887 and references therein.

CHC*H*PMe$_3$), 2.36 (s, 2, C*H*$_2$SiMe$_3$), 2.35 and 1.13 (d of an AB q, 2, $^2J_{HH}$ = 8 Hz, C*H*$_2$SiMe$_3$), 1.65 (d, 9, $^2J_{PH}$ = 13.4 Hz, P*Me*$_3$), 0.04 (s, 18, CH$_2$Si*Me*$_3$), −0.17 (s, 9, CH$_2$Si*Me*$_3$). ^{13}C NMR (CD$_3$CN): δ 228.3 (dd, 1, $^1J_{CH}$ = 122 Hz, $^2J_{PC}$ = 10 Hz, Re*C*HCHPMe$_3$), 85.0 (dd, 1, $^1J_{CH}$ = 163 Hz, $^1J_{PC}$ = 85 Hz, CH*C*HPMe$_3$), 38.3 (t, 2, $^1J_{CH}$ = 118 Hz, *C*H$_2$SiMe$_3$), 37.0 (t, 1, $^1J_{CH}$ = 117 Hz, *C*H$_2$SiMe$_3$), 12.9 (dd, 3, $^1J_{CH}$ = 111 Hz, $^1J_{PC}$ = 59 Hz, P*Me*$_3$), 4.0 (q, 3, $^1J_{CH}$ = 118 Hz, CH$_2$Si*Me*$_3$), 2.2 (q, 6, $^1J_{CH}$ = 118 Hz, CH$_2$Si*Me*$_3$). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 5.78. IR (NaCl, Nujol, cm^{-1}): ν(Re–O) 982 (s) (ν(Re–^{18}O) 921 (s)); 1367 (vw), 1359 (vw), 1320 (w), 1299 (s), 1260 (w), 1245 (w), 1239 (s), 1149 (m), 1043 (w), 998 (s), 953 (s), 937 (s), 905 (m), 850 (s), 832 (s), 771 (s), 753 (w), 747 (w), 702 (w), 689 (w), 680 (m), 660 (m), 618 (w), 610 (w).

Re(O)Me$_3$(CHCH(PMe$_3$)), 1b. To a frozen (−196 °C) solution of Re(O)Me$_3$(PMe$_3$) [prepared *in situ* from 0.100 g, 0.23 mmol, of Re(O)Me$_2$Cl(PMe$_3$)$_2$] in toluene (50 mL) was added ethyne (3.5 mmol) via a vacuum manifold. The mixture was allowed to warm to room temperature and then stirred for 1 h. This yielded a red-orange solution and dark solid. The mixture was filtered, and the filtrate was then reduced in volume in vacuo to yield a white precipitate. The solution was again filtered. The filtrate was reduced in volume in vacuo and then cooled to −20 °C. This produced red-orange crystals (yield 0.032 g, 0.09 mmol, 40%). Anal. Calcd for Re(O)PC$_8$H$_{20}$: C, 27.50; H, 5.77. Found: C, 27.77; H, 6.02.

^{1}H NMR (C$_6$D$_6$): δ 12.59 (dd, 1, $^3J_{HH}$ = 17.4 Hz, $^3J_{PH}$ = 36.0 Hz, ReC*H*CHP), 2.74 (dd, 1, $^3J_{HH}$ = 16.9 Hz, $^2J_{PH}$ = 35.4 Hz, ReCHC*H*P), 2.62 (s, 3, Re*Me*), 2.26 (s, 6, Re*Me*), 0.29 (d, 9, J_{PH} = 14.1 Hz, ReP*Me*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 232.0 (d, 1, $^2J_{PC}$ = 6.2 Hz, Re*C*HCHP), 79.3 (d, 1, $^1J_{PC}$ = 88.0 Hz, ReCH*C*HP), 33.4 (s, 2, Re*Me*), 25.0 (s, 1, Re*Me*), 12.6 (d, J_{PC} = 58 Hz, P*Me*$_3$). ^{31}P{^{1}H} (C$_6$D$_6$): δ 5.2 (s, CHCH*P*Me$_3$). IR (CsI, Nujol, cm^{-1}): ν(Re–O) 998 (s); 1481 (sh), 1329 (w), 1251 (m), 1212, (m), 1188 (w), 1101 (m), 982 (s), 941 (s), 910 (m), 870 (m), 820 (m), 747 (s), 699 (m), 670 (w).

[Re(O)Me$_2$(CHCH(PMe$_3$))$_2$]Cl, 2a. A solution of Re(O)Me$_2$Cl(PMe$_3$)$_2$ (0.150 g, 0.36 mmol) in toluene (50 mL) was frozen (−196 °C) and the flask evacuated. Ethyne (1.5 mmol) was then condensed into the flask via a calibrated vacuum manifold. The mixture was allowed to warm to room temperature and then stirred for 2 days. Over this time a dark solid formed. The solution was filtered through a glass frit, and the solid was washed with additional toluene (3 × 25 mL). The solid on the frit was then transferred to another Schlenk flask. Washing the solid with acetonitrile (3 × 30 mL) yielded a deep red solution. The acetonitrile solution was then reduced in volume, and toluene (10 mL) was added. Cooling to −20 °C yielded a red-orange solid. The analysis and yield reported below are based on material dissolved in methylene chloride and then stripped *in vacuo* to remove acetonitrile solvent of crystallization (yield 0.084 g, 50%). Anal. Calcd for ReP$_2$OClC$_{12}$H$_{28}$: C, 30.54; H, 5.98. Found: C, 30.60; H, 6.11.

^{1}H NMR (CH$_3$CN): δ 11.69 (dd, 2, $^3J_{HH}$ = 17.5 Hz, $^3J_{PH}$ = 32.5 Hz, ReC*H*CHP), 4.31 (dd, 2, $^3J_{HH}$ = 17.5 Hz, $^2J_{PH}$ = 29.8 Hz, ReCHC*H*P), 1.70 (d, 18, $^2J_{PH}$ = 14 Hz, P*Me*$_3$), 1.60 (s, 6, ReC*H*$_3$). ^{13}C{^{1}H} NMR (CH$_3$CN): δ 221.3 (d, 2, $^2J_{PC}$ = 9.4 Hz, Re*C*HCHP), 89.3 (d, 2, $^1J_{PH}$ = 78.4 Hz, ReCH*C*HP), 26.8 (s, 2, Re*Me*), 10.9 (d, 6, $^1J_{PH}$ = 41.0 Hz, P*Me*$_3$). ^{31}P{^{1}H} (CH$_3$CN): δ 10.5 (s, CHCH*P*Me$_3$). IR (CsI, Nujol, cm^{-1}): ν(Re–O) 1006 (s) (ν(Re–^{18}O) 960; 1430 (w), 1282 (m), 1162 (w), 957 (s), 948 (s), 875 (w), 682 (m), 524 (m), 511 (m).

[Re(O)Me$_2$(CHCH(PMe$_2$Ph))$_2$]Cl, 2b. This compound was prepared by a procedure analogous to the one used for the preparation of **2a**. The analysis and yield reported below are based on material dissolved in methylene chloride and then stripped *in vacuo* to remove acetonitrile solvent of crystallization (yield 65%). Anal. Calcd for ReP$_2$ClOC$_{22}$H$_{32}$: C, 44.33; H, 5.41. Found: C, 44.49; H, 5.77.

^{1}H NMR (CH$_3$CN): δ 11.73 (dd, 2, $^3J_{HH}$ = 17.7 Hz, $^3J_{PH}$ = 32.5 Hz, ReC*H*CHP), 7.85 (m, 4, PMe$_2$*Ph*), 7.64 (m, 4, PMe$_2$*Ph*), 7.22 (m, 2, PMe$_2$*Ph*), 4.30 (dd, 2, $^3J_{HH}$ = 17.7 Hz, $^2J_{PH}$ = 29.8 Hz, ReCHC*H*P), 2.06 (d, 6, $^2J_{PH}$ = 9.4 Hz, ReP(*Me*$_2$Ph)), 2.01 (d, 6, $^2J_{PH}$ = 9.4 Hz, ReP(*Me*$_2$Ph)), 1.70 (s, 6, ReC*H*$_3$). ^{13}C{^{1}H} NMR (CH$_3$CN): δ 220.7 (d, 2, $^2J_{PC}$ = 9.4 Hz, Re*C*HCHP), 134.4 (s, 2, PMe$_2$*Ph*), 132.3 (d, 4, J_{PC} = 9.4 Hz, PMe$_2$*Ph*), 130.5 (d, 4, J_{PC} = 11.5 Hz, PMe$_2$*Ph*), 92.2 (d, 2, $^1J_{PH}$ = 83.2 Hz, ReCH*C*HP), 29.5 (s, 2, Re*Me*), 11.6 (d, 2, $^1J_{PH}$ = 40.0 Hz, ReP*Me*$_2$Ph), 11.1 (d, 2, $^1J_{PH}$ = 40.2 Hz, ReP*Me*$_2$Ph). ^{31}P{^{1}H} (CH$_3$CN): δ 9.9 (s, CHCH*P*Me$_2$Ph). IR (CsI, Nujol, cm^{-1}): ν(R–O) 981 (s) (ν(Re–^{18}O) 945); 1500 (s), 1379 (s), 1299 (m), 1261 (m), 1239, (m), 1204 (w), 1152 (m), 1116 (s), 960 (s), 932 (s), 871 (m), 816 (m), 729 (m), 596 (w), 508 (w), 488 (m).

Reaction of [Re(O)Me$_2$(PMe$_3$)$_2$(CH$_3$CN)][BF$_4$] with Ethyne. Ethyne (0.2 mmol) was added via a vacuum manifold to a frozen acetonitrile-*d*$_3$ solution of [Re(O)Me$_2$(PMe$_3$)$_2$(CH$_3$CN)][BF$_4$] (0.025 g, 0.05 mmol). The solution was allowed to warm to room temperature and then stirred for 12 h. During this time the color became an intense red. The ^{1}H NMR spectrum for the solution is identical to that of **2a**.

Re(O)(CH$_2$SiMe$_3$)$_2$(CHCH(PMe$_3$))(CHCH(CH$_2$SiMe$_3$)), 3. This compound is a byproduct in the synthesis of **1a**. The yield was variable depending upon reaction conditions but was never more than 10% of the major product (<5% overall), as determined by ^{1}H NMR of the stripped CH$_3$CN extracts. Repeated recrystallizations of **1a** yielded a supernantant in which **3** is the major component because **3** is more soluble in CH$_3$CN than **1a**.

^{1}H NMR (CD$_3$CN): δ 12.34 (dd, 1, $^3J_{HH}$ = 17.2 Hz, $^3J_{PH}$ = 33.7 Hz, C*H*CHPMe$_3$), 8.32 (broad d, 1, $^3J_{HH}$ = 11.6 Hz, C*H*CHCH$_2$SiMe$_3$), 6.37 (d of t, 1, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 11.6 Hz, CHC*H*CH$_2$SiMe$_3$), 3.64 (dd, 1, $^3J_{HH}$ = 17.4 Hz, $^2J_{PH}$ = 33.2 Hz, CHC*H*PMe$_3$), 2.50 and 1.05 (d of an AB q, 2, $^2J_{HH}$ = 8.0 Hz, C*H*$_2$SiMe$_3$), 0.87 (broad d, 2, $^3J_{HH}$ = 8.0 Hz, CHCHC*H*$_2$SiMe$_3$), 1.69 (d, 9, $^2J_{PH}$ = 13.8 Hz, P*Me*$_3$), 0.01 (s, 18, CH$_2$Si*Me*$_3$), −0.05 (s, 9, CH$_2$Si*Me*$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 229.5 (s, 1, Re*C*HCHPMe$_3$), 180.8 (s, 1, Re*C*HCHCH$_2$SiMe$_3$), 119.5 (s, 1, ReCH*C*HCH$_2$SiMe$_3$), 88.0 (d, $^1J_{PC}$ = 86.7 Hz, CH*C*HPMe$_3$), 37.4 (s, 2, *C*H$_2$SiMe$_3$), 24.6 (s, 1, ReCHCH*C*H$_2$SiMe$_3$), 12.7 (d, 3, $^1J_{PC}$ = 58.6 Hz, P*Me*$_3$), 2.30 (s, 6, CH$_2$Si*Me*$_3$), −1.14 (s, 3, ReCHCHCH$_2$Si*Me*$_3$). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 6.42.

Re(O)Me$_3$(HC≡CMe), 4a. To a frozen (−196 °C) solution of Re(O)Me$_3$(PMe$_3$) [prepared *in situ* from 0.125 g, 0.30 mmol, of Re(O)Me$_2$Cl(PMe$_3$)$_2$] in toluene (50 mL) was added propyne (1.0 mmol) via a vacuum manifold. The solution was allowed to warm to room temperature and then stirred for 1 h. This yielded a yellow solution which was reduced in volume to yield a white precipitate. The solution was filtered. Stripping the filtrate gave a yellow oil (yield 0.034 g, 40%). Anal. Calcd for ReOC$_6$H$_{13}$: C, 25.08; H, 4.56. Found: C, 25.23; H, 4.31.

^{1}H NMR (C$_6$D$_6$): δ 8.13 (s, 1, *H*C≡CMe), 2.44 (s, 3, HC≡C*Me*), 2.19 (s, 3, Re*Me*), 2.18 (d, 3, $^4J_{HH}$ = 1.5 Hz, Re*Me*), 1.92 (s, 3, Re*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 148.9 (s, 1, HC≡*C*Me), 139.4 (s, 1, H*C*≡CMe), 41.5 (s, 1, Re*Me*), 28.3 (s, 2, Re*Me*), 11.0 (s, 1, HC≡C*Me*). IR (CsI, Nujol, cm^{-1}): ν(Re—O) 1005 (s) (ν(Re—^{18}O) 957); ν(C≡C) 1745 (w); 1611 (m), 1449 (w), 1422 (s), 1318 (m), 1290 (w), 1172 (w), 1126 (w), 1074 (w), 1042 (w), 936 (s), 892 (w), 807 (m), 762 (m), 703 (w), 520 (br).

Re(O)Me$_3$(MeC≡CMe), 4b. This compound was prepared from Re(O)Me$_2$Cl(PMe$_3$)$_2$ (0.125 g, 0.30 mmol) and MeC≡CMe (1.0 mmol) by a procedure analogous to the one used for the preparation of **4a**. The solvent was removed from the reaction mixture and the residue extracted with a warm 1:1 toluene/hexane mixture. The solvent was removed in vacuo to leave a yellow oil (yield 0.035 g, 39%). Anal. Calcd for ReOC$_7$H$_{15}$: C, 27.90; H, 5.02. Found: C, 28.04; H, 4.84.

^{1}H NMR (C$_6$D$_6$): δ 2.35 (s, 6, *Me*C≡C*Me*), 2.15 (s, 6, Re*Me*), 1.84 (s, 3, Re*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 143.5 (s, 2, Me*C*≡*C*Me), 41.4 (s, 1, Re*Me*), 28.3 (s, 2, Re*Me*), 9.2 (s, 2, *Me*C≡CRe*Me*). IR (CsI, Nujol, cm^{-1}): ν(Re—O) 995 (s); ν(C≡C) 1810 (m); 1449 (w), 1403 (m), 1301 (m), 1152 (w), 1063 (w), 945 (s), 902 (w), 852 (m), 762 (m), 512 (w).

Re(O)Me$_3$(EtC≡CEt), 4c. To a red solution of Re(O)Me$_3$PMe$_3$ [prepared *in situ* from 0.125 g, 0.30 mmol, of Re(O)Me$_2$Cl(PMe$_3$)$_2$] in toluene (50 mL) was added 3-hexyne (0.068 mL, 0.050 g, 0.60 mmol) via a gastight syringe. The solution, which changed to a yellow color within 5 min, was stirred for 1 h. The solution volume was reduced in vacuo by 50% and then 5 mL of pentane was added, yielding a white precipitate. The solution was filtered, and the solvent was removed from the filtrate in vacuo to give a yellow oil (yield 0.034 g, 0.14 mmol, 48%). Anal. Calcd for $\mathrm{ReOC_9H_{19}}$: C, 32.81; H, 5.81. Found: C, 32.70; H, 5.78.

^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.72 (AB part of an $\mathrm{ABX_3}$, 4, $^2J_{\mathrm{HH}} \approx {}^3J_{\mathrm{HH}} \approx 7.6$ Hz, $\mathrm{Me}CH_2\mathrm{C{\equiv}C}$), 2.35 (s, 6, Re*Me*), 1.88 (s, 3, Re*Me*), 1.02 (t, 6, $^3J_{\mathrm{HH}} = 7.6$ Hz, $Me\mathrm{CH_2C{\equiv}C}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 146.1 (s, 2, $\mathrm{Et}C{\equiv}C$), 42.0 (s, 1, Re*Me*), 27.4 (s, 2, Re*Me*, 18.6 (s, 2, $C\mathrm{H_3CH_2C{\equiv}C}$), 13.5 (s, 2, $\mathrm{CH_3}CH_2\mathrm{C{\equiv}C}$). IR (CsI, Nujol, cm^{-1}): ν(Re—O) 1004 (s) (ν(Re—^{18}O) 948); ν(C≡C) 1818 (w); 1440 (m), 1375 (w), 1305 (m), 1285 (m), 1244 (w), 1237 (s), 1204 (w), 1182 (w), 1158 (s), 1128 (w), 983 (s), 937 (w), 901 (w), 800 (w), 741 (w), 530 (m).

Re(O)Me$_3$(HC≡CPh), 4d. This compound was prepared from $\mathrm{Re(O)Me_2Cl(PMe_3)_2}$ (0.150 g, 0.36 mmol) and HC≡CPh (0.20 mL, 1.85 mmol) by a procedure analogous to that used for the preparation of **4c**. The product is a waxy solid (yield 0.050 g, 0.14 mmol, 40%). Anal. Calcd for $\mathrm{ReOC_{11}H_{15}}$: C, 37.81; H, 4.33. Found: C, 38.29; H, 4.74.

^{1}H NMR ($\mathrm{C_6D_6}$): δ 8.55 (s, 1, *H*C≡CPh), 7.28 (m, 2, HC≡C*Ph*), 7.08 (m, 3, HC≡C*Ph*, 2.52 (s, 3, Re*Me*), 2.14 (s, 3, Re*Me*), 2.11 (s, 3, Re*Me*). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 143.7 (s, 1, HC≡*C*Ph), 138.7 (d, 1, $J_{\mathrm{CH}} = 225$ Hz, H*C*≡CPh), 131.4 (dt, 2, $^1J_{\mathrm{CH}} = 163$ Hz, $^3J_{\mathrm{CH}} = 7.1$ Hz, HC≡C*Ph*), 129.7 (dt, 2, $^1J_{\mathrm{CH}} = 157.0$ Hz, $^3J_{\mathrm{CH}} = 6.7$ Hz, HC≡C*Ph*), 128.9 (dt, 1, $^1J_{\mathrm{CH}} = 160$ Hz, $^3J_{\mathrm{CH}} = 6.7$ Hz, HC≡C*Ph*), 128.8 (s, 1, HC≡C*Ph*), 43.4 (q, 1, $J_{\mathrm{CH}} = 132.2$ Hz, Re*Me*), 32.7 (q, 1, $J_{\mathrm{CH}} = 132.3$ Hz, Re*Me*), 29.3 (q, 1, $J_{\mathrm{CH}} = 128.9$ Hz, Re*Me*). IR (CsI, Nujol, cm^{-1}): ν(Re—O) 992 (s); ν(C≡C) 1792 (m); 1404 (sh), 1350 (m), 1304 (m), 1150 (w), 1098 (w), 1010 (w), 970 (w), 900 (w), 895 (w), 795 (m), 770 (m), 650 (w).

Re(O)Me$_3$(PhC≡CPh), 4e. This compound was prepared from $\mathrm{Re(O)Me_2Cl(PMe_3)_2}$ (0.100 g, 0.23 mmol) and PhC≡CPh (0.064 g, 0.36 mmol) by a procedure similar to that used for the preparation of **4a**. The product is a pale yellow crystalline solid (yield 0.065 g, 0.15 mmol, 66%). Anal. Calcd for $\mathrm{ReOC_{17}H_{19}}$: C, 47.98; H, 4.50. Found: C, 48.21; H, 4.88.

^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.28 (m, 4, *Ph*C≡C), 7.13 (m, 4, *Ph*C≡C), 7.04 (m, 2, *Ph*C≡C), 2.40 (s, 6, Re*Me*), 2.29 (s, 3, Re*Me*). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 147.5 (s, 2, *C*≡*C*Ph), 132.0 (s, 2, *Ph*C≡C*Ph*), 130.5 (s, 2, *Ph*C≡C*Ph*), 129.2 (s, 2, *Ph*C≡C*Ph*), 129.0 (s, 2, *Ph*C≡C*Ph*), 128.8 (s, 2, *Ph*C≡C*Ph*), 128.3 (s, 2, *Ph*C≡C*Ph*), 44.7 (s, 1, Re*Me*), 33.2 (s, 2, Re*Me*). IR (CsI, Nujol, cm^{-1}): ν(Re—O) 1000 (s); ν(C≡C) 1837 (m); 1431 (m), 1419 (m), 1304 (m), 1285 (m), 1244 (w), 1206 (w), 1200 (w), 957 (s), 947 (s), 936 (s), 853 (m), 782 (m), 670 (m), 526 (w), 488 (w).

X-ray Crystallography for Re(O)(CH$_2$SiMe$_3$)$_3$(CHCH(PMe$_3$)), 1a. A crystal data summary is given in Table I, and atomic coordinates are in Table V. The crystals were grown by slowly cooling a saturated acetonitrile solution (−30 °C). In a nitrogen filled glovebag, a crystal was attached to a glass fiber with a small amount of stopcock grease. The sample was then quickly transferred to the diffractometer where it was immersed in a cold nitrogen stream. A lattice determination suggested an orthorhombic cell. The structure was solved by a combination of direct methods and Fourier techniques. Hydrogen atoms were located in a difference Fourier and refined isotropically in the final cycles. A final difference Fourier was featureless with the largest peak being 0.95 e Å^{-3}. The absolute configuration shown in the figure is correct for the molecule in the crystal studied, based on a comparative refinement of the two enantiomers.

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10) for Re(O)(CH$_2$SiMe$_3$)$_3$(CHCH(PMe$_3$)) (1a)^a

atom	*x*	*y*	*z*	B_{iso}
Re(1)	7553.1(3)	555.5(3)	2741.0(3)	11
O(2)	7536(7)	440(6)	1515(5)	18
C(3)	7557(9)	−803(7)	3368(7)	14
C(4)	7525(10)	−1101(8)	4306(7)	14
P(5)	7434(3)	−2349(2)	4681(2)	12
C(6)	8400(10)	−2736(10)	5427(12)	20
C(7)	6383(9)	−2550(11)	5376(13)	22
C(8)	7429(13)	−3187(9)	3658(8)	25
C(9)	8957(8)	617(11)	3245(11)	17
Si(10)	9898(2)	−91(3)	2593(3)	18
C(11)	11067(11)	154(13)	3194(13)	25
C(12)	10006(10)	305(12)	1297(10)	22
C(13)	9698(8)	−1516(10)	2669(11)	19
C(14)	6131(8)	690(13)	3295(10)	17
Si(15)	5204(2)	46(3)	2563(3)	21
C(16)	5368(10)	−1341(10)	2430(13)	26
C(17)	4018(9)	290(14)	3162(14)	28
C(18)	5140(9)	584(14)	1302(13)	27
C(19)	7563(11)	2113(8)	3146(8)	18
Si(20)	7738(2)	2600(2)	4414(2)	21
C(21)	6969(12)	1937(11)	5333(10)	29
C(22)	8979(9)	2552(12)	4855(11)	25
C(23)	7366(10)	3967(8)	4367(9)	21

^{a} Isotropic values are calculated by using the formula found in: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [Re(O)Me$_2$(CHCH(PMe$_2$Ph))$_2$]Cl·CH$_3$CN (2b·CH$_3$CN)^a

atom	*x*	*y*	*z*	*U*(eq)
Re	2054(1)	3532(1)	7683(1)	24(1)
P(1)	1948(1)	837(1)	9687(1)	26(1)
P(2)	−901(1)	1315(1)	7138(1)	30(1)
Cl	675(1)	7348(1)	852(1)	41(1)
O	1964(2)	5091(3)	7752(2)	36(1)
C(1)	3544(3)	3005(5)	7843(3)	37(2)
C(2)	2169(5)	2933(7)	6601(3)	37(2)
C(3)	2057(3)	2647(5)	8656(3)	27(2)
C(4)	2234(3)	1446(5)	8862(3)	29(2)
C(5)	723(3)	2755(5)	7445(2)	27(2)
C(6)	352(4)	1613(5)	7282(3)	30(2)
C(30)	−413(5)	6326(6)	8464(3)	51(2)
C(31)	354(5)	5739(7)	8980(3)	45(2)
N	−1005(5)	6809(8)	8073(3)	89(3)
C(11)	1000(4)	−278(6)	9484(3)	35(2)
C(12)	1568(5)	2054(6)	10246(3)	40(2)
C(13)	2972(3)	117(5)	10252(3)	28(2)
C(14)	2874(5)	916(6)	10690(3)	45(2)
C(15)	3654(5)	−1331(7)	11199(4)	58(2)
C(16)	4524(5)	−700(7)	11270(3)	56(2)
C(17)	4635(4)	308(6)	10820(3)	50(2)
C(18)	3865(4)	715(6)	10309(3)	41(2)
C(21)	−1226(5)	206(7)	7793(3)	48(2)
C(22)	−1570(4)	2728(6)	7212(3)	38(2)
C(23)	−1274(4)	684(5)	6231(3)	32(2)
C(24)	−792(4)	1053(6)	5668(3)	39(2)
C(25)	−1102(5)	647(7)	4951(3)	49(2)
C(26)	−1883(5)	−150(6)	4801(4)	54(2)
C(27)	−2369(5)	−548(6)	5350(3)	53(2)
C(28)	−2069(4)	−109(5)	6070(3)	43(2)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

X-ray Crystallography for [Re(O)Me$_2$(CHCH(PMe$_2$Ph))$_2$]Cl·CH$_3$CN, 2b·CH$_3$CN. A crystal data summary is given in Table I, and atomic coordinates are in Table VI. The crystals for study were grown by low temperature vapor diffusion of diethyl ether into a saturated acetonitrile solution (4 °C; 10 days). In a nitrogen filled glovebag, a crystal was attached to a glass fiber with a small amount of stopcock grease. The sample was then quickly transferred to the diffractometer where it was immersed in a cold nitrogen stream. During collection the intensities of three check reflections were measured after every 60 reflections. A linear decay correction (ca. 7.5% average decrease in intensity after 120 h of exposure), a semiempirical absorption correction based on ψ scans of 6 reflections near $\chi = 90°$, and Lorentz and polarization corrections were applied to the data.

Direct methods readily revealed the positions of the rhenium, phosphorus, and chlorine atoms. Standard difference map techniques were used to find the remaining non-hydrogen atoms.

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Re(O)Me$_3$(PhC≡CPh) (4e)[a]

atom	*x*	*y*	*z*	*U*(eq)
Re	4079(1)	2500	2747(1)	19(1)
O	4218(5)	2500	−363(14)	37(3)
C(1)	4288(5)	3590(4)	4227(16)	33(2)
C(2)	5378(6)	2500	4149(20)	28(3)
C(3)	2830(4)	2855(4)	3543(12)	24(2)
C(4)	2282(4)	3509(3)	3774(12)	20(2)
C(5)	1695(4)	3583(4)	5734(14)	27(2)
C(6)	1151(5)	4191(4)	5844(15)	31(2)
C(7)	1176(5)	4718(4)	4029(15)	29(2)
C(8)	1764(5)	4659(4)	2046(15)	29(2)
C(9)	2320(4)	4057(4)	1941(12)	23(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed all of the hydrogen atom positions. An attempted isotropic refinement of the hydrogens produced unacceptable thermal parameters for one hydrogen attached to C(1) and the hydrogen attached to C(5). The hydrogen atoms attached to C(1) and C(5) were therefore placed in calculated positions ($U_{iso}(H) = 1.2U_{iso}(C)$; $d_{C-H} = 0.96$ Å) for refinement. Refinement was performed to convergence with this model. The final difference map contained three peaks (1.21, 1.13, and 1.07 e Å^{-3}) located within 1.07 Å of the rhenium. All other peaks were less than 0.92 e Å^{-3}.

X-ray Crystallography for Re(O)Me$_3$(PhC≡CPh), 4e. A crystal data summary is given in Table I, and atomic coordinates are in Table VII. The crystals for study were grown at low temperature from a saturated hexane solution (−20 °C; 2 days). In air, a crystal was quickly attached to a glass fiber with a minimum amount of stopcock grease. It was then transferred to the diffractometer where it was immersed in a cold nitrogen stream. The intensities of three check reflections were measured after every 60 reflections; the crystal did not decay during the 48 h of collection. A semiempirical absorption correction based on ψ scans of 10 reflections near $\chi = 90°$ and Lorentz and polarization corrections were applied to the data.

Systematic absences were consistent with the space groups *Pnma* and *Pna*2$_1$. The *E* statistics suggested that the centrosymmetric space group *Pnma* was the correct choice. Direct methods readily revealed the position of the rhenium atom located on a mirror plane. Standard difference map techniques were used to find the remaining non-hydrogen atoms. The hydrogen atoms were placed in calculated positions ($U_{iso}(H) = 1.2U_{iso}(C)$; $d_{C-H} = 0.96$ Å) for refinement. An extinction correction was applied in the final cycles of refinement. The final difference map contained one peak (1.46 e Å^{-3}) located near the rhenium atom. All other peaks were less than 0.85 e Å^{-3}.

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Supplementary Material Available: Tables of anisotropic thermal parameters, H-atom coordinates, and complete bond lengths and bond angles for Re(O)(CH$_2$SiMe$_3$)$_3$(CHCH(PMe$_3$)) and packing diagrams for **2b**·CH$_3$CN and **4e** (15 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors can be obtained from the authors.

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