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Reactions of the Tungsten–Carbyne Complex $W(\equiv CMe)Cl(PMe_3)_4$ with π-Acceptor Ligands: Carbon Monoxide, Alkynes, and Alkenes

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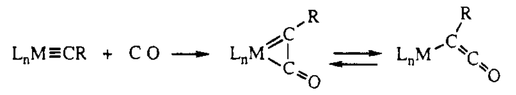
The tungsten–carbyne complex $W(\equiv CCH_3)Cl(PMe_3)_4$ (**1**) reacts with carbon monoxide to initially form the monocarbonyl adduct $W(\equiv CCH_3)Cl(PMe_3)_3(CO)$, which reacts further with CO to give an oxametallacyclopentenone complex, $\overline{W[OC(PMe_3){=}CMeC}(O)]Cl(CO)_2(PMe_3)_2$ (**3**). An X-ray crystal structure of **3** shows a seven coordinate tungsten complex with the metal bound to an acyl carbon and an enolate oxygen of the metallacycle, which results from an unusual double carbonylation of the carbyne ligand. Crystal data for $\mathbf{3}{\cdot}C_4H_8O$, at 24 °C: monoclinic, $P2_1/c$, $a = 14.945(3)$ Å, $b = 9.259(3)$ Å, $c = 20.226(3)$ Å, $\beta = 102.27(1)°$, $Z = 4$, $R = 0.035$, $R_w = 0.040$. Reaction of **1** with 2 equiv of *p*-tolyl isocyanate gives CO and the tungsten–ureato-*N,N′* complex $W(\equiv CCH_3)Cl[(NTol)_2C{=}O](PMe_3)_2$. Alkynes react with **1** to displace two PMe_3 ligands and form the first examples of carbyne–alkyne complexes, $W(\equiv CCH_3)Cl(RC{\equiv}CR')(PMe_3)_2$ ($RC{\equiv}CR'$ = $MeC{\equiv}CMe$, $PhC{\equiv}CPh$, $HC{\equiv}C^tBu$]. The diphenylacetylene and *tert*-butylacetylene complexes rearrange to give the new carbyne–alkyne complexes $W(\equiv CPh)Cl(CH_3C{\equiv}CPh)(PMe_3)_2$ and $W(\equiv C^tBu)Cl(CH_3C{\equiv}CH)(PMe_3)_2$, respectively. These rearrangements resemble alkyne metathesis, in that the carbyne ligand is exchanged with one end of the alkyne ligand. Vinylalkoxysilanes react with **1** to give carbyne–alkene complexes, $W(\equiv CCH_3)Cl[CH_2{=}CHSi(OMe)_3](PMe_3)_2$ and $W(\equiv CCH_3)Cl[CH_2{=}CHSi(OEt)Me_2](PMe_3)_2$, in which the silane appears to be bound through both the alkene and silyl ether functionalities.

Introduction

Since the first carbyne complexes $W(\equiv CR)X(CO)_4$ were synthesized by Fischer in 1973,[1] the chemistry of metal–carbon triple bonds has been an area of considerable interest.[2] Reactions of carbyne complexes with a variety of unsaturated ligands that give new C–C bonds have been explored extensively.[3] For example, carbyne complexes can undergo coupling with CO to form η^1- and η^2-ketenyl complexes (eq 1)[4] and can function as alkyne metathesis catalysts (eq 2).[5] Metathesis activity has been reported for a number of high-valent carbyne or "Schrock-type" alkylidyne complexes but not for low-valent "Fischer-type" carbynes, which can be precursors for catalysts in the polymerization of alkynes and cycloalkenes.[6] The reactions of carbynes with unsaturated organic substrates are typically proposed to occur through coupling at the metal center, but there are no reports of carbyne–alkyne complexes and carbyne–alkene species are rare.[7]



(1)

$$L_nM{\equiv}CR + R'C{\equiv}CR' \longrightarrow L_nM{\equiv}CR' + R'C{\equiv}CR \qquad (2)$$

We recently reported the facile preparation of a stable Fischer carbyne complex without carbonyl ligands, $W(\equiv CMe)Cl(PMe_3)_4$ (**1**).[8] Complex **1** has an unusual affinity for certain unsaturated organic ligands. This report describes double carbonylation of the carbyne ligand to give a novel metallacycle complex, carbyne–alkyne complexes, and the first example of stoichiometric alkyne metathesis by a Fischer carbyne complex.[9]

Results

Reaction with Carbon Monoxide. A THF solution of $W(\equiv CMe)Cl(PMe_3)_4$ (**1**) reacts with ~1 atm of CO at 65 °C to initially give a bright yellow solution of the

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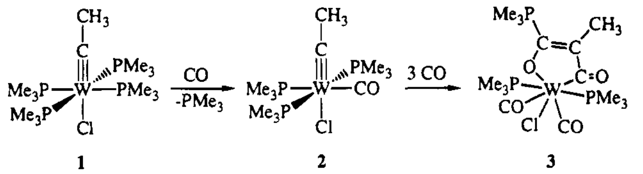
Table 1. Selected NMR and IR Data for W(≡CCH$_3$)Cl(CO)(PMe$_3$)$_3$ (2) and W[OC(PMe$_3$)═C(CH$_3$)C(O)]Cl(PMe$_3$)$_2$(CO)$_2$ (3)[a]

compd no.	^{1}H NMR[b]	^{13}C{^{1}H} NMR	IR (cm^{-1}, C_6D_6)
2	1.60 (t, 3, 18H, trans P*Me*$_3$'s)[c] 1.51 (d, 7, 9H, cis P*Me*$_3$)[c] 1.73 (quartet, 5, 3H, ≡CC*H*$_3$)[c]	226.8 (dt, J_{WC} = 150, J_{PC} = 45, J_{PC} = 7, *C*O)[c] 211.2 (t, J_{CP} = 7, ≡*C*CH$_3$)[c]	ν_{CO} 1891
3	1.21, 1.34 (d, 9, 18H, 2 W−P*Me*$_3$)[d] 1.74 (d, 2, 3H, ═C(C*H*$_3$)−)[d] 1.97 (d, 13, 9H, −C(P*Me*$_3$)═)[d]	254.5, 252.1 (m, W(*C*O)$_2$)[e] 235.6 (broad s, J_{WC} = 136, W−*C*(O)−)[e] 178.7 (dd, J_{PC} = 88, J_{CC} = 6, W−O−*C*(PMe$_3$)═)[e]	ν_{CO} 1900, 1809 $\nu_{-C(O)-}$ 1509 ν_{C-O} 1064

[a] For additional data, see Experimental Section. [b] Spectra reported as δ (multiplicity, *J* (Hz), no. of hydrogens, assignment). [c] In THF-d_8 at 24 °C. [d] In CD_2Cl_2 at −40 °C. [e] From reaction of **1** with 99% ^{13}CO; in THF-d_8 at −40 °C.

Scheme 1. Reaction of W(≡CCH$_3$)Cl(PMe$_3$)$_4$ (1) with CO



monocarbonyl adduct W(≡CMe)Cl(CO)(PMe$_3$)$_3$ (**2**, Scheme 1). IR and NMR spectra of **2** are similar to those of the closely related compounds W(≡CAr)Cl(CO)(PMe$_3$)$_3$, (Ar = Ph, *p*-tolyl).[10] A virtual triplet and a doublet (2:1) in the ^{1}H NMR of **2** indicate the *mer* geometry of the three phosphine ligands, and the methyl group on the carbyne is split by the three phosphine ligands to give a quartet (Table 1). The CO stretching frequency occurs in the IR at 1891 cm^{-1}, which was confirmed by the reaction of **1** with ^{13}CO ($\nu_{^{13}CO}$ = 1852 cm^{-1}). Complex **2** is not isolable, however, because it reacts further with 3 equiv of CO to give the unusual tungsten−oxametallacyclopentenone W[OC(PMe$_3$)═C-MeC(O)]Cl(CO)$_2$(PMe$_3$)$_2$ (**3**), which precipitates out of the THF solution.

Bright orange **3** is isolated in 70% yield on stirring a THF solution of **1** under ~1 atm of CO at 65 °C overnight. It is sparingly soluble in THF and benzene but very soluble in CH_2Cl_2. An X-ray crystal structure of **3** shows a seven-coordinate tungsten center, bound to two phosphine ligands, two carbonyl groups, a chloride, and the two ends of an unusual metallacycle (Figure 1). The metallacycle contains the original carbyne ligand (CMe), two molecules of carbon monoxide, and a PMe$_3$ group. The tungsten is bound to an acyl carbon at one end and an enolate oxygen at the other; the PMe$_3$ group is bound to the α-carbon of the enolate. The five atoms of the metallacycle are planar to within 0.03 Å. Bond lengths and angles within the metallacycle are given in Figure 2, while other metrical data are collected in Table 2. The valence bond structure shown for the metallacycle is a good representation of the bonding. The C(2)−C(3) distance of 1.348(9) Å is typical for C−C double bonds (1.34 Å),[11] the C(1)−C(2) bond of 1.482(9) Å is a common sp^2−sp^2 single bond (1.48 Å),[11] and the C(3)−O(2) distance of 1.313(8) Å is only slightly shorter than typical oxygen−sp^2-carbon bonds (1.34 Å).[11] There appears to be little ylide character to the C(3)−P(1) bond (1.823(7) Å), as it is longer than typical P═C bonds.[12]

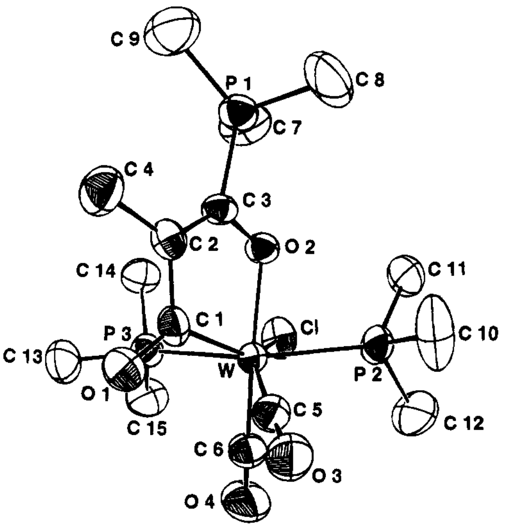


Figure 1. ORTEP of W[OC(PMe$_3$)C═C(CH$_3$)C(O)](Cl-(CO)$_2$(PMe$_3$)$_2$ (**3**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

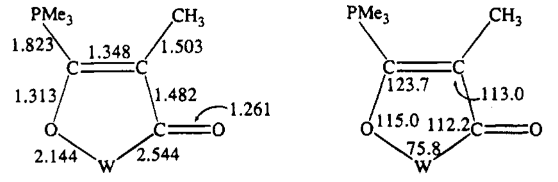


Figure 2. Bond distances (Å) and angles (deg) within the metallacycle in **3**. Estimated errors for the distances and angles are ≤0.009 Å and ≤0.6°.

The NMR and IR spectra of **3** are consistent with the solid-state connectivity (see Table 1 and the Experimental Section). Two carbonyl bands are observed in the IR spectrum in CD_2Cl_2 solution (1900, 1809 cm^{-1}), along with an acyl stretch at 1509 cm^{-1} and a C−O single-bond stretch at 1064 cm^{-1}. These assignments were confirmed using ^{13}CO to give the ^{13}CO-labeled metallacycle complex. Complex **3** is fluxional on the NMR time scale at room temperature, such that the phosphine ligands on the metal center give a broad lump in the ^{1}H NMR. Cooling the solution to −40 °C, however, gives a pair of doublets for two inequivalent phosphine ligands in the ^{1}H and ^{31}P NMR. The other phosphine, which is not attached to the metal center,

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $\overline{W[OC(PMe_3)=CMeC}(O)]Cl(CO)_2(PMe_3)_2 \cdot C_4H_8O$ (3)[a]

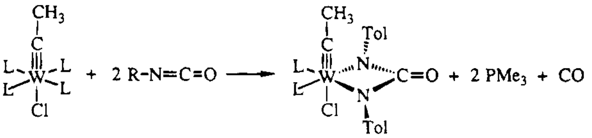
	Bond Distances		
W−Cl	2.544(2)	W−P(2)	2.499(2)
W−P(3)	2.534(2)	W−C(6)	1.964(9)
W−C(5)	1.913(8)		
	Bond Angles		
Cl−W−P(2)	78.76(7)	Cl−W−P(3)	79.46(7)
Cl−W−O(2)	82.32(13)	Cl−W−C(1)	144.2(2)
Cl−W−C(5)	148.2(2)	Cl−W−C(6)	87.8(3)
P(2)−W−P(3)	157.56(7)	P(2)−W−O(2)	79.08(12)
P(2)−W−C(1)	123.3(2)	P(2)−W−C(5)	79.0(2)
P(2)−W−C(6)	99.3(2)	P(2)−W−O(2)	92.71(12)
P(3)−W−C(1)	73.7(2)	P(3)−W−C(5)	123.2(2)
P(3)−W−C(6)	85.2(3)	O(2)−W−C(1)	75.8(2)
O(2)−W−C(5)	115.2(2)	O(2)−W−C(6)	170.1(3)
C(1)−W−C(5)	67.7(3)	C(1)−W−C(6)	112.6(3)
C(5)−W−C(6)	73.7(4)	W−C(5)−O(3)	176.5(6)
W−C(6)−O(4)	178.2(9)	C(3)−C(2)−C(4)	127.0(7)
W−C(1)−O(1)	129.6(5)	O(1)−C(1)−C(2)	118.2(6)
P(1)−C(3)−C(2)	129.7(6)	C(1)−C(2)−C(4)	120.0(6)
P(1)−C(3)−O(2)	106.4(5)		

[a] See also Figure 2.

gives a doublet in the ^{1}H NMR and a singlet in the ^{31}P NMR, at both 24 and −40 °C.

Other peaks are observed in NMR spectra taken during the reaction of **1** with CO to give **3**, but no intermediates besides **2** have been identified. The reaction does not produce significant amounts of **3** when CH_2Cl_2 is used as a solvent, although formation of the CO adduct **2** is observed in fair yield.

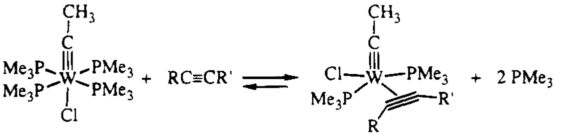
Reaction with Isocyanates. *tert*-Butyl isocyanate and acetonitrile do not react with **1** at room temperature, and heating these reaction mixtures gives only paramagnetic products. Two equivalents of *p*-tolyl isocyanate, however, reacts with **1** in benzene solution at 24 °C to give a new compound, whose NMR and IR spectra suggest formulation as the tungsten−ureato-*N,N'* complex $W(\equiv CCH_3)Cl[(NTol)_2C=O](PMe_3)_2$ (Tol = *p*-MeC_6H_4 (**4**); eq 3). When the reaction is carried out in a sealed NMR tube, the carbonyl adduct **2** is also observed, indicating that CO is also generated. The formation of **4** is very sensitive to reaction conditions, and the formation of **2** can be avoided by using a reaction vessel with more head space. While **4** has been isolated as a brown solid, its instability in solution over 1 day at ambient temperatures has precluded obtaining X-ray-quality crystals or satisfactory elemental analyses.



L = PMe3 **4** (3)

The ^{1}H NMR of **4** shows a virtually coupled pair of PMe_3 ligands, two equivalent *p*-tolyl groups, and the methyl group of the carbyne ligand. The $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) has a triplet (J_{PC} = 18 Hz) at 297.8 ppm, indicating the presence of a carbyne carbon bound to a metal center that coordinates two phosphines. A plane of symmetry is suggested by the equivalence of the phosphine and tolyl groups. A singlet at 159.6 ppm is also observed in the (proton coupled) ^{13}C NMR spectrum, and the solution IR spectrum (C_6D_6) has a strong band at 1668 cm^{-1}, consistent with a C=O group of a ureato-*N,N'* ligand.[13,14] This reaction of **1**, in which the carbyne is a spectator ligand, contrasts with the reported reaction of $(dme)Cl_3W\equiv C^tBu$ with cyclohexyl isocyanate.[15] The high-valent alkylidyne complex gives an imido complex in which the isocyanate is incorporated into an unusual azacarboxylate ligand.

Reactions with Alkynes. Terminal and internal acetylenes react reversibly with $W(\equiv CMe)Cl(PMe_3)_4$ (**1**) in benzene or THF solution to give the first examples of carbyne−alkyne complexes, $W(\equiv CMe)Cl(RC\equiv CR')(PMe_3)_2$ (**5**, **6**, **8**; eq 4). The internal alkyne 2-butyne (1.2 equiv) reacts with a 0.05 M THF solution of **1** over 3 h at 80 °C, to displace two phosphine ligands and yield yellow $W(\equiv CMe)Cl(MeC\equiv CMe)(PMe_3)_2$ (**5**) in 80% yield (K_{eq} ≈ 0.2 M at 80 °C). Removal of the volatiles shifts the equilibrium toward starting material such that isolation of **5** has not been possible. Continued heating over 1 week results in decomposition to unidentified paramagnetic products. The ^{1}H NMR spectrum of **5** shows a single resonance for the two 2-butyne methyl groups and a virtual triplet for the phosphine ligands (which give a singlet in the ^{31}P NMR; Table 3). The carbyne carbon in the ^{13}C NMR appears at 321.2 ppm as a triplet (J_{PC} = 19 Hz), showing coupling to two phosphine ligands. The resonance for the two alkyne carbons at 167.7 ppm, however, is a doublet (J_{PC} = 15 Hz) because the phosphines are magnetically inequivalent and only one of the PC couplings is large.



(4)

R = R' = Me (**5**)
R = R' = Ph (**6**)
R = ^{t}Bu, R' = H (**8**)

Diphenylacetylene reacts with **1** over 12 h at 70 °C to form mainly the acetylene adduct $W(\equiv CMe)Cl(PhC\equiv CPh)(PMe_3)_2$ (**6**) (60%), but also a new complex **7** (35%) and a trace of unreacted **1** (5%) appear. Complex **6** is analogous to the 2-butyne carbyne complex **5**, as the alkyne displaces two phosphine ligands and its ^{1}H NMR spectrum (Table 3) shows a triplet for a pair of phosphines and a triplet (J_{PH} = 5.8 Hz) for the methyl group on the carbyne. Complex **6** slowly isomerizes (2 weeks at 24 °C) to give 100% conversion to **7** (63% isolated yield from **1**). NMR spectra identify **7** as an isomer of **6**, with a phenylcarbyne group and a 1-phenylpropyne ligand (Scheme 2). Thus, exchange of ≡CMe and ≡CPh groups has occurred. ^{13}C NMR spectra of **7** show a characteristic carbyne resonance (319.8 ppm) and two alkyne resonances (175.6, 174.6 ppm), due to the asymmetry of the alkyne ligand. This asymmetry

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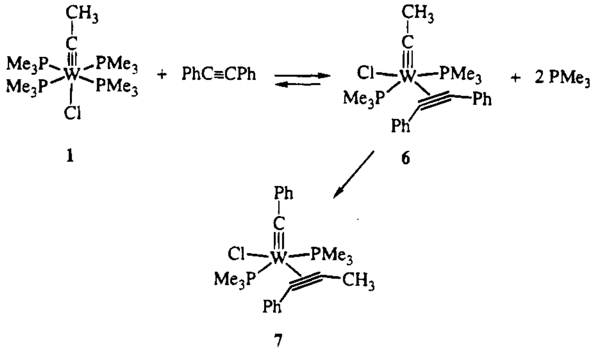
[15] Weiss, K.; Schubert, U.; Schrock, R. R. *Organometallics* **1986**, *5*, 397−398.

Table 3. Selected NMR Data (ppm; J in Hz) for Carbyne−Alkyne Complexes

compd	^{1}H NMR	^{31}P{^{1}H} NMR	^{13}C{^{1}H} NMR
$W(\equiv CMe)Cl(PMe_3)_2(MeC\equiv CMe)^a$ (**5**)	2.67 (t, $^4J_{PH} = 6$, W≡C*Me*) 2.52 (s, *Me*C≡C*Me*)	9.3 (s, $J_{WP} = 191$)	321.2 (t, $J_{PC} = 19$, W≡*C*Me) 167.7 (d, $J_{PC} = 15$, Me*C*≡*C*Me)
$W(\equiv CMe)Cl(PMe_3)_2(PhC\equiv CPh)^b$ (**6**)	2.91 (t, $^4J_{PH} = 6$, ≡C*Me*)	3.3 (s, $J_{WP} = 195$)	*c*
$W(\equiv CPh)Cl(PMe_3)_2(MeC\equiv CPh)^b$ (**7**)	2.57 (t, $^4J_{PH} = 1.3$, *Me*C≡CPh)	5.4 (d, $J_{PH} = 93$, $J_{WP} = 187$) 3.4 (d, $J_{PP} = 93$, $J_{WP} = 189$)	319.8 (t, $J_{PC} = 18$, W≡*C*Ph) 175.6 (dd, $J_{PC} = 7$, $J_{P'C} = 21$, MeC≡*C*Ph) 174.6 (m, Me*C*≡CPh)
$W(\equiv CMe)Cl(PMe_3)_2(HC\equiv C^tBu)^b$ (**8**)	9.42 (m, *H*C≡C^{t}Bu) 2.77 (t, $^4J_{PH} = 6$, ≡C*Me*) 1.38 (s, HC≡C^t*Bu*)	8.1 (d, $J_{PP} = 84$, $J_{WP} = 191$) −2.9 (d, $J_{PP} = 84$, $J_{WP} = 192$)	321.0 (t, $J_{PC} = 19$, W≡*C*Me) 158.3 (m, ^{t}Bu*C*≡CH) 155.5 (m, ^{t}BuC≡*C*H)
$W(\equiv C^tBu)Cl(PMe_3)_2(HC\equiv CMe)^b$ (**9**)	9.38 (m, *H*C≡CMe) 2.78 (s, HC≡C*Me*) 0.96 (s, ^{t}*Bu*C≡W)	3.7, 3.9^d ($J_{WP} = 191$)	331.6 (t, $J_{PC} = 15$, W≡*C*^{t}Bu) 173.1 (dd, $J_{PC} = 11$, $J_{P'C} = 17$, HC≡*C*Me) 155.4 (d of m, $J_{CH} = 186$, H*C*≡CMe)^e

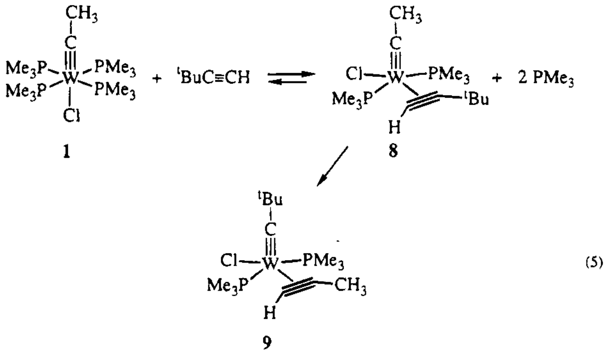
^{a} In THF-d_8. ^{b} In C_6D_6. ^{c} No ^{13}C NMR obtained due to low concentration of **6** in solution. ^{d} Two peaks of a second-order spectrum. ^{e} Proton coupled.

Scheme 2. Reaction of $W(\equiv CCH_3)Cl(PMe_3)_4$ (1) with Diphenylacetylene



also makes the phosphine ligands inequivalent in **7** (in contrast to **5** and **6**). The methyl group, which is now on the coordinated alkyne ($CH_3C\equiv CPh$), has a small coupling constant (J_{PH} = 1.3 Hz) compared to the coupling constant (J_{PH} = 5.8) of the methyl group on the carbyne in **6**.

Terminal acetylenes also displace PMe_3 ligands from **1** to give carbyne−alkyne complexes. A pale yellow benzene solution of **1** (0.05 M) reacts with 1 equiv of *tert*-butylacetylene to give a slightly darker yellow solution of $W(\equiv CMe)Cl(^tBuC\equiv CH)(PMe_3)_2$ (**8**) in 60% yield after 1 day at 24 °C ($K_{eq} \approx 5 \times 10^{-3}$ M at 24 °C). Isolation, however, is difficult since removal of the volatiles shifts the equilibrium back to starting material. Complex **8** is identified by its NMR spectra, which are quite similar to those of **7** since both have an unsymmetrical acetylene ligand (Table 3). The phosphine ligands and the acetylenic carbons are inequivalent. The acetylenic proton is shifted characteristically downfield to give a multiplet at 9.42 ppm in the ^{1}H NMR.[16]



If the reaction mixture is left at room temperature for 2 weeks, the solution darkens and complex **8** decays to give an ~80% yield of a new product (**9**) plus small amounts (15% by ^{31}P NMR) of the known *tert*-butylcarbyne complex $W(\equiv C^tBu)Cl(PMe_3)_4$[17] (5% of unreacted **8** is also present). The major product **9** is tentatively assigned as the metathesis product $W(\equiv C^tBu)Cl(HC\equiv CMe)(PMe_3)_2$ (eq 5), on the basis of its ^{1}H, ^{31}P, and ^{13}C NMR spectra (Table 3). As in the reaction of $PhC\equiv CPh$ (Scheme 2), there is exchange of the methylcarbyne ligand in **1** for one of the ends of the acetylene ligand, in this case the $\equiv C^tBu$ fragment. The phosphine ligands in **9** are inequivalent because of the asymmetry of the alkyne ligand, but they are quite close in chemical shift in the ^{1}H and ^{31}P NMR spectra (although not so close by ^{13}C NMR). The carbyne and alkyne resonances for **9** are similar to those for its isomeric precursor **8**, though shifted. Thus, the ^{t}Bu resonance is at δ 1.38 when part of the alkyne ligand in **8** but shifts to δ 0.96 in **9**, where it is attached to the carbyne carbon (compare 0.99 ppm for the ^{t}Bu group in $W(\equiv C^tBu)Cl(PMe_3)_4$[17]). The methyl group is a triplet when attached to the carbyne carbon but a singlet when part of the alkyne ligand. We have not observed free propyne in this reaction, but the indirect evidence strongly suggests that $\equiv$CMe and $\equiv C^tBu$ groups have exchanged in converting **8** to **9**. The reaction of **1** with 3-hexyne proceeds similarly, with slow formation of the known $W(\equiv CCH_2CH_3)Cl(PMe_3)_4$[8] as well as a mixture of carbyne−alkyne products. Again, products result from exchange of the carbyne group ($\equiv$CMe) with one end of the alkyne ($\equiv$CEt).

The NMR spectra of **5**−**9** define the orientation of most of the ligands in the carbyne−alkyne complexes, assuming that they all adopt the same basic structure. The phosphines are equivalent in complexes with symmetrical alkyne ligands but inequivalent for complexes of $RC\equiv CR'$. Thus, the phosphines must both lie *cis* to the carbyne ligand, which always appears as a triplet in the ^{13}C{^{1}H} NMR (J_{PC} = 15−20 Hz). The alkyne ligand must lie perpendicular to the M≡CR vector and must not be rapidly rotating at ambient temperatures, as this would equilibrate the phosphine ligands in $RC\equiv CR'$ complexes. The ^{1}H NMR resonances for the PMe_3 ligands in **7** and **8** do not coalesce at 70 °C, which indicates that the barriers to alkyne rotation are $\Delta G^{\ddagger} \geq 19$ and 17 kcal/mol for **7** and **8**, respectively. Two structures are consistent with these data: a pseudo-

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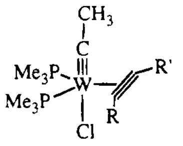
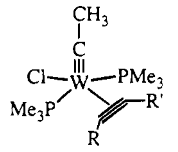
[16] Templeton, J. A. *Adv. Organomet. Chem.* **1989**, *29*, 1−100.

[17] Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322−6329.

trigonal-bipyramidal structure with the carbyne and chloride ligands in the *trans* axial positions (**A**), and a square pyramidal structure with an apical carbyne ligand and *trans* phosphine ligands (**B**). The two



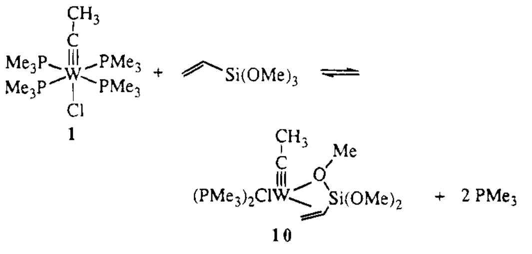
A



B

structures are quite similar and can be interconverted by moving the chloride from *trans* to the carbyne to roughly *trans* to the alkyne. The observed P–P coupling constants (93 Hz for **7**) appear to be consistent with either structure, as they are intermediate between *cis* and *trans* couplings in octahedral tungsten(IV) complexes: compare the 4 Hz *cis* coupling in $W(O)Cl_2(PMe_3)_3$[18] and the ca. 160 Hz *trans* couplings in $W(O)Cl_2(CH_2{=}CHR)(PMePh_2)_2$.[19]

Reactions with Vinylalkoxysilanes. $W(\equiv CMe)Cl(PMe_3)_4$ (**1**) is unreactive with simple alkenes. Heating with 5 equiv of propene or ethylene in benzene gives no apparent reaction after 1 week at 69 °C. Vinyltrimethylsilane, $CH_2{=}CHSiMe_3$, also does not bind to **1**, even when a large excess (40 equiv) of silane is present. Complex **1** does, however, react with vinylalkoxysilanes. Heating a 0.05 M THF solution of 1 with 1.2 equiv of vinyltrimethoxysilane at 69 °C forms the carbyne–alkene complex $W(\equiv CMe)Cl[CH_2{=}CHSi(OMe)_3](PMe_3)_2$ (**10**) in 95% yield by ^1H NMR (eq 6). The displacement

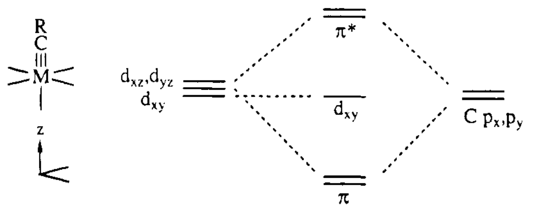


(6)

of 2 equiv of phosphine by the vinylsilane is an equilibrium process, with $K_{eq} \approx 2 \times 10^{-1}$ M at 69 °C; cooling the solution shifts the equilibrium back to the starting materials ($K_{eq} \approx 1 \times 10^{-3}$ M at 24 °C). This unfavorable equilibrium makes clean isolation of **10** difficult. The bromide analog $W(\equiv CMe)Br[CH_2{=}CHSi(OMe)_3](PMe_3)_2$ (**11**) is also accessible from reaction of $W(\equiv CMe)Br(PMe_3)_4$ with $CH_2{=}CHSi(OMe)_3$, although only in low yields ($K_{eq} \approx 2 \times 10^{-6}$ M at 69 °C, $K_{eq} \approx 2 \times 10^{-8}$ M at 24 °C). Only one alkoxy substituent is needed to observe binding, as $CH_2{=}CHSiMe_2(OEt)$ also reacts with **1** to give an equilibrium amount of the carbyne–alkene complex $W(\equiv CMe)Cl[CH_2{=}CHSi(OEt)Me_2](PMe_3)_2$ (**12**) ($K_{eq} \approx 6 \times 10^{-3}$ M at 80 °C). In contrast, excess allyltrimethoxysilane, $CH_2{=}CHCH_2Si(OMe)_3$, does not displace PMe_3 from **1** at 69 °C.

The carbyne–alkene complexes **10-12** were identified by NMR spectroscopy. The ^1H NMR spectra all show two inequivalent phosphine ligands (two doublets), a triplet for the methylcarbyne (coupled to the two phosphine ligands), and a set of resonances for one vinylsilane ligand. The vinylalkoxysilane ligands could bind solely through the vinyl group or as a chelating ligand. There is no direct evidence for coordination of an alkoxy group, as the three methoxy groups in **10** are equivalent by ^1H and ^{13}C NMR even at −40 °C. Still, we favor a chelated structure in which there is rapid exchange of bound and unbound OMe groups. The chelated structure provides a rationale for why one vinylsilane displaces two PMe_3 ligands and for why only alkoxy-substituted silanes bind to tungsten. Steric effects alone cannot explain the loss of two PMe_3 ligands on coordination of $CH_2{=}CHSi(OMe)_3$, since this ligand binds to the sterically very similar $WX_2(PMe_3)_4$ with loss of only one PMe_3 (X = Cl, Br).[8] Without alkoxide coordination, the metal center would be 16-electron, which seems unlikely. Possible structures for these complexes are discussed below.

Chart 1



Discussion

Carbyne–Alkyne, –Alkene, and –Carbonyl Complexes. $W(\equiv CMe)Cl(PMe_3)_4$ (**1**) exhibits unusual reactivity, binding alkenes and alkynes and coupling with 2 equiv of CO. In part this reactivity is due to the lability of the phosphine ligands due to steric crowding, as we have documented for the sterically similar $MX_2(PR_3)_4$ complexes.[8,20] Complexes **1** also appear to have a high affinity for π-acid ligands and engage in significant π-back-bonding. This is indicated by the stretching frequency in the carbonyl adduct **2**, 1891 cm^{-1}. The tungsten center is quite electron rich because the PMe_3 ligands are strongly σ donating and are poor π-acceptors.

The electronic structure of octahedral carbyne and alkylidyne complexes is well established, with the metal–carbon π bonds being formed from overlap of the carbon p_x,p_y orbitals with the metal d_{xz},d_{yz} components of the σ-nonbonding t_{2g} set (Chart 1, the M≡C bond is taken as the z axis).[21] These molecules can be viewed as Fischer carbynes, which implies that a CR^+ fragment stabilizes filled metal d_{xz},d_{yz} orbitals, while description as Schrock-type alkylidynes implies that a CR^{3-} ligand destabilizes empty metal d_{xz},d_{yz} orbitals. Chart 1 qualitatively applies to both cases, the key difference being the relative energy of the metal d_π and carbon p_π orbitals. In both cases, d_{xy} is the only nonbonding level, and it holds the two electrons in the d^2 compounds described here. Since this orbital lies *cis* to the metal–

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[18] Carmona, E.; Sanchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797.

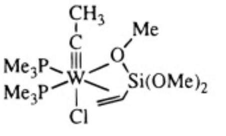
[19] Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261–1277.

[20] Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402–10411.

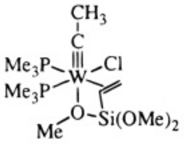
[21] (a) Reference 2, especially ref 2e, Chapter 3. (b) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley: New York, 1988; Chapter 2 and references therein. (c) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 489–496. (d) Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203–5208.

carbon triple bond, the π-acid ligands must lie *cis* to the multiple bond as well.[19,21] This is consistent with the spectroscopic data and the structure proposed for the carbonyl adduct **2**.

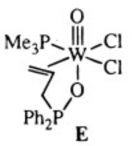
Single faced π-acceptor ligands such as alkenes and alkynes must lie perpendicular to the M≡C bond in order to overlap with d_{xy}, as observed in all carbyne–alkene complexes.[2] Identical arguments have been advanced to explain the orientation of alkene and alkyne ligands in d^2 oxo and imido complexes and related species.[19,21,22] Assuming this orientation, two structures are possible for the chelated vinylsiloxide complexes **10–12**: the coordinated ether oxygen can then be either *cis* or *trans* to the carbyne, as shown in **C** and **D**.



C



D



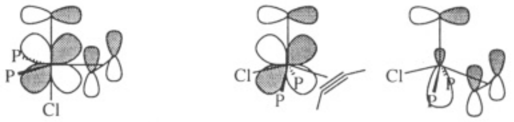
E

Structure **D** is similar to the structurally characterized bidentate coordination of an allylphosphine oxide ligand to a tungsten–oxo center (**E**),[23] although the chelate ring is one atom longer in this case. The allyl siloxide $CH_2{=}CHCH_2Si(OMe)_3$ would form a chelate ring similar to **E**; therefore its lack of binding is likely electronic in origin, the additional methylene reducing the inductive effect of the silicon.

The bonding in the carbyne–alkyne complexes is more complicated because of the presence of π-donation from the alkyne $\pi_\perp$. This creates a "π-conflict" because there are no nonbonding empty d_π orbitals to interact with the alkyne $\pi_\perp$. If the carbyne is viewed as CR^+, then the metal d_π orbitals are filled and the alkyne faces a filled–filled interaction. In the alkylidyne perspective, CR^{3-} and the alkyne compete for bonding with a single empty metal d orbital. π-Conflicts of this type have been discussed by Mayr, Templeton, and others and provide an elegant rationale for the coupling of two carbyne ligands at a metal center.[24] Mayr has also suggested that such π-conflicts should destabilize octahedral carbyne–alkyne complexes.[24a]

Alkynes react with **1** to displace *two* phosphine ligands; therefore, complexes **5–9** are five-coordinate, not octahedral, species. This is likely a result of the π-conflict. Steric effects cannot explain the lower coordination number, because alkynes replace only one PMe_3 on reaction with the sterically very similar $WCl_2(PMe_3)_4$, and the $WCl_2(RC{\equiv}CR)(PMe_3)_3$ products are quite stable.[25] **1** is an 18-electron complex; thus, either **5–9** are 16-electron or they utilize donation from the alkyne $\pi_\perp$ orbital. The ^{13}C NMR chemical shifts of the alkyne ligands, δ 150–180, are indicative of three-electron-donor alkynes,[16] indicating substantial $\pi_\perp$-donation. Similarly, the chemical shift of δ 9.4 for the acetylenic protons in **8** and **9** are indicative of three-electron-donor alkynes in bis(alkyne) complexes.[16] Thus, the alkyne adducts **5–9** have figured out how to form metal–carbon triple bonds and accept π-donation from the alkyne ligand, therefore approaching 18-electron species. It should be noted that the ^{13}C resonance for the carbyne carbon shifts far downfield from **1** (253 ppm) to ca. 320 ppm in **5–9**, indicating that the metal–carbon triple bond is perturbed by the presence of the alkyne.

The spectroscopic data for the carbyne–alkyne complexes, as noted above, indicate a C_s structure consistent with either trigonal-bipyramidal (tbp) or square-pyramidal (sp) structures (**A** and **B**). Bonding in a tbp geometry differs from the octahedral case primarily in the *xy* plane, with the $d_{x^2-y^2}$ orbital losing some σ^* character. However, $d_{x^2-y^2}$ is not of the right symmetry to accept electrons from the alkyne $\pi_\perp$. The tungsten d_{xz} orbital that is involved in the octahedral π-conflict is not very different in the tbp structure. **A1** shows the in-phase combination of the d_{xz}, the carbyne $p_{\pi,x}$, and the alkyne $\pi_\perp$ orbitals illustrating the π-conflict. Moving from octahedral to square-pyramidal (sp) coordination, however, creates a roughly nonbonding hybrid orbital trans to the carbyne (**B2**) that can overlap well with the alkyne $\pi_\perp$. In addition, the carbyne–tungsten–alkyne angle likely is larger than 90° in the sp structure, reducing the alkyne interaction with the d_{xz} (**B1**). These effects allow a partial separation of the carbyne and alkyne π bonding, minimizing the π-conflict. The alkyne $\pi_\perp$ donation proposed in **B2** is very similar to that observed in extended Hückel and *ab initio* calculations on pseudotetrahedral $Re(O)X(RC{\equiv}CR)$ compounds.[26] On the basis of these qualitative bonding arguments, we believe that the carbyne–alkyne adducts most likely adopt the square-pyramidal structure **B**.



A1
trigonal bipyramidal

B1 B2
square pyramidal

Carbyne Reactivity. Alkyne Metathesis Reactions. In 1975, Katz proposed that carbyne complexes are the catalytic species in alkyne metathesis, where coupling between the carbyne and acetylene occurs through metallacyclobutadiene derivatives.[27] The formation of a carbyne–alkyne intermediate is probably the first step in this mechanism (eq 7). The development of well-defined alkyne metathesis catalysts and extensive mechanistic work by Schrock have provided strong support for this general mechanism.[28] All of the

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(22) (a) Tungsten(IV)–oxo–alkynes: Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248–1253 and ref 19 (also for oxo–alkene complexes). (b) Rhenium(V)–oxo–alkynes: Hoffman, D. M.; Huffman, J. C.; Lappas, D.; Wiedra, D. A. *Organometallics* **1993**, *12*, 4312–4320 and references therein. (c) Tantalum(III)–imido–alkynes: Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860. (d) Tungsten(IV)–imido–alkynes and –alkenes: Nielson, A. J.; Ware, D. C. *Polyhedron* **1990**, *9*, 603–610. Clark, C. R.; Nielson, A. J.; Rickard, C. E. F.; Ware, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1173. (e) Tungsten–carbene–alkyne: Mayr, A.; Lee, K. S.; Kjelsberg, M. A.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 6079.

(23) Brock, S. L.; Mayer, J. M. *Inorg. Chem.* **1991**, *30*, 2138–2143.

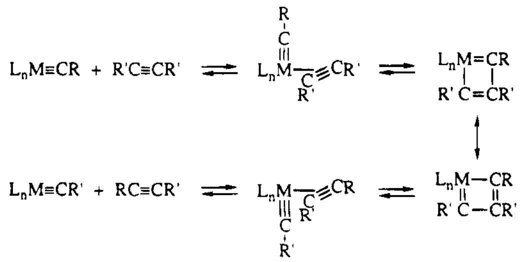
(24) (a) Mayr, A. *Comments Inorg. Chem.* **1990**, *10*, 227–266. (b) References 4, 16, 21d, and 22b.

(25) Clark, G. R.; Nielson, A. J.; Rae, A. D.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1992**, 1069. Nielson, A. J.; Boyd, P. D. W.; Clark, G. R.; Hunt, T. A.; Metson, J. B.; Rickard, C. E. F.; Schwerdtfeger, P. *Polyhedron* **1992**, *11*, 1419–1421. Barrera, J.; Sabat, M.; Harman, W. D. *Organometallics* **1993**, *12*, 4381–4390.

(26) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454–7462. Cundari, T. R.; Conry, R. R.; Spaltenstein, E.; Critchlow, S. C.; Hall, K. A.; Tahmassebi, S. K.; Mayer, J. M. *Organometallics* **1994**, *13*, 322–331.

(27) Katz, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 1592.

(28) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342–348. See also ref 2e, pp 174–178, and 220–224.



(7)

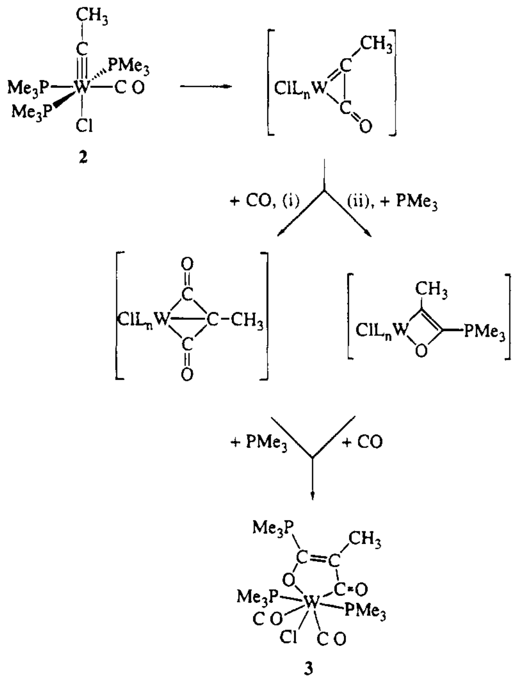
Schrock catalysts, to our knowledge, are d^0 species (counting as CR^{3-}). The reactions reported here are the first examples of metathesis-type reactivity for Fisher carbynes, which are d^2 species when counted as CR^{3-}. It must be emphasized, however, that our reactions are very slow and not catalytic—these are very poor alkyne metathesis reagents.

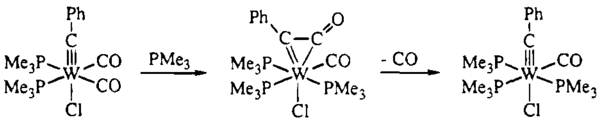
The substantial barrier to alkyne metathesis can be traced to the presence of the two nonbonding electrons (Chart 1). The pair of electrons provide a back-bonding interaction that stabilizes alkyne complexes—this is likely one of the reasons they are observable—but the stabilization makes it more difficult to form the metallacyclobutadiene intermediate. The back-bonding requires that the alkyne be oriented perpendicular to the carbyne, and there appears to be a significant rotational barrier (≥17 kcal/mol) to align the alkyne with the carbyne, as is required for ring closure. This suggests that Fisher carbyne complexes will in general not be active metathesis reagents.

The carbyne–alkyne complexes **6**–**9** all provide evidence of metathesis reactivity. (Metathesis in the 2-butyne complex **5** may be occurring, but it is a degenerate reaction.) The conversion of $W(\equiv CMe)Cl(PhC\equiv CPh)(PMe_3)_2$ (**6**) to the phenylcarbyne–1-phenylpropyne isomer $W(\equiv CPh)Cl(MeC\equiv CPh)(PMe_3)_2$ (**7**) is the only example of a clean rearrangement to a single product (Scheme 2). This is likely due to enhanced thermodynamic stability of the phenylcarbyne ligand in **7**, consistent with molecular orbital calculations showing aryl stabilization of the metal–carbon triple bond.[29] In addition, aryl alkyne ligands appear to bind more strongly to tungsten, because of their higher π-acidity, so that there is less loss of alkyne from the rearranged product. In the case of the terminal acetylene $^tBuC\equiv CH$, $W(\equiv CMe)Cl(^tBuC\equiv CH)(PMe_3)_2$ (**8**) is formed at room temperature and slowly isomerizes to give products including the metathesis products $W(\equiv C^tBu)Cl(HC\equiv CMe)(PMe_3)_2$ (**9**) and $W(\equiv C^tBu)Cl(PMe_3)_4$[17] (eq 5). In this case no particular product appears to be favored, and a detailed understanding is complicated by free propyne not being observed in the NMR of the reaction mixture. Metatheses of terminal acetylenes by Schrock carbynes are also not very clean reactions, due to deprotonation of intermediate metallacyclobutadienes, polymerization, and other side reactions.[30] However, no polymerization or deprotonated metallacyclobutadienes were observed in the reactions of **1** with acetylenes.

Double Carbonylation of the Carbyne Ligand. The coupling of two molecules of CO with a carbyne ligand—$W(\equiv CMe)Cl(PMe_3)_4$ (**1**) + 2CO → $\overline{W[OC(PMe_3)=CMeC(O)]}Cl(CO)_2(PMe_3)_2$ (**3**) (Scheme 1)—has not, to our knowledge, previously been observed.[2,3] The reaction pathway leading to **3** has not been established but likely occurs by initial CO substitution, converting **1** to **2**, followed by coupling to give an η^1- or η^2-ketenyl complex (Scheme 3).[31] Formation of a ketenyl ligand by coupling of a carbyne ligand with a coordinated CO is well precedented[2-4,32] and a ketenyl complex is observed on dissolving the closely related phenylcarbyne complex *cis*-$W(\equiv CPh)X(CO)_2(PMe_3)_2$ in neat PMe_3 (eq 8).[32] Under these reaction conditions—CH_2Cl_2 or PMe_3 solvent and no excess carbon monoxide—loss of CO occurs to give the substituted product analogous to **2** (eq 8).[32]

Scheme 3. Possible Reaction Pathways for the Formation of 3





(8)

We also observe primarily formation of a carbyne–carbonyl product on reaction of **1** with CO in CH_2Cl_2 solvent, but in THF the ketenyl proceeds on to the insoluble metallacycle complex **3**. The insolubility likely provides one driving force for the formation of of **3**, and excess CO is clearly required. The ketenyl intermediate could proceed to **3** in two ways: insertion of a second CO followed by phosphine attack at the electrophilic ketene carbon (Scheme 3, path i), or initial phosphine attack at the ketenyl ligand to give an enolate ligand, followed by CO insertion (path ii). The lack of reaction of the phenylketenyl group in eq 8 with neat PMe_3

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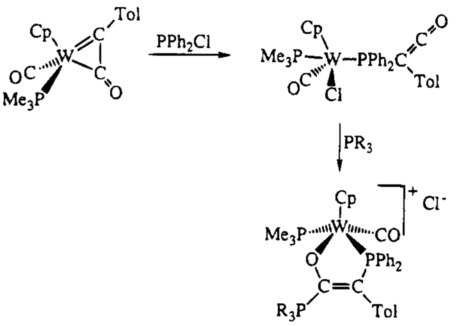
[29] Ushio, J.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5892–5901 and ref 21c.

[30] Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554 and ref 28.

[31] A reviewer suggested the η^1-ketenyl form, which adds PMe_3 to give $L_nClW{-}C(Me){=}C({-}O){-}PMe_3$, also η^1. We favor the η^2 forms, on the basis of the very similar Mayr η^2-ketenyl complex[32] and the electron deficiency of the tungsten center.

[32] Mayr, A.; Lee, T.-Y.; Kjelsberg, M. A.; Lee, K. S. *Organometallics* **1994**, *13*, 2512–2515 and references therein.

suggests the former route, trapping of the ketenyl ligand by added CO (path i). A related enolate metallacycle has been formed from an η^2-ketenyl ligand by initial insertion of PPh_2^+ followed by phosphine attack at the ketene carbon (eq 9; R′ = Me, Et, *i*-Pr, *n*-Bu).[33] Phosphine attack at a coordinated vinylidene has also been observed.[34]



(9)

Experimental Section

Reactions were performed under nitrogen using standard vacuum line techniques. Compounds were handled and stored in a continuous nitrogen flow glovebox. Solvents were dried using standard techniques.[35] CO (Matheson) and ^{13}CO (99.9%, Cambridge) were used without further purification. Silyl reagents (Petrarch) and alkynes (Aldrich) were dried over sodium and distilled before use, except diphenylacetylene, which was sublimed before use. $W(\equiv CMe)Cl(PMe_3)_4$ (**1**) and $W(\equiv CMe)Br(PMe_3)_4$ were prepared as previously described.[8] NMR spectra were recorded on a Varian VXR-300 using C_6D_6 as solvent unless noted otherwise; ^{13}C NMR were taken at 75.4 MHz; ^{31}P NMR were taken at 121.4 MHz. ^1H NMR are reported as δ (multiplicity, *J*, number of H's, assignment). ^1H and ^{13}C chemical shifts are reported in ppm referenced to solvent peaks or tetramethylsilane; ^{31}P spectra are externally referenced to 85% H_3PO_4. Coupling constants are reported in Hz. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, BC, Canada.

Reactions which were not done on a preparative scale were performed in NMR tubes. An NMR tube sealed to a ground-glass joint is charged with reagents and solvent in the drybox and then capped with a Teflon valve. The tube is frozen at −196 °C and evacuated on the vacuum line; any other reagents are vacuum-transferred into the tube, and the tube is sealed with a torch.

$W[OC(PMe_3){=}CMeC(O)]Cl(CO)_2(PMe_3)_2$ (3). A 200 mL-thick walled glass bomb sealed with a teflon stopcock was charged with **1** (220 mg, 4.0×10^{-4} mol), THF (7 mL), and ~1 atm of CO. Heating at 65 °C overnight caused the pale yellow solution to turn golden, with formation of a yellow-orange precipitate. In a frit apparatus, the reaction mixture was cooled at −76 °C for 1 h. Filtration and drying *in vacuo* gave 0.176 g (68%) of yellow-orange solids of **3**. Selected ^1H and ^{13}C NMR data: see Table 1. ^1H NMR (CD_2Cl_2, 25 °C): 2.04 (d, $^2J_{PH} = 14$, 9H, $\text{-}C[P(CH_3)_3]{=}$), 1.80 (d, $^4J_{PH} = 3$, 3H, $=C(CH_3)-$), 1.3 (broad s, 18H, 2 $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 14.3 (s, $=C(PMe_3)$), −7.5 (broad lumps, 2 PMe_3). $^{31}P\{^1H\}$ (CD_2Cl_2, −40 ° C): −3.3 (d, $J_{PP} = 154$, $J_{WP} = 220$, $W-PMe_3$), −8.8 (d, $J_{PP} = 154$, $J_{WP} = 195$, $W\text{-}PMe_3'$), 16.3 (s, $\text{-}C(PMe_3){=}$); $^{13}C\{^1H\}$ NMR (THF-d_8, −50 °C) 14.2 (d, $J_{PC} = 27$, $WP(CH_3)_3$), 13.6 (d, $J_{PC} = 29$, $WP(CH_3)_3$), 9.3 (d, $J_{PC} = 53$, $-C[P(CH_3)_3]{=}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −50 °C): 135.1 (d, $J_{PC} = 37$, $=C(CH_3)-$), 9.2 (s, $=C(CH_3)-$). Anal. Calcd for $WClP_3O_4C_{15}H_{30}\cdot 0.7C_4H_8O$: C, 34.09; H, 5.72; O, 12.00. Found: C, 33.78; H, 5.56; O, 12.41.

Reaction of CO and ^{13}CO with $W(\equiv CMe)Cl(PMe_3)_4$ (1). An NMR tube was loaded with 15 mg of **1**, 0.5 mL of THF-d_8, and ca. 200 Torr of CO and sealed with a torch. The pale yellow solution was heated for 18 h at 79 °C to give a gold-yellow solution. ^1H NMR showed the formation of 20% $W(\equiv CMe)Cl(CO)(PMe_3)_3$ (**2**) + unreacted **1**. The tube was broken open in the drybox, and the volatiles were removed from the reaction mixture. A similar reaction mixture with ~0.5 atm of ^{13}CO was heated for 4.5 h at 79 °C, at which point an ^1H NMR spectrum showed formation of $W(\equiv CMe)(^{13}CO)Cl(PMe_3)_3$; the metallacycle product **3** grew in at ambient temperatures over a few days. Selected $^{13}C\{^1H\}$ and ^1H NMR for **2**: see Table 1. IR (C_6D_6) for **2**: ν_{CO} 1891 cm^{-1}, $\nu_{^{13}CO}$ = 1852 cm^{-1} (calcd 1849 cm^{-1}). For $W(\equiv CMe)(^{13}CO)Cl(PMe_3)_3$ (**2**-^{13}CO; THF-d_8): $^{31}P\{^1H\}$ NMR −20.2 (dd, $^2J_{PP} = 21$, $^2J_{CP} = 7$, $J_{WP} = 275$, 2 *trans* PMe_3), −25.8 (dt, $^2J_{PP} = 21$, $^2J_{CP} = 45$, $J_{WP} = 217$, 1 *cis* PMe_3). $^{13}C\{^1H\}$ NMR 226.8 (dt, $^2J_{PC} = 45$, $^2J_{PC} = 7$, $J_{WC} = 150$, W-CO), 211.2 (t, $^2J_{PC} = 7$, $\equiv CCH_3$), 21.0 (t, $J_{PC} = 13$, 2 *trans* $P(CH_3)_3$), 20.8 (s, $\equiv CCH_3$), 20.6 (d, $J_{PC} = 17$, 1 *cis* $P(CH_3)_3$). For $W[O^{13}C(PMe_3){=}CMe^{13}C(O)]Cl(CO)_2(PMe_3)_2$ (**3**-$^{13}C_2$): $^{13}C\{^1H\}$ NMR (−40 °C, THF-d_8) 254.5, 252.1 (m, $W(CO)_2$), 235.6 (broad s, $J_{WC} = 136$, $W\text{-}C(O)-$), 178.7 (dd, $^1J_{PC} = 88$, $^2J_{CC} = 6$, $W\text{-}O\text{-}C(PMe_3){=}$); IR ($C_6D_6$, cm^{-1}, calculated values in parentheses): 1855 (1858), 1768 (1769) $\nu_{13C=O}$; 1478 (1474) $\nu_{-(13C=O)-}$.

Reaction of 1 with *p*-Tolyl Isocyanate. A 200 mL glass bomb was loaded with **1** (250 mg, 0.45 mmol), THF (10 mL), and *p*-tolyl isocyanate (0.19 mL, 1.5 mmol). Stirring at 24 °C for 3 days gave a dark brown solution. Removal of the volatiles and recrystallization from THF/pentane at −76 °C gave 0.170 g of cocoa brown solids of $W(\equiv CCH_3)Cl[(NTol)_2C{=}O](PMe_3)_2$ (**4**) (yield 60%). ^1H NMR (C_6D_6): 8.15, 7.15 (2 broad singlets, 4H each, 2 C_6H_4Me), 3.92 (t, $^4J_{PH} = 4$, 3H, $\equiv CCH_3$), 2.20 (s, 6H, 2 $C_6H_4CH_3$), 1.06 (t, $^2J_{PH} = 4$, 18H, 2 $P[CH_3]_3$). $^{31}P\{^1H\}$ NMR (THF-d_8): 1.6 (s, $J_{WP} = 283$). $^{13}C\{^1H\}$ NMR (C_6D_6): 14.2 (t, 13, $P(CH_3)_3$), 20.9 (s, 2 $C_6H_4CH_3$), 32.6 (s, $\equiv CCH_3$), 297.8 (t, $^2J_{PC} = 18$, $\equiv CMe$); ^{13}C: 123.4 (m, 4 ortho or meta CH), 128.5 (m, 4 ortho or meta CH), 128.8 (s, 2C, para carbons), 147.5 (s, 2 ipso carbon), 159.6 [s, $(NTol)_2C{=}O)$]. IR (C_6D_6, cm^{-1}): 1668, 1508, 952 (st), 1332, 1328, 928 (w).

Reaction of 1 with 2-Butyne. A pale yellow solution of **1** (12 mg, 2.2×10^{-5} mol) and 1.2 equiv of $MeC\equiv CMe$ (19 Torr in 25.7 mL) in 0.5 mL of THF-d_8 was refluxed in a sealed NMR tube for 3 h at 80 °C. The solution became bright yellow and contained 80% $W(\equiv CMe)Cl(MeC\equiv CMe)(PMe_3)_2$ (**5**) ($K_{eq} \approx 0.2$ M at 80 °C) by ^1H NMR. ^1H NMR (THF-d_8): 2.67 (t, $^4J_{PH} = 6$, 3H, $W\equiv CCH_3$), 2.52 (s, 6H, $CH_3C\equiv CCH_3$), 1.65 (t, 4, 18H, 2 $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (THF-d_8): 9.3 (s, $J_{WP} = 191$). $^{13}C\{^1H\}$ NMR (THF-d_8): 321.2 (t, $^2J_{PC} = 19$, $W\equiv CCH_3$), 167.7 (d, $^2J_{PC} = 15$, $CH_3C\equiv CCH_3$), 37.1 (s, $W\equiv CCH_3$), 17.8 (s, $CH_3C\equiv CCH_3$), 16.6 (d, 11, $P(CH_3)_3$), 16.8 (d, 11, $P(CH_3)_3$).

Preparation of $W(\equiv CPh)Cl(MeC\equiv CPh)(PMe_3)_2$ (7). A 200 mL thick-walled glass bomb was loaded with **1** (220 mg, 4.0×10^{-4} mol), $PhC\equiv CPh$ (150 mg, 1.2 equiv), and 25 mL of toluene, and the solution was refluxed at 65 °C for 2 weeks. $W(\equiv CMe)Cl(PhC\equiv CPh)(PMe_3)_2$ (**6**) was observed by ^1H and $^{31}P\{^1H\}$ NMR but was not concentrated enough to observe in a $^{13}C\{^1H\}$ NMR spectrum. The reaction proceeds slowly for 2 weeks more at room temperature. The volatiles were removed to give a brown oil, which was redissolved in Et_2O, cooled at 0 °C for 1 h, and filtered to give 130 mg of dark yellow **7** (63% yield). For **6**: ^1H NMR 6.9 (m, 4H, phenyl resonances), 7.0

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Table 4. Crystal Data for W[OC(PMe$_3$)=CMeC(O)]Cl(CO)$_2$(PMe$_3$)$_2$·C$_4$H$_8$O (3)

formula	WClP$_3$O$_5$C$_{19}$H$_{38}$
fw	658.74
cryst size	0.12 × 0.30 × 0.72 mm
unit cell[a]	monoclinic
a	14.945(3) Å
b	9.259(3) Å
c	20.226(3) Å
β	102.27(1)°
V	2734.8(20) Å^3
Z	4
ϱ(calc)	1.600 g/cm^3
space group	$P2_1/c$ (No. 14)
systematic extinctions	$0k0$, $k = 2n$; $h00$, $l = 2n$
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (0.710 73 Å)
monochromator	graphite
temp	24 °C
scan mode	$\theta - 2\theta$
scan range	$\Delta\theta = 0.80° + 0.347 \tan\theta$
scan rate	4.1°/min
max 2θ	50°
octants collected	$h, \pm k, l$
decay[b]	7.4%
abs coeff,[c] μ	46.1 cm^{-1}
transmissn factors	0.9999–0.6850 (av = 0.8571)
no. of rflns measd	5331
no. of rflns after averaging	5125
no. of unique obs rflns ($I > 3\sigma(I)$)	3356
no. of params refined	262
R[d]	0.035
R_w	0.040
goodness of fit	1.133
residual electron density	±0.8 e/Å^3

[a] Calculated from a least-squares fit of the setting angles of 24 reflections from all octants with 25° < 2θ < 35° tuned on Friedel-related pairs (±2θ). [b] Based on three standard reflections with 2$\theta \approx$ 24° measured every 500 reflections. Linear decay correction was applied. [c] Empirical absorption correction was applied. [d] $R = \sum||F_o| - |F_c||$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = [\sigma^2_{count} + (0.05F^2)^2]/4F^2$. Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination*; Wiley: New York, 1989; Chapter 9, p 229, and Chapter 17, p 388.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2) for W[OC(PMe$_3$)=CMeC(O)]Cl(CO)$_2$(PMe$_3$)$_2$·C$_4$H$_8$O (3)

atom	x	y	z	B(eq)[a]
W	2786.5(2)	1539.1(3)	964.2(1)	3.138(5)
Cl	1422.0(14)	506(3)	1372.7(11)	5.64(5)
P(1)	3353.4(14)	−2802(2)	31.4(10)	3.86(5)
P(2)	3550(2)	504(3)	2083.0(9)	4.24(5)
P(3)	1519.7(14)	1975(2)	−67.3(10)	4.02(5)
O(1)	3699(4)	2771(6)	−190(2)	4.5(1)
O(2)	2949(3)	−670(5)	694(2)	3.4(1)
O(3)	4566(4)	3338(6)	1319(3)	5.7(1)
O(4)	2246(6)	4529(7)	1451(3)	9.2(2)
O(5)	1610(6)	−2130(10)	−1685(4)	9.8(2)
C(1)	3452(5)	1674(8)	95(3)	3.3(1)
C(2)	3575(4)	234(8)	−193(3)	3.2(2)
C(3)	3293(5)	−857(7)	154(3)	3.0(1)
C(4)	3992(5)	109(9)	−805(4)	4.5(2)
C(5)	3891(5)	2649(8)	1162(4)	4.0(2)
C(6)	2450(6)	3442(9)	1264(4)	5.3(2)
C(7)	2280(6)	−3491(10)	143(5)	6.5(2)
C(8)	4253(8)	−3499(10)	689(5)	7.2(3)
C(9)	3544(8)	−3444(10)	−757(5)	6.9(3)
C(10)	4791(7)	359(13)	2253(5)	7.9(3)
C(11)	3248(7)	−1319(9)	2266(4)	6.1(2)
C(12)	3345(9)	1514(12)	2796(4)	8.6(3)
C(13)	1692(6)	2859(10)	−837(4)	5.6(2)
C(14)	1018(6)	266(10)	−415(4)	5.2(2)
C(15)	549(6)	2956(11)	112(5)	7.0(3)
C(16)	1547(9)	−1056(13)	−2173(6)	9.6(4)
C(17)	814(10)	−1524(15)	−2766(7)	11.8(5)
C(18)	279(9)	−2540(20)	−2484(7)	11.9(5)
C(19)	835(10)	−2990(20)	−1849(6)	12.4(5)

[a] Anisotropically refined atoms given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

(m, 6H, phenyl resonances), 2.91 (t, $^4J_{PH}$ = 6, 3H, $\equiv$CCH_3), 1.40 (t, 5, 18H, 2 P(CH_3)$_3$); ^{31}P{^{1}H} NMR 3.3 (s, J_{WP} = 195). For **7**: ^{1}H NMR 7.0–7.4 (m, 10H, phenyl resonances), 2.57 (t, $^4J_{PH}$ = 1.3, 3H, CH_3C$\equiv$CPh), 1.52 (d, 8.5, 9H, P(CH_3)$_3$), 1.39 (d, 8.5, 9H, P(CH_3)$_3$); ^{31}P{^{1}H} NMR 5.4 (d, J_{PP} = 93, J_{WP} = 187), 3.4 (d, J_{PP} = 93, J_{WP} = 189); ^{13}C{^{1}H} NMR 319.8 (t, $^2J_{PC}$ = 18, W$\equiv$$C$Ph), 16.8 (d, J_{PC} = 20, P(CH$_3$)$_3$), 16.4 (d, J_{PC} = 20, P(CH$_3$)$_3$); ^{13}C NMR (proton coupled) 175.6 (dd, $^2J_{PC}$ = 7, $^2J_{PC}$ = 21, MeC$\equiv$$C$Ph), 174.6 (m, Me$C$$\equiv$CPh), 150.7 (s, ipso-carbon of Ph), 148.7 (s, ipso-carbon of Ph), 18.7 (q, J_{CH} = 134, CH$_3$C$\equiv$CPh). Anal. Calcd WClP$_2$C$_{22}$H$_{31}$: C, 45.81; H, 5.42. Found: C 45.51, H, 5.27.

Reaction of 1 with *tert*-Butylacetylene. A pale yellow solution of **1** (12 mg, 2.2 × 10^{-5} mol) and 1.2 equiv of ^{t}BuC$\equiv$CH (19 Torr in a 25.7 mL bulb) in 0.5 mL of C$_6$D$_6$ were sealed in an NMR tube to give a pale green solution of W($\equiv$CMe)Cl(^{t}BuC$\equiv$CH)(PMe$_3$)$_2$ (**8**) in 60% yield after 1 day at 24 °C ($K_{eq} \approx 5 \times 10^{-3}$ M at 24 °C). Further heating resulted in decomposition (loss of signal in the ^{1}H and ^{31}P NMR); an ^{1}H NMR spectrum of the volatiles from the reaction mixture showed only ^{t}BuC$\equiv$CH and PMe$_3$. Reaction of **1** and ^{t}BuC$\equiv$CH at ambient temperatures for 2 weeks gave, by ^{31}P{^{1}H} NMR, 80% W($\equiv$C^{t}Bu)Cl(HC$\equiv$CMe)(PMe$_3$)$_2$ (**9**), 5% **1**, and 15% W[$\equiv$C-^{t}Bu]Cl(PMe$_3$)$_4$. The last product was identified by comparison of its ^{1}H, ^{13}C, and ^{31}P NMR spectra to the values reported in the literature.[17] For **8**: ^{1}H NMR 9.42 (m, 1H, HC$\equiv$C^{t}Bu), 2.77 (t, $^4J_{PH}$ = 6, 3H, $\equiv$CCH_3), 1.64 (d, 8, 9H, P(CH_3)$_3$), 1.44 (d, 8, 9H, P(CH_3)$_3$), 1.38 (s, 9H, HC$\equiv$CC(CH_3)$_3$). ^{31}P{^{1}H} NMR 8.1 (d, J_{PP} = 84, J_{WP} = 191), −2.9 (d, J_{PP} = 84, J_{WP} = 192); ^{13}C{^{1}H} NMR 321.0 (t, $^2J_{PC}$ = 19, W$\equiv$$CCH_3$), 158.3 (m, ^{t}Bu$C$$\equiv$CH), 155.5 (m, ^{t}BuC$\equiv$$C$H), 37.1 (s, W$\equiv$C$CH_3$), 32.5 (s, HC$\equiv$C$CMe_3$), 27.2 (s, HC$\equiv$CC($CH_3$)$_3$), 18.8 (d, 27, P($CH_3$)$_3$), 16.2 (d, 28, P($CH_3$)$_3$). For **9**: ^{1}H NMR 9.38 (m, 1H, HC$\equiv$CCH$_3$), 2.78 (s, 3H, HC$\equiv$CCH_3), 1.53 (m, 18H, 2 P(CH_3)$_3$), 0.96 (s, 9H, W$\equiv$CC(CH_3)$_3$); ^{31}P{^{1}H} NMR 3.7, 3.9 (2 peaks of a second-order spectrum, J_{WP} = 191); ^{13}C{^{1}H} NMR 331.6 (t, $^2J_{PC}$ = 15, W$\equiv$$C^t$Bu), 173.1 (dd, $^2J_{PC}$ = 11, $^2J_{P'C}$ = 17, HC$\equiv$$CCH_3$), 16.9 (dd, $J_{P'C}$ = 9, J_{PC} = 19, P(CH$_3$)$_3$), 17.6 (dd, J_{PC} = 8, $J_{P'C}$ = 19, P'(CH$_3$)$_3$); ^{13}C (proton coupled) 155.4 (d of m, J_{CH} = 186, MeC$\equiv$$C$H), 51.7 (s, W$\equiv$C$CMe_3$), 32.1 (quartet, J_{CH} = 125, W$\equiv$CC(CH$_3$)$_3$), 20.9 (quartet, J_{CH} = 126, CH$_3$C$\equiv$CH).

Reaction of 1 with 3-Hexyne. A pale yellow solution of **1** (12 mg, 2.2 × 10^{-5} mol) and CH$_3$CH$_2$C$\equiv$CCH$_2$CH$_3$ (48 Torr in 25.7 mL) reacted in 0.5 mL of C$_6$D$_6$ for 2 weeks at 24 °C in a sealed NMR tube. ^{31}P NMR spectra of the yellow solution showed 10% **1**, 35% W($\equiv$CCH$_2$CH$_3$)Cl(PMe$_3$)$_4$,[8] and 55% carbyne–alkyne products (peaks at 5 ppm). The ^{1}H NMR spectra were complex with overlapping peaks, so that the carbyne–alkyne products could not be assigned, although a methylcarbyne–alkyne product is suggested by a triplet at 2.82 ppm (J_{PH} = 6 Hz) in the ^{1}H NMR (compare Table 3).

W($\equiv$CMe)Cl[CH$_2$=CHSi(OMe)$_3$](PMe$_3$)$_2$ (10). A solution of **1** (12 mg, 2.2 × 10^{-5} mol), vinyltrimethoxysilane (10 μL, 6.6 × 10^{-5} mol), and THF-d_8 (0.5 mL) were refluxed at 80 °C in a sealed NMR tube overnight. NMR spectra showed formation of pale yellow-green **10** in 95% yield. NMR (THF-d_8) for **10**: ^{1}H 3.36 (s, 9H, Si(OMe)$_3$), 1.99 (t, $^4J_{PH}$ = 6, 3H, $\equiv$CCH_3), 1.58 (d, 8, 9H, PMe_3), 1.52 (d, 8, 9H, PMe_3), 0.62, 0.84, 1.25 (3 m, 1H each, C$H_a$$H_b$=C$H_c$Si(OMe)$_3$); ^{31}P{^{1}H}: 4.4 (d, J_{PP} = 120, J_{WP} = 236), −7.2 (d, J_{PP} = 120, J_{WP} = 212); ^{13}C{^{1}H} NMR 277.0 (t, $^2J_{PC}$ = 19, W$\equiv$$C$Me), 50.8 (s, Si(O$CH_3$)$_3$), 27.8 (d, $^3J_{PC}$ = 11, W$\equiv$CCH$_3$), 18.4, 13.1 (2 m, CH$_2$=CHSi), 16.2, 15.3 (2 d, J_{PC} = 27, 2 P[CH$_3$]$_3$).

W($\equiv$CMe)Br[CH$_2$=CHSi(OMe)$_3$](PMe$_3$)$_2$ (11) was observed on reaction of WBr$_2$(PMe$_3$)$_4$ (14 mg, 2.2 × 10^{-5} mol) with excess vinyltrimethoxysilane (50 μL, 3.3 × 10^{-4} mol) in C$_6$D$_6$ at 69 °C overnight. W($\equiv$CMe)Br(PMe$_3$)$_4$ formed initially and then reacted further with vinyltrimethoxysilane to give **11**.

The spectral data were obtained from these *in situ* reactions. ^{1}H NMR (C$_6$D$_6$): 3.31 (s, 9H, CH$_2$=CHSi(O*Me*)$_3$), 2.00 (t, $^4J_{PH}$ = 6, 3H, ≡CC*H*$_3$), 1.70 (d, 8, 9H, P*Me*$_3$), 1.49 (d, 8, 9H, P*Me*$_3$). ^{31}P{^{1}H} NMR: −0.9 (d, J_{PP} = 110, J_{WP} = 232), −11.9 (d, J_{PP} = 110, J_{WP} = 209). The small equilibrium constant for formation of **11** precluded obtaining ^{13}C NMR spectra and prevented resolution of the vinyl resonances in the ^{1}H NMR.

W(≡CMe)Cl[CH$_2$=CHSi(OEt)Me$_2$](PMe$_3$)$_2$ (12). A solution of **1** (12 mg, 2.2 × 10^{-5} mol), CH$_2$=CHSi(OEt)Me$_2$ (6 μL, 3.7 × 10^{-5} mol), and THF-*d*$_8$ (0.5 mL) were refluxed at 80 °C in a sealed NMR tube overnight. NMR spectra showed 60% conversion to pale yellow-green **12** (K_{eq} ≈ 6 × 10^{-3} M at 80 °C, measured at 24 °C). NMR (THF-*d*$_8$) for **12**: ^{1}H 3.25 (m, 2H, Si[OC*HH'*CH$_3$]), 2.01 (t, $^4J_{PH}$ = 6, 3H, ≡CC*H*$_3$), 1.64, (d, 8, 9H, P*Me*$_3$), 1.55 (d, 8, 9H, P*Me*$_3$), 0.86 (t, 6, 3H, Si(OCH$_2$C*H*$_3$)), 0.24 (s, 3H, SiMe'*Me*), the other SiMe' resonance is presumably hidden under the free ligand peaks; ^{31}P{^{1}H} 4.3 (d, J_{PP} = 121), −8.5 (d, J_{PP} = 121).

X-ray Structure of W[OC(PMe$_3$)=CMeC(O)]Cl(CO)$_2$(PMe$_3$)$_2$ (3). Yellow-orange crystals of **3** were grown by slow evaporation of solvent from a THF solution. The crystals were mounted in capillary tubes in the drybox and sealed under an atmosphere of nitrogen. The crystal data collection and solution were performed as previously described[36] (Table 4). The structure was solved using the SHELX direct methods structure package and refined with full-matrix least squares. All non-hydrogen atoms were refined anisotropically. All isotropic hydrogen atoms were placed in calculated positions (C−H = 0.95 Å) and confirmed by a difference map. The atomic coordinates and equivalent thermal parameters are listed in Table 5.

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Supplementary Material Available: A figure giving additional atom labeling and tables of positional parameters for H atoms, anisotropic thermal parameters, bond distances and angles, torsion angles, and least-squares planes for **3** (7 pages). Ordering information is given on any current masthead page.

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[36] Erickson, T. K. G.; Bryan, J. C.; Mayer, J. M. *Organometallics* **1988**, *7*, 1930.