Carbon Suboxide as a C_1 Reagent. Sequential Cleavage of CO from C_3O_2 at a Metal Center To Give $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$ and $WCl_2(CO)(PMePh_2)_2(\equiv CPMePh_2)$

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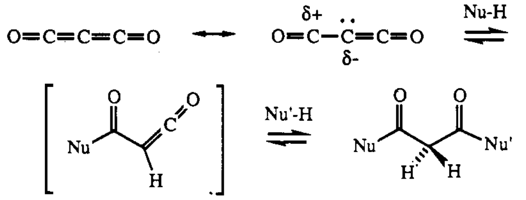
Received February 2, 1989

Carbon suboxide (O=C=C=C=O) reacts with toluene solutions of $WCl_2(PMePh_2)_4$ (1) in a 1:1 stoichiometry to afford $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$ (2) in high yield. The reaction is formally analogous to the reported reactions of 1 with other heterocumulenes (O=C=O, RN=C=O, and RN=C=NR) except that in the cases of these latter three reagents, tungsten oxo or imido complexes are formed whereas in the case of C_3O_2, a C—C rather than a C—O or C—N bond is cleaved; the probable resulting ketenylidene intermediate is apparently trapped by $PMePh_2$ to give the novel (diphenylmethylphosphoranylidene)ketene derivative. 2 crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 11.400$ (4) Å, $b = 16.029$ (4) Å, $c = 21.569$ (9) Å, and $\beta = 97.13$ (3)°. The least-squares refinement converged to $R(F) = 0.041$ and $R_w(F) = 0.052$ for the 4333 unique data with $F > 3\sigma(F)$. At 35 °C in $CHCl_3$ solution, 2 undergoes an irreversible loss of CO to give the unusual tungsten phosphinocarbyne complex $WCl_2(CO)(PMePh_2)_2(\equiv CPMePh_2)$ (3). Carbon suboxide thus serves as a carbon atom synthon by sequential loss of two molecules of carbon monoxide. Treatment of toluene solutions of 1 with (triphenylphosphoranylidene)ketene, $O=C=CPPh_3$, affords a triphenylphosphine analogue of 3, $WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)$ (4), in excellent yield. 4 crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$, $a = 11.283$ (2) Å, $b = 14.932$ (3) Å, $c = 24.947$ (6) Å, and $\beta = 100.55$ (2)°. The least-squares refinement converged to $R(F) = 0.041$ and $R_w(F) = 0.043$ for the 5205 unique data with $F_o > 3\sigma(F_o)$. The phosphinocarbyne ligand of 4 is bound to W in a nearly linear fashion, with W–C(2)–P(3) = 171.2 (5)°, and the W–C(2) bond distance of 1.823 (7) Å is typical of W–C triple-bond distances found in other structures.

Introduction

Carbon suboxide (O=C=C=C=O) has been the subject of extensive studies by organic[1] and physical[2] chemists since its discovery in 1906 by Otto Diels,[3] but the inorganic reaction chemistry of C_3O_2 has only recently come under investigation.[4-7] This is somewhat surprising because the established modes of reactivity between C_3O_2 and organic molecules suggest some intriguing synthetic possibilities for its use as a reagent in organometallic systems. Most reactions involving carbon suboxide and organic substrates can be divided into two general classes: (1) nucleophilic additions to C_3O_2 and (2) photoreactions involving C_3O_2 fragmentation (i.e., sequential loss of CO).[1] By far the more common of these reaction types involves nucleophilic attack of C_3O_2 (at C-1) in accord with an important contribution to the ground-state structure from a dipolar Lewis structure as depicted in eq 1. In organic[1] and main-group[5] systems, α-carbonylketene intermediates like that shown in eq 1 are strongly implicated in reactions of C_3O_2, but they cannot be isolated. In contrast, we have recently shown in transition-metal systems that some metal–hydrido species undergo facile 1,2-insertion reactions with C_3O_2 to afford remarkably stable (perhaps for steric reasons) *formylketenyl* complexes (e.g., $Re\{C(CHO)CO\}(CO)_2(PPh_3)_2$ and $W\{C(CHO)CO\}(CO)_2(NO)(PPh_3)_2$).[6] The potential for preparing other new types of ketene-containing species using this methodology is obvious; for example, the hydridic or protic nature of a metal hydride could determine whether the hydrogen adds to C-1 or C-2, in accord with the resonance structures for C_3O_2 given in eq 1.[8]



(1)

Carbon suboxide is also attractive as a synthetic source of the "C_2O" and "C" fragments in transition-metal sys-

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(1) For a review of the organic reaction chemistry of C_3O_2, see: Kappe, T.; Ziegler, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 491.

(2) For a review of the physical chemistry of C_3O_2; see: *Gmelins Handbuch der Anorganischen Chemie*; Verlag-Chemie: Weinheim, 1970; Kohlenstoff, C, Section 1, Syst. No. 14, p 75 ff.

(3) (a) Diels, O.; Wolf, B. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 689. (b) Diels, O.; Meyerheim, G. *Ibid.* **1907**, *40*, 355.

(4) (a) Kolomnikov, I. S.; Koreshkov, Yu. D.; Lobeeva, T. S.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 1132. (b) Paiaro, G.; Pandolfo, L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 288. (c) Paiaro, G.; Pandolfo, L. *Ibid.* **1981**, *20*, 289. (d) Paiaro, G.; Pandolfo, L.; Segala, P. *Congr. Naz. Chim. Inorg.*, [*Atti*], *12th* **1979**, 77. (e) Pandolfo, L.; Paiaro, G.; Valle, G.; Ganis, P. *Gazz. Chim. Ital.* **1985**, *115*, 59. (f) Pandolfo, L.; Paiaro, G.; Valle, G.; Ganis, P. *Ibid.* **1985**, *115*, 65. (g) Pandolfo, L.; Paiaro, G. *Ibid.* **1985**, *115*, 561. (h) Pandolfo, L.; Morandini, F.; Paiaro, G. *Ibid.* **1985**, *115*, 711. (i) Pandolfo, L.; Paiaro, G. *J. Mol. Catal.* **1984**, *27*, 343.

(5) (a) Pandolfo, L.; Bressan, M.; Paiaro, G. *Gazz. Chim. Ital.* **1986**, *116*, 471. (b) Pandolfo, L.; Paiaro, G.; Vettori, V. *Ibid.* **1987**, *117*, 781. (c) Pandolfo, L.; Paiaro, G. *Ibid.* **1988**, *118*, 577. (d) Ganis, P.; Paiaro, G.; Pandolfo, L.; Valle, G. *Organometallics* **1987**, *7*, 210.

(6) Hillhouse, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7772.

(7) (a) List, A. K.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 4855. (b) List, A. K.; Hillhouse, G. L.; Rheingold, A. L. *Ibid.* **1988**, *110*, 6926.

(8) The charge distribution in C_3O_2 determined from ESCA data is as follows: O (−0.28), C1 (+0.45), C2 (−0.33).[9a] These data are consistent with calculated values.[9b-d] (a) Gelius, U.; Allan, C. J.; Allison, D. A.; Siegbahn, H.; Siegbahn, K. *Chem. Phys. Lett.* **1971**, *11*, 224. (b) Olsen, J. F.; Burnelle, J. J. *J. Phys. Chem.* **1969**, *73*, 2298. (c) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2191. (d) Sabin, J. R.; Kim, H. *J. Chem. Phys.* **1972**, *56*, 2195.

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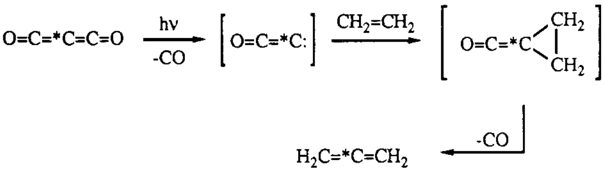
tems. Interest here stems from the reported photoreaction of C_3O_2 to give the ketenylidene fragment :C=C=O, which is itself formally capable of decarbonylation and is consequently a carbon atom synthon.[9] A striking example of the use of carbon suboxide as a C-synthon is seen when it is irradiated with 300-nm light in an ethylene atmosphere to produce allene.[10] As shown in eq 2, the central



(2)

carbon atom of C_3O_2 undergoes a formal insertion into the olefinic bond of ethylene and becomes the central atom of the product allene (with overall production of 2 equiv of CO). There is literature precedent to suggest that C_3O_2 can be a useful precursor to the "C_2O" fragment in inorganic systems, an example of which is illustrated in eq 3.[4c,g] The characterization of these products as ketenylidene complexes relies mainly on infrared data ($\nu_{CCO} \sim 2080$ cm^{-1}), but none have been structurally characterized.

$$[RhCl(C_8H_{14})_2]_2 + C_3O_2 \xrightarrow{py} [(C_8H_{14})(CO)(py)Rh(\mu\text{-}C_2O)Cl]_2 \quad (3)$$

We are currently exploring the organometallic reaction chemistries of C_3O_2 and the related (triphenylphosphoranylidene)ketene, O=C=CPPh$_3$,[11] with an eye toward their utilization as precursors (in thermal or photochemical decarbonylation reactions) to ketenylidene and carbide moieties, as well as other unusual C_1 and C_2 ligands. In this regard, we have investigated the reactions of these molecules with $WCl_2(PMePh_2)_4$, a complex known to participate in bond cleavage reactions with other heterocumulenes.[12] Herein we report the results of these studies, including evidence that carbon suboxide can undergo sequential carbon–carbon bond breaking reactions at a metal center (with loss of 2 equiv of carbon monoxide) to give, first, $WCl_2(CO)(PMePh_2)_2\{C,C'{:}\eta^2\text{-}C(O)CPMePh_2\}$ and then $WCl_2(CO)(PMePh_2)_2(\equiv CPMePh_2)$. Some of these results have been previously reported in preliminary form.[7]

Experimental Section

General Considerations. All compounds were handled in an inert-atmosphere glovebox, and reactions were carried out under an argon atmosphere by using standard high-vacuum and Schlenk techniques using dry, air-free solvents. NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 by using a Chicago-built 500-MHz instrument (^1H), a Varian XL-400 spectrometer (^{13}C, 100.6 MHz), a General Electric QE-300 spectrometer (^{13}C, 75.5 MHz), and a Nicolet NTC-200 spectrometer (^{31}P, 81 MHz). Elemental analyses were performed by Dornis and Kolbe (West Germany) and Desert Analytics (Tucson, AZ). Carbon monoxide (Matheson) was used directly from a lecture bottle. Carbon suboxide (C_3O_2) was prepared by the dehydration of malonic acid and stored as a liquid at −78 °C in the dark.[13] Carbon suboxide specifically labeled with 20% ^{13}C at the central carbon position was prepared from the appropriate commercially available labeled malonic acid (Cambridge Isotope Laboratories). (Triphenylphosphoranylidene)ketene (Ph_3PCCO) was prepared by the action of $NaN(SiMe_3)_2$ on $Ph_3PCHC(O)OMe$,[14a] which in turn was prepared by the reaction of Na_2CO_3 with $[Ph_3PCH_2C(O)OMe][Br]$.[14b] $WCl_2(PMePh_2)_4$ was synthesized according to the literature method.[15]

Preparation of $\mathbf{WCl_2(CO)(PMePh_2)_2\{C,C'{:}\eta^2\text{-}C(O)CPMePh_2\}}$ (2). C_3O_2 (1.8 mmol) was condensed into a flask containing 1.69 g (1.6 mmol) of $WCl_2(PMePh_2)_4$ suspended in 15 mL of toluene. The mixture was stirred for 12 h at ambient temperature and filtered and the precipitate washed with petroleum ether (15 mL) to give 1.32 g (81% yield) of **2**·C_7H_8. Recrystallization from CH_2Cl_2 gave solvent-free **2** as a blue, air-sensitive powder. For **2**: ^1H NMR ($CDCl_3$) δ 1.94 ($OCCP\mathit{Me}Ph_2$, d, 3 H, J_{PH} = 14.2 Hz), 2.03 (W–$P\mathit{Me}Ph_2$, t, 6 H, J_{PH} = 4.0 Hz), 7.0–8.0 ($PMe\mathit{Ph}_2$, m, 30 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 3.3 (W–$\mathit{P}MePh_2$, s with W satellites, 2 P, J_{PW} = 275 Hz), 24.6 ($OCC\mathit{P}MePh_2$, s, 1 P); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 10.26 ($OCCP\mathit{Me}Ph_2$, d, J_{PC} = 59.7 Hz), 13.15 (W–$P\mathit{Me}Ph_2$, t, J_{PC} = 15.5 Hz), 124–138 ($PMe\mathit{Ph}_2$, m), 183.44 ($OC\mathit{C}PMePh_2$, dt, $^1J_{PC}$ = 56.5, $^2J_{PC}$ = 7.0 Hz), 211.94 ($O\mathit{C}CPMePh_2$, d, J_{PC} = 12.1 Hz), 219.6 (W–$\mathit{C}O$, br s); IR (Fluorolube mull) ν_{CO} = 1910 cm^{-1}, $\nu_{C=O}$ = 1673 cm^{-1}. Anal. Calcd for $C_{42}H_{39}Cl_2O_2P_3W$: C, 54.63; H, 4.26; W, 19.91. Found: C, 54.29; H, 3.96; W, 20.08. $\mathbf{WCl_2(CO)(PMePh_2)_2\{C,C'{:}\eta^2\text{-}C(O)^{13}C\text{–}PMePh_2\}}$ (**2**-^{13}C) was analogously prepared (20% ^{13}C enrichment) from O=C=^{13}C=C=O; the enhanced resonance in the ^{13}C NMR spectrum is the doublet-of-triplets at δ 183.4.

Preparation of $\mathbf{WCl_2(CO)(PMePh_2)_2(\equiv CPMePh_2)}$ (3). A 0.51-g (0.6-mmol) sample of **2** was dissolved in $CHCl_3$ (25 mL) and maintained at 35 °C for 48 h. The volume of solution was reduced to 5 mL, and Et_2O was added to give a pink precipitate. Recrystallization from cold CH_2Cl_2 gave red-purple crystals of **3** (0.21 g, 51% yield). For **3**: ^1H NMR ($CDCl_3$) δ 1.26 (C–$P\mathit{Me}Ph_2$, d, 3 H, J_{PH} = 13.2 Hz), 2.20 (W–$P\mathit{Me}Ph_2$, t, 6 H, J_{PH} = 3.6 Hz), 6.9–7.6 ($PMe\mathit{Ph}_2$, m, 30 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 10.7 (W–$\mathit{P}MePh_2$, d with W satellites, 2 P, J_{PP} = 4, J_{PW} = 285 Hz), −2.4 (C–$\mathit{P}MePh_2$, t with W satellites, 1 P, J_{PP} = 4, J_{PW} = 194 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 0.04 M $Cr(acac)_3$) δ 12.3 (C–$P\mathit{Me}Ph_2$, d, J_{PC} = 61 Hz), 14.7 (W–$P\mathit{Me}Ph_2$, t, J_{PC} = 14 Hz), 124–140 ($PMe\mathit{Ph}_2$, m), 218.7 (C–$PMePh_2$, t, J_{PC} = 12 Hz), 244.6 (W–$\mathit{C}O$, q, J_{PC} = 5 Hz); IR (Fluorolube mull) ν_{CO} = 1903 cm^{-1}. Anal. Calcd for $C_{41}H_{39}Cl_2OP_3W$: C, 55.00; H, 4.39. Found: C, 53.89; H, 4.17. $\mathbf{WCl_2(CO)(PMePh_2)_2(\equiv ^{13}CPMePh_2)}$ (**3**-^{13}C) was analogously prepared (20% ^{13}C enrichment) from **2**-^{13}C; the enhanced resonance in the ^{13}C NMR spectrum is the *triplet* at δ 219.

Preparation of $\mathbf{WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)}$ (4). $WCl_2(PMePh_2)_4$ (2.44 g, 2.3 mmol) and Ph_3PCCO (0.70 g, 2.3 mmol) were suspended in 30 mL of toluene. The suspension was stirred for 8 h at 35 °C, during which time the suspension darkened in color. The resulting mixture was filtered, and the precipitate was washed with toluene (5 mL) and then with petroleum ether (5 mL) to give 1.86 g (84% yield) of solvent-free, purple **4**. For **4**: ^1H NMR ($CDCl_3$) δ 2.16 (W–$P\mathit{Me}Ph_2$, t, 6 H, J_{PH} = 3.8 Hz), 6.8–7.7 (*Ph*, m, 35 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 10.2 (W–$\mathit{P}MePh_2$, d with W satellites, 2 P, J_{PP} = 4, J_{PW} = 285 Hz), −1.6 (C–$\mathit{P}Ph_3$, t with W satellites, 1 P, J_{PP} = 4, J_{PW} = 196 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 0.04 M $Cr(acac)_3$) δ 15.0 (W–$P\mathit{Me}Ph_2$, t, J_{PC} = 14 Hz), 123.6 (C–$P\mathit{Ph}_3$, d, J_{PC} = 90 Hz), 127.0 (W–$PMe\mathit{Ph}_2$, t, J_{PC} = 4 Hz), 127.5 (W–$PMe\mathit{Ph}_2$, t, J_{PC} = 4 Hz), 128.7 (C–$P\mathit{Ph}_3$, d, J_{PC} = 13 Hz), 132.3 (C–$P\mathit{Ph}_3$, d, J_{PC} = 2 Hz), 132.5 (W–$PMe\mathit{Ph}_2$, t, J_{PC} = 5 Hz), 132.9 (C–$P\mathit{Ph}_3$, d, J_{PC} = 10 Hz), 133.4 (W–$PMe\mathit{Ph}_2$, t, J_{PC} = 5 Hz), 136.5 (W–$PMe\mathit{Ph}_2$, t, J_{PC} = 21 Hz), 139.8 (W–$PMe\mathit{Ph}_2$, t, J_{PC} = 19 Hz), 215.4 (C–PPh_3, t, J_{PC} = 10 Hz), 245.9 (W–$\mathit{C}O$, q, J_{PC} = 5 Hz); IR (Fluorolube mull) ν_{CO} = 1905 cm^{-1}.

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(9) (a) Williamson, D. G.; Bayes, K. D. *J. Am. Chem. Soc.* **1968**, *90*, 1957. (b) Peterson, R. F., Jr.; Wolfgang, R. L. *J. Chem. Soc., Chem. Commun.* **1968**, 1201. (c) Smith, R. N.; Smith, R. A.; Young, D. A. *Inorg. Chem.* **1966**, *5*, 145. (d) For a C_2O review, see: *Gmelins Handbuch der Anorganischen Chemie*; Verlag-Chemie: Weinheim, 1970; Kohlenstoff, C, Section 1, Syst. No. 14, p 71 ff.

(10) (a) Mullen, R. T.; Wolf, A. P. *J. Am. Chem. Soc.* **1968**, *84*, 3214. (b) Bayes, K. D. *Ibid.* **1968**, *84*, 4077. (c) Willis, C.; Bayes, K. D. *Ibid.* **1966**, *88*, 3203. (d) Kirmse, W. *Carbene, Carbenoide, und Carbenanaloga*; Verlag-Chemie: Weinheim, 1969; pp 156, 231.

(11) (a) Daly, J. J.; Wheatly, P. J. *J. Chem. Soc. A* **1966**, 1703. (b) Matthews, C. N.; Birum, G. H. *Tetrahedron Lett.* **1966**, 5707.

(12) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826.

(13) Glemser, O. In *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Brauer, Ed.; Academic: New York, 1963; p 648 ff.

(14) (a) Bestmann, H. J.; Sandmeier, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 634. (b) Bestmann, H. J.; Kratzer, O. *Chem. Ber.* **1962**, *95*, 1894.

(15) Sharp, P. R. *Organometallics* **1984**, *3*, 1217.

Table I. Selected Bond Distances and Angles for $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$

(a) Bond Distances (Å)

W-Cl(1)	2.474 (2)	W-C(3)	1.996 (8)
W-Cl(2)	2.575 (2)	O(1)-C(1)	1.175 (12)
W-P(1)	2.554 (2)	O(2)-C(2)	1.200 (11)
W-P(2)	2.520 (2)	C(2)-C(3)	1.368 (12)
W-C(1)	1.921 (10)	P(3)-C(3)	1.753 (8)
W-C(2)	2.146 (9)		

(b) Bond Angles (deg)

Cl(1)-W-Cl(2)	83.2 (1)	P(1)-W-C(3)	99.7 (2)
Cl(1)-W-P(1)	84.6 (1)	P(2)-W-C(1)	90.5 (3)
Cl(1)-W-P(2)	81.9 (1)	P(2)-W-C(2)	96.7 (2)
Cl(1)-W-C(1)	85.8 (3)	P(2)-W-C(3)	92.9 (2)
Cl(1)-W-C(2)	152.8 (2)	C(1)-W-C(2)	67.0 (3)
Cl(1)-W-C(3)	168.0 (2)	C(1)-W-C(3)	105.1 (3)
Cl(2)-W-P(1)	84.4 (1)	C(2)-W-C(3)	38.3 (3)
Cl(2)-W-P(2)	90.8 (1)	W-C(1)-O(1)	176.2 (8)
Cl(2)-W-C(1)	168.7 (2)	W-C(2)-O(2)	147.8 (6)
Cl(2)-W-C(2)	124.0 (2)	W-C(2)-C(3)	64.9 (5)
Cl(2)-W-C(3)	86.1 (2)	W-C(3)-P(3)	149.7 (5)
P(1)-W-P(2)	166.2 (1)	W-C(3)-C(2)	76.8 (5)
P(1)-W-C(1)	91.8 (2)	O(2)-C(2)-C(3)	147.2 (8)
P(1)-W-C(2)	96.7 (2)	C(2)-C(3)-P(3)	133.0 (7)

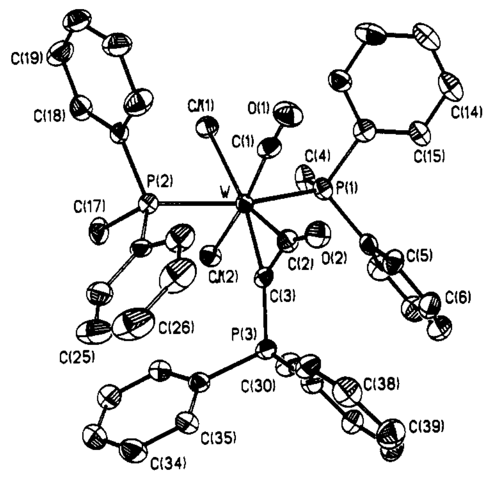


Figure 1. A perspective view of $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$ (2) showing the atom-labeling scheme (40% probability ellipsoids). The hydrogen atoms have been omitted for clarity.

Anal. Calcd for $C_{46}H_{41}Cl_2OP_3W$: C, 57.70; H, 4.32. Found: C, 56.64; H, 4.16.

Crystal Structure Determination of 2. Crystals of 2 suitable for an X-ray diffraction study were obtained by the slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of the complex. 2 crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 11.400$ (4) Å, $b = 16.029$ (4) Å, $c = 21.569$ (9) Å, and $\beta = 97.13$ (3)°. The least-squares refinement converged to $R(F) = 0.041$ and $R_w(F) = 0.052$ for the 4333 unique data with $F > 3\sigma(F)$. Complete crystallographic details pertaining to the refinement of the structure, tables of atomic coordinates, thermal parameters, and structure factors were reported in the preliminary communication (and its supplementary material) and therefore are not repeated here.[7] However, for the benefit of the discussion, selected bond angles and distances are given in Table I and a perspective view of the complex along with the atom numbering scheme is shown in Figure 1.

Crystal Structure Determination of 4. Crystals of 4 suitable for an X-ray diffraction study were grown by the slow diffusion of benzene into a saturated methylene chloride solution. Table II contains a summary of the crystallographic data. The sample was mounted in epoxy cement on a glass fiber. Preliminary photographic evidence and systematic absences in the reflection data uniquely determined the monoclinic space group $P2_1/c$. The data were empirically corrected for absorption by using a six-parameter pseudoellipsoid model, and the structure was solved by heavy-atom methods. The phenyl rings were constrained to rigid hexagons with C–C distances of 1.395 Å. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were treated as idealized, updated isotropic contributions (C–H = 0.96 Å). All computations used the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI). Figure 2 shows a perspective view of the molecule along with the atom-numbering scheme. Atomic coordinates and isotropic thermal parameters are given in Table III, and selected bond distances and angles are given in Table IV. Complete listings of bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates with their isotropic thermal parameters, and observed and calculated structure factors are given in the supplementary material.

Table II. Crystallographic Data for $WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)$

(a) Crystal Data

formula	$C_{46}H_{41}Cl_2OP_3W$	Z	4
crystal system	monoclinic	D(calcd), g cm^{-3}	1.539
space group	$P2_1/c$	color	purple
a, Å	11.283 (2)	size, mm	0.14 × 0.15 × 0.36
b, Å	14.932 (3)	temp, K	294
c, Å	24.947 (6)	μ(Mo Kα), cm^{-1}	32.0
β, deg	100.55 (2)	T_{max}/T_{min}	1.29
V, Å^3	4132 (1)		

(b) Data Collection

diffractometer	Nicolet R3m	rflns collected	7779
radiation	Mo Kα	indpdt rflns	7279
wavelength (λ), Å	0.71073	R(merge), %	5.6
monochromator	graphite	obs rflns ($3\sigma(F_o)$)	5205
scan limits, deg	$4 \le 2\theta \le 50$	std rflns	3 std/157 rflns
scan method	Wyckoff	std variation, %	±1

(c) Refinement

$R(F)$, %	4.08	Δ/σ(final)	0.04
$R_w(F)$, %	4.28	$\Delta(\rho)$, e A^{-3}	1.22
GOF	1.19	N_o/N_v	13.2

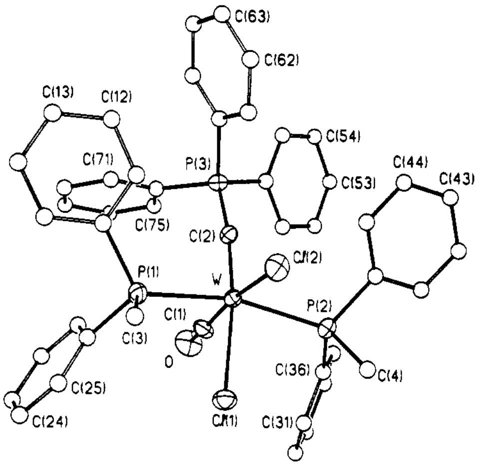


Figure 2. A perspective view of $WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)$ (4) showing the atom-labeling scheme (40% probability ellipsoids). The phosphorus bound substituents are shown as arbitrary-sized spheres, and the hydrogen atoms have been omitted for clarity.

Results and Discussion

Carbon suboxide reacts cleanly in a 1:1 stoichiometric fashion with toluene solutions of $WCl_2(PMePh_2)_4$ (1) to afford slate-blue crystals of $WCl_2(CO)(PMePh_2)_2\{C,C':\eta^2\text{-}C(O)CPMePh_2\}$ (2) as the 1:1 toluene solvate in high yield (eq 4). The identification of 2 as a novel (methyldiphenylphoranylidene)ketene complex of tungsten follows directly from its distinctive spectral characteristics (IR; ^1H, ^{13}C, and ^{31}P NMR) and a single-crystal X-ray diffraction study (discussed below). The infrared spectrum of 2 exhibits two strong bands corresponding to C–O

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)$

	x	*y*	*z*	*U*^{a}
W	3178.0 (3)	1217.7 (2)	1435.1 (1)	26.6 (1)
P(1)	2755 (2)	1285 (2)	406.2 (8)	36.0 (6)
P(2)	4008 (2)	754 (1)	2408.4 (8)	34.0 (7)
P(3)	1131 (2)	2926 (1)	1641.8 (8)	31.3 (6)
Cl(1)	4988 (2)	358 (1)	1216.3 (9)	44.4 (7)
Cl(2)	2025 (2)	−222 (1)	1349.3 (9)	48.0 (9)
C(1)	4260 (7)	2272 (6)	1511 (3)	40 (3)
O	4846 (5)	2903 (4)	1573 (3)	59 (2)
C(2)	2053 (6)	2032 (5)	1558 (3)	30 (2)
C(3)	2735 (10)	172 (6)	78 (4)	66 (4)
C(4)	4506 (8)	−412 (6)	2485 (4)	54 (3)
C(11)	282 (5)	1483 (3)	277 (2)	43 (3)
C(12)	−862	1751	14	51 (3)
C(13)	−992	2251	−466	57 (4)
C(14)	21	2483	−682	55 (3)
C(15)	1165	2216	−420	46 (3)
C(16)	1296	1715	60	36 (3)
C(21)	3932 (5)	2845 (4)	244 (2)	65 (4)
C(22)	4757	3375	34	92 (5)
C(23)	5478	2995	−304	105 (7)
C(24)	5374	2086	−432	104 (7)
C(25)	4550	1556	−222	69 (4)
C(26)	3829	1935	116	49 (3)
C(31)	6411 (5)	1230 (4)	2502 (2)	58 (4)
C(32)	7428	1762	2669	69 (5)
C(33)	7395	2456	3040	63 (4)
C(34)	6345	2617	3245	56 (4)
C(35)	5328	2086	3079	45 (3)
C(36)	5360	1392	2707	40 (3)
C(41)	3454 (4)	669 (5)	3465 (2)	68 (5)
C(42)	2663	631	3834	77 (5)
C(43)	1424	707	3647	66 (4)
C(44)	976	822	3092	72 (5)
C(45)	1767	861	2724	58 (4)
C(46)	3006	784	2910	41 (3)
C(51)	2532 (4)	3301 (4)	2640 (2)	46 (3)
C(52)	2747	3617	3176	59 (4)
C(53)	1792	3929	3409	65 (4)
C(54)	622	3924	3107	83 (5)
C(55)	407	3607	2572	60 (4)
C(56)	1362	3295	2338	38 (3)
C(61)	−723 (4)	1705 (3)	1458 (2)	41 (3)
C(62)	−1924	1444	1302	53 (4)
C(63)	−2812	2085	1131	60 (4)
C(64)	−2499	2988	1115	66 (4)
C(65)	−1298	3249	1271	51 (4)
C(66)	−410	2607	1442	37 (3)
C(71)	1030 (5)	3811 (3)	659 (2)	48 (3)
C(72)	1305	4496	322	60 (4)
C(73)	1956	5241	548	73 (4)
C(74)	2332	5302	1112	82 (5)
C(75)	2058	4617	1449	52 (3)
C(76)	1407	3871	1223	36 (3)

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

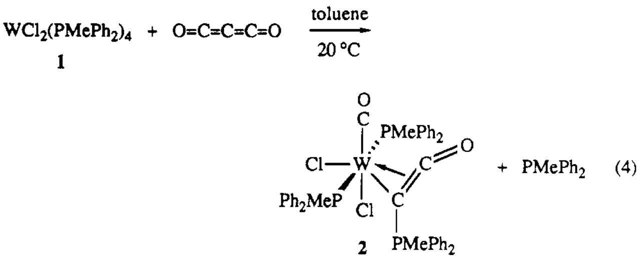
Table IV. Selected Bond Distances and Angles for $WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)$

(a) Bond Distances (Å)

W–C(2)	1.823 (7)	W–P(1)	2.525 (2)
W–C(1)	1.981 (8)	W–P(2)	2.534 (2)
W–Cl(1)	2.555 (2)	C(1)–O	1.146 (10)
W–Cl(2)	2.501 (2)	C(2)–P(3)	1.729 (8)

(b) Bond Angles (deg)

P(1)–W–P(2)	162.4 (1)	Cl(1)–W–Cl(2)	88.5 (1)
P(1)–W–Cl(1)	79.2 (1)	Cl(1)–W–C(1)	85.2 (2)
P(1)–W–Cl(2)	87.1 (1)	Cl(1)–W–C(2)	168.3 (2)
P(1)–W–C(1)	93.7 (2)	Cl(2)–W–C(1)	173.4 (2)
P(1)–W–C(2)	97.8 (2)	Cl(2)–W–C(2)	102.7 (2)
P(2)–W–Cl(1)	84.1 (1)	C(1)–W–C(2)	83.6 (3)
P(2)–W–Cl(2)	86.7 (1)	W–C(2)–P(3)	171.2 (5)
P(2)–W–C(1)	90.7 (2)	W–C(1)–O	176.2 (8)
P(2)–W–C(2)	99.7 (2)		



stretches for the newly formed carbon monoxide ligand (1910 cm^{-1}) and the ketenyl ylide (1673 cm^{-1}).[16] The $^{31}P\{^1H\}$ NMR spectrum of **2** contains two resonances of relative intensity 2:1, with the larger having ^{183}W satellites (the two $PMePh_2$ ligands) and the smaller having none (since the phosphorus of the OC_2PMePh_2 ligand is no longer bound to tungsten). The ^1H NMR spectrum likewise shows two distinct types of methyl resonances, a virtual triplet (indicating a pair of trans $PMePh_2$ ligands) and a doublet (arising from the OC_2PMePh_2 ligand). In addition to typical Me and Ph carbon resonances, the $^{13}C\{^1H\}$ NMR spectrum of **2** contains a broad resonance for W—CO (δ 220, unresolved coupling), a doublet for W(OCCPMePh$_2$) (δ 212; $^2J_{PC}$ = 12 Hz), and a doublet-of-triplets for W(OCCPMePh$_2$) (δ 183; $^2J_{PC}$ = 7, $^1J_{PC}$ = 57 Hz).[16] The latter assignment was confirmed by spectral measurements of 20% isotopically enriched $WCl_2(CO)(PMePh_2)_2\{C,C'{:}\eta^2\text{-}C(O)^{13}CPMePh_2\}$ (**2**-^{13}C), prepared from **1** and O=C=^{13}C=C=O (20% ^{13}C).

The reaction depicted in eq 4 is an interesting one from several perspectives. It is formally analogous to the reported reactions of **1** with other heterocumulenes (O=C=O, RN=C=O, and RN=C=NR) except that in the cases of these latter three reagents, tungsten–oxo or –imido complexes are formed whereas in the case of C_3O_2, a C–C rather than a C–O or C–N bond is cleaved (eq 5–7).[12] In

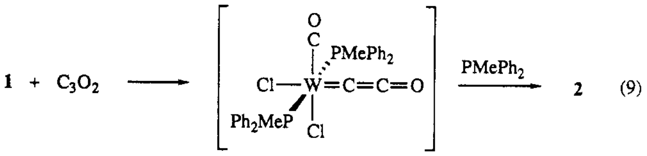
$$1 + O{=}C{=}O \rightarrow W(O)Cl_2(CO)(PMePh_2)_2 + 2PMePh_2 \quad (5)$$

$$1 + RN{=}C{=}O \rightarrow W(NR)Cl_2(CO)(PMePh_2)_2 + 2PMePh_2 \quad (6)$$

$$1 + RN{=}C{=}NR \rightarrow W(NR)Cl_2(CNR)(PMePh_2)_2 + 2PMePh_2 \quad (7)$$

$$1 + O{=}CR_2 \rightarrow W(O)Cl_2(CR_2)(PMePh_2)_2 + 2PMePh_2 \quad (8)$$

the light of these reactions, and that of some ketones with **1**[17] (eq 8), it seems likely that the reaction of C_3O_2 with **1** proceeds by way of a ketenylidene intermediate that is subsequently trapped by $PMePh_2$ to give **2** (eq 9). At-



tempts to intercept this putative ketenylidene intermediate by carrying out the reaction in the presence of phosphine traps such as MeI and 9-BBN were not successful and yielded **2** in undiminished yields. The phosphine-trapping results suggest that if nucleophilic addition of $PMePh_2$ to a [W=C=C=O] moiety is mechanistically important in the formation of **2**, then it is perhaps an intramolecular

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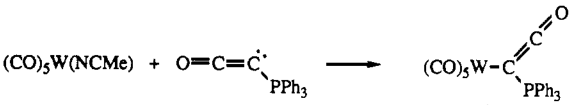
[16] The IR and ^{13}C NMR spectral data for **2** are diagnostic for an η^2-ketenyl complex. For a recent review that includes tabulations of such data for related ketene, ketenyl, and ketenylidene complexes, see: Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

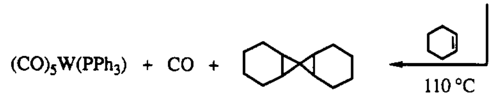
[17] Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213.

process involving a *tris(phosphine)* intermediate like $[W(CO)Cl_2(CCO)(PMePh_2)_3]$. Similarly, the reaction of **1** with one-half equivalent of C_3O_2 gives **2** stoichiometrically based on C_3O_2, along with unreacted $WCl_2(PMePh_2)_4$; an intermediate ketenylidene complex did not undergo a second C–C bond activation with the excess **1** to give a $W_2(\mu_2\text{-}C)$ moiety.

It has been demonstrated that triphenylphosphoranylidene ketene (Ph_3PC_2O) forms a stable complex in $(CO)_5W(\eta^1\text{-}C(CO)PPh_3)$ (eq 10)[18] and that upon thermolysis in the presence of cyclohexene, this complex decomposes to yield $(CO)_5W(PPh_3)$ and 7,7′-spirobinorcarane (eq 11).[18a] **2**, however, is the first example of a complex containing an η^2,4-electron donor ligand of this type, and so we set out to determine whether it was susceptible to "carbon atom extrusion" reactions like that shown in eq 11 or if its reaction chemistry was more akin to that of the η^2-ketenyl complexes of the general type $M\{C,C'\text{:}\eta^2\text{-}C(CO)R\}$[16,19] that it closely resembles both spectroscopically (see above) and structurally (discussed in detail below).



(10)



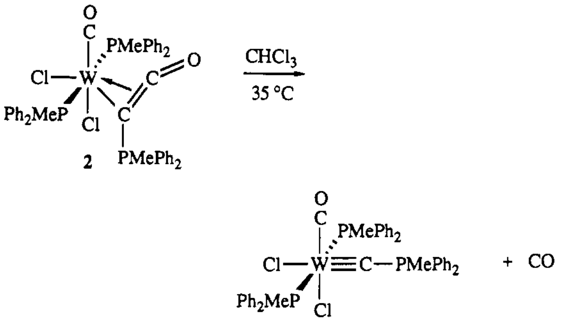
(11)

Mild thermolysis of **2** in $CHCl_3$ (35 °C, 48 h) results in extrusion of carbon monoxide and cleavage of the C–C bond of the (phosphoranylidene)ketene ligand to give a phosphinocarbyne complex of tungsten, $WCl_2(CO)(PMePh_2)_2(\equiv CPMePh_2)$ (**3**), as a red-purple precipitate in about 50% isolated yield (eq 12). The phosphinocarbyne ligand, although unusual, has precedence in two other tungsten systems. Schrock has reported the preparation and structural characterization of $[W_2(\equiv CPMe_3)_2Cl_4(PMe_3)_4{}^{2+}][AlCl_4{}^-]_2$, a dimer containing two terminal (trimethylphosphino)carbyne ligands (see eq 13),[20] and Templeton recently described the isolation of $[Tp'W(CO)_2(\equiv CPEt_3)^+][PF_6{}^-]$ (Tp′ = hydrido(3,5-dimethylpyrazolyl)borate) according to the reaction shown in eq 14.[21] Although CO migration from an η^2-ketenyl ligand

$$W(\equiv CH)(PMe_3)_4Cl + AlCl_3 + C_2Cl_6 \rightarrow [W_2(\equiv CPMe_3)_2Cl_4(PMe_3)_4][AlCl_4]_2 \tag{13}$$

$$Tp'W(CO)_2(\equiv CSMe) + PEt_3 \rightarrow [Tp'W(CO)_2(\equiv CPEt_3)^+] \tag{14}$$

(to give OC—M≡C—R) is thought to be involved in the isomerization of *cis,cis*-$WCl(\equiv CPh)(CO)_2(PMe_3)_2$ to *trans,trans*-$WCl(\equiv CPh)(CO)_2(PMe_3)_2$ catalyzed by PMe_3 (eq 15),[19i] the reaction depicted in eq 12 is essentially the *reverse* of the most common ketenyl ligand formation reaction: carbonylation of a carbyne ligand, $OC—M\equiv C—R \rightarrow M\{C(CO)R\}$.[16,19] Carbon monoxide, however, does not react with **3** (1 atm, 20 °C) to regenerate **2**. Taken as a whole, the reaction sequence represented by eq 4 and eq 12 (i.e., $1 + C_3O_2 \rightarrow 3 + CO$) constitutes stepwise cleavage of 2 equiv of CO from carbon suboxide to afford a new C_1 fragment.

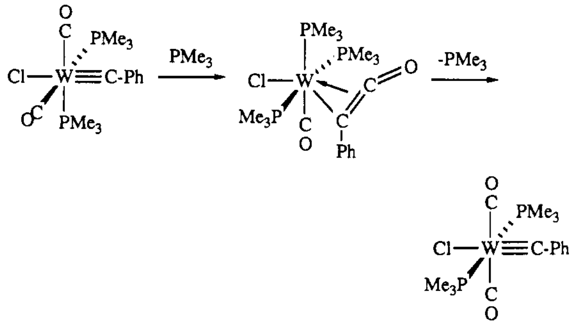


2 **3** (12)

Table V. Selected ^{13}C and ^{31}P NMR Data for W≡C—PR$_3$ Complexes

complex	δ(^{13}C) (W≡*C*—PR$_3$)	δ(^{31}P) (W≡C—*P*R$_3$)
$[W_2(\equiv CPMe_3)_2Cl_4(PMe_3)_4{}^{2+}][AlCl_4{}^-]_2$[a]	241.9 (br s)	6.8 (s, $^2J_{PW}$ = 166 Hz)
$[Tp'W(CO)_2(\equiv CPEt_3)^+][PF_6{}^-]$[b]	not reported	30.1 (s, $^2J_{PW}$ = 150 Hz)
$[Tp'W(CO)_2(\equiv CPMe_3)^+][PF_6{}^-]$[b]	253.4 (s)	16.7 (s, $^2J_{PW}$ = 147 Hz)
$WCl_2(CO)(PMePh_2)_2(\equiv CPMePh_2)$ (**3**)[c]	218.7 (t, $^2J_{PC}$ = 12 Hz)	−2.4 (t, $^3J_{PP}$ = 4, $^2J_{PW}$ = 194 Hz)
$WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)$ (**4**)[c]	215.4 (t, $^2J_{PC}$ = 10 Hz)	−1.6 (t, $^3J_{PP}$ = 4, $^2J_{PW}$ = 196 Hz)

[a] Reference 20. [b] Tp′ = hydrido(3,5-dimethylpyrazolyl)borate; ref 21. [c] This work.



(15)

The spectroscopic properties of **3**, particularly aspects of its ^{13}C and ^{31}P NMR spectra associated with the $W\equiv CPMePh_2$ unit (see Table V for comparisons with similar complexes), are interesting. First, the $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits two resonances with ^{183}W satellites, a doublet at δ 10.7 (2 P, W-*P*MePh$_2$; $^3J_{PP}$ = 4, $^1J_{PW}$ = 285 Hz) and a triplet at δ −2.4 (1 P, W≡C—*P*MePh$_2$; $^3J_{PP}$ = 4, $^2J_{PW}$ = 194 Hz). The magnitudes of $^3J_{PP}$ and $^2J_{PW}$ are surprisingly large and are in the ranges typical of simple meridional $PMePh_2$ ligands (i.e., all attached *directly* to W). These large couplings for the $CPMePh_2$ ligand are probably a consequence of its linear (sp-hybridized at C) geometry since the "bent" OC_2PMePh_2 ligand of **2** does not exhibit such coupling. Moreover, the resonance for

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[18] (a) Berke, H.; Lindner, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 667. (b) Lindner, E.; Berke, H. *Chem. Ber.* **1974**, *107*, 1360.

[19] (a) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474. (b) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M. *Z. Naturforsch., B* **1983**, *38B*, 1419. (c) Kreissl, F. R.; Sieber, W. J.; Alt, H. G. *Chem. Ber.* **1984**, *117*, 2527. (d) Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Ibid.* **1977**, *110*, 3782. (e) Kreissl, F. R.; Friedrich, P.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 102. (f) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Ibid.* **1976**, *15*, 632. (g) Fischer, E. O.; Filippou, A. C.; Alt, H. G.; Ackermann, K. *J. Organomet. Chem.* **1983**, *254*, C21. (h) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 310. (i) Mayr, A.; Kjelsberg, M. A.; Lee, K. S.; Asaro, M. F.; Hsieh, T.-C. *Organometallics* **1987**, *6*, 2610. (j) Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A. *J. Organomet. Chem.* **1983**, *258*, C37. (k) Kreissl, F. R.; Sieber, W.; Wolfgruber, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 493.

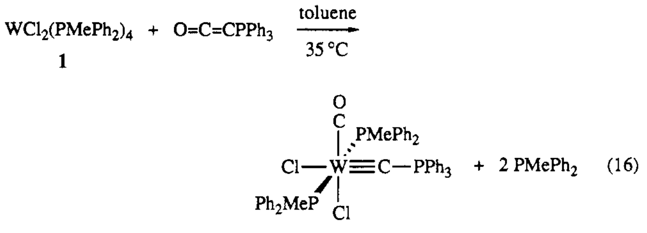
[20] Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476.

[21] Bruce, A. E.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1987**, *6*, 1350.

the carbonyl carbon atom of 3 appears as a pseudoquartet at δ 245, with $^2J_{PC} \sim {}^3J_{PC} = 5$ Hz (again, as would be expected for simple meridional $PMePh_2$ ligands). However, the resonance for the carbyne carbon atom of the $W{\equiv}CPMePh_2$ moiety appears as a *triplet* in the ^{13}C NMR spectrum (δ 219; $^2J_{PC} = 12$ Hz) with *no observable* $^1J_{PC}$ *coupling*! As shown in Table V, this is a peculiar characteristic common to the other reported transition-metal phosphinocarbyne complexes[20,21] and can be contrasted to $^1J_{PC} = 192$ Hz in $[Ph_3P{-}C{\equiv}C{-}Me^+]$[22] and $^1J_{PC} = 56.5$ Hz in 2. This extraordinary combination of unusual coupling constants led us to incorrectly formulate 3 as $WCl_2(CO)(PMePh_2)_3$ in a preliminary report[7a] that was subsequently corrected.[7b,23] Indeed, it was only upon obtaining (a) ^{13}C NMR data for the specifically ^{13}C-enriched (20%) derivative $WCl_2(CO)(PMePh_2)_2({\equiv}{}^{13}CPMePh_2)$ (3-^{13}C) and (b) a crystal structure of a PPh_3 analogue (see below) that we became entirely convinced of the identity of 3.

Ketenyl complexes often react with Lewis acids to effect the transformation of the ketenyl ligand into an oxyalkyne ligand (i.e., $M\{C(CO)R'\} + R^+ \rightarrow M\{R'C{\equiv}COR\}^+$),[24] so we investigated the reactions of 2 with $[Me_3O^+][BF_4^-]$, $CF_3SO_3SiMe_3$, and $AlCl_3$ anticipating the possible formation of novel $M\{Ph_2MeP{-}C{\equiv}C{-}OR\}^+$ and $M\{Ph_2MeP{-}C{\equiv}COAlCl_3\}$ complexes. Such species were not observed as products in any of these reactions. Instead, benzene-insoluble (CH_2Cl_2 soluble) products with spectroscopic properties (IR; ^{31}P NMR) similar to those of 3 were formed (suggestive of cationic phosphinocarbyne complexes related to 3), but none could be isolated in pure form.

Reaction of 1 with a stoichiometric amount of $Ph_3PC{=}C{=}O$ proceeds smoothly (C_7H_8 solution, 8 h, 35 °C) to give air-stable $WCl_2(CO)(PMePh_2)_2({\equiv}CPPh_3)$ (4) that can be isolated as purple crystals in excellent yield (eq 16). This (triphenylphosphino)carbyne complex has been characterized spectroscopically as well as by a single-crystal X-ray diffraction study. The spectroscopic properties of 4 are (not surprisingly) very similar to those of 3 that were discussed in detail above, and pertinent data are summarized in Table V for comparison. Specifically, the unusual spectral features associated with the $W{\equiv}CPMePh_2$ ligand of 3 are also observed for the $W{\equiv}CPPh_3$ ligand in the ^{13}C and ^{31}P NMR spectra of 4. The reaction shown in eq 16 is related in obvious ways to those depicted in eq 4–8; the impressive variety of "oxidative cleavage" reactions involving substrates with multiple bonds in which 1 participates is quite striking. As in the case of carbon

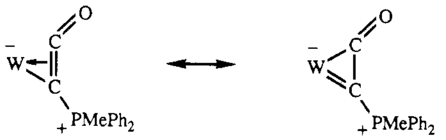


4

suboxide, a C—C bond is also cleaved in the reaction of $Ph_3PC{=}C{=}O$ with 1, with no observed intermediates. We have also examined the reaction of 1 with the bis(ylide) compound $(Ph_3P)_2C$ but were unable to observe any products of oxidative cleavage; the lack of reactivity might be a consequence of the steric bulk of $(Ph_3P)_2C$.

Molecular Structure of $WCl_2(CO)(PMePh_2)_2\{C,C'{:}\eta^2\text{-}C(O)CPMePh_2\}$. The crystal structure of 2 consists of well-separated molecules in the unit cell, with no significant inter- or intramolecular nonbonded contacts. Listings of selected bond angles and distances are given in Table I, and a perspective view of the complex is illustrated in Figure 1. The coordination geometry about W is approximately octahedral with the η^2-C(O)CPMePh$_2$ ligand occupying one site in the coordination sphere. All of the atoms in 2 except for P(1), P(2), and the Me and Ph groups are nearly coplanar, with the largest deviation from the least-squares plane being 0.15 Å for Cl(2).

The most interesting features of the structure, as expected, are associated with the unusual η^2-C(O)CPMePh$_2$ ligand. Coordination of the phosphoranylideneketene ligand to W in this η^2 fashion allows the metal center to attain an 18-electron configuration. The C(2)–C(3) bond distance (1.37 (1) Å) suggests significant double-bond character in this linkage (using the Pauling radii and hybridization correction, the bond order is ~1.5),[25] and the P(3)–C(3) distance (1.753 (8) Å) is significantly longer than the corresponding distance usually found in phosphoranylidenes (~1.67–1.70 Å).[26,27] The C(2)–O(2) bond length (1.200 (11) Å) is typical of that found in aldehydes and ketones.[25] Partial multiple-bond character is indicated in the W–C(3) bond, with this distance (1.996 (8) Å) being substantially shorter that for the W—C(2) bond (2.146 (9) Å); these can be compared to W—C single (2.258 (9) Å for $W{-}CH_2CMe_3$) and double (1.942 (9) Å for $W{=}CHCMe_3$) bond lengths found in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$.[31] These data are most consistent with a model consisting of a resonance average of forms A and B.



A B

The metrical parameters associated with the η^2-C(O)CPMePh$_2$ ligand are remarkably similar (in all pertinent bond angles and distances) to the corresponding ones of η^2-ketenyl ligands in related W(II) complexes that have been structurally characterized.[19a,d,e,g] A noteworthy structural feature common to all of these η^2-ketenyl complexes as well as to 2 is the presence of a carbon monoxide coligand that is always proximal to (i.e., cisoid) and aligned in the same direction as the ketenyl carbonyl group, as shown in C. Isomers such as D or other rotational isomers are never observed.

Molecular Structure of $WCl_2(CO)(PMePh_2)_2({\equiv}CPPh_3)$. Compound 4 represents the second example of

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(22) (a) Albright, T. A. *Org. Magn. Reson.* **1976**, *8*, 489. (b) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 2946. (c) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1975**, *40*, 3437.

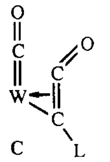
(23) Additionally, 3 and the related complex 4 repeatedly gave low carbon content in their elemental analyses, even for pure, crystalline samples.

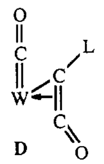
(24) For examples of η^2-ketenyl → oxyalkyne ligand transformations, see ref 19a, 19b, 19j, and 19k. For examples of related carbyne + CO → oxyalkyne ligand transformations, see: (a) Fischer, E. O.; Friedrich, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 327. (b) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766.

(25) Pauling, L. *The Nature of the Chemical Bond*; 3rd ed.; Cornell University: Ithaca, NY, 1960.

(26) (a) Schmidbaur, H.; Schier, A.; Neugebauer, D. *Chem. Ber.* **1983**, *116*, 2173. (b) Schmidbaur, H.; Schier, A.; Milewski-Mahrla, B.; Schubert, U. *Ibid.* **1982**, *115*, 722. (c) For a comprehensive bibliography of phosphorus ylide structures, see ref 1 and 2 in: Vincent, M. A.; Schaefer, III, H. F.; Schier, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1983**, *105*, 3806.

(27) The structure of $O{=}C{=}CPPh_3$ has been determined.[11a] Pertinent metrical parameters of the O—C—C—P framework include the following: O—C = 1.185 (6), C—C = 1.210 (10), C—P = 1.648 (7) Å; O—C—C = 175.6 (8), C—C—P = 145.4 (7)°.


C


D

a structurally characterized phosphinocarbyne complex, the other being Schrock's dimeric $[W_2(\equiv CPMe_3)_2Cl_4(PMe_3)_4{}^{2+}][AlCl_4{}^-]_2$.[20] The molecular structure of 4 is shown in Figure 2, and listings of selected bond distances and angles are given in Table IV. There are no unusually short inter- or intramolecular nonbonded contacts. The ligands form a slightly distorted pseudooctahedral array about the central W atom, with cis chlorides (Cl(1)–W–Cl(2) = 88.5 (1)°) and trans disposed diphenylmethylphosphine ligands (P(1)–W–P(2) = 162.4 (1)°). Although the two phosphorus atoms of the $PMePh_2$ ligands are chemically and magnetically equivalent (one ^{31}P resonance), as can be seen from the structure and the ^{13}C NMR data, there are two sets of chemically inequivalent Ph groups associated with the $PMePh_2$ ligands of 4.

The (triphenylphosphino)carbyne ligand ($Ph_3P{-}C^{2-}$) is isolobal with the oxo ligand (O^{2-}), and in 4 it acts as a 4-electron donor and gives the d^2 metal center its full 18-electron complement. This isolobal analogy is reflected in the structural similarities between 4 and $W(O)Cl_2(CO)(PMePh_2)_2$.[12] The $CPPh_3$ ligand is situated trans to a chloride ligand and exerts a modest trans lengthening influence on Cl(1) with respect to Cl(2) that is trans to the carbonyl ligand (2.555 (2) Å vs 2.501 (2) Å); the magnitude of this trans influence is only slightly less than that observed for the oxo ligand of $W(O)Cl_2(CO)(PMePh_2)_2$ (Δ = 0.09 Å). The ligand is bound to W in a nearly linear fashion (W–C(2)–P(3) = 171.2 (5)°) with a short W–C(2) bond length of 1.823 (7) Å that is in the range (1.75–1.83 Å)[28] typical of the W–C triple-bond distance observed in various tungsten alkylidyne complexes (cf. 1.759 (9) Å in $[(t\text{-}BuO)_3W(\equiv CMe)]_2$;[29] 1.82 (2) Å in $CpW(CO)_2(\equiv C\text{-tolyl})$;[30] 1.785 (8) Å in $W(\equiv CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$[31]). The metrical parameters for the $W\equiv C{-}PPh_3$ fragment of 4 are identical, within experimental error, with the corresponding values observed in $[W_2(\equiv CPMe_3)_2Cl_4(PMe_3)_4{}^{2+}][AlCl_4{}^-]_2$ (where W–C = 1.83 (3) Å; C–P = 1.71 (3) Å; W–C–P = 174.0 (19)°).[20]

Conclusions

We have demonstrated the sequential cleavage of 2 equiv of carbon monoxide from a molecule of carbon suboxide (O=C=C=C=O) at a tungsten center. The first CO extrusion reaction yields a complex, $WCl_2(CO)(PMePh_2)_2\{C,C'{:}\eta^2\text{-}C(O)CPMePh_2\}$ (**2**), in which the "C_2O" fragment has been incorporated as a phosphoranylidene ketene ligand. Complex **2** is then subject to another facile CO loss to yield $WCl_2(CO)(PMePh_2)_2(\equiv CPMePh_2)$ (**3**), a compound in which a "C" fragment, whose origin was shown by labeling studies to be the central carbon atom of C_3O_2, is present as a (diphenylmethylphosphino)carbyne ligand. A triphenylphosphine derivative, $WCl_2(CO)(PMePh_2)_2(\equiv CPPh_3)$ (**4**), can be directly prepared by oxidative cleavage of a C=C bond of $Ph_3PC{=}C{=}O$ by $WCl_2(PMePh_2)_4$. Both **2** and **4** have been structurally characterized by X-ray diffraction methods. X-ray structural characterization of **4** was particularly important because unusual coupling constants (^{13}C, ^{31}P NMR) associated with the phosphinocarbyne ligands in **3** and **4** made unambiguous characterization of these complexes difficult. These results are important ones in our study of the organometallic chemistry of carbon suboxide and phosphoranylidene ketenes because they provide clear, structural evidence that these molecules can be useful synthons to novel C_1 and C_2 organometallic fragments.

Acknowledgment. Financial support of the National Science Foundation (Grant CHE-8818607), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a fellowship from the Alfred P. Sloan Foundation (1989–1991) is sincerely appreciated by G.L.H. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant (NIH-CA-14599). We wish to thank Prof. William Kaska for providing us with samples of Ph_3PC_2O and $(Ph_3P)_2C$ and for helpful discussions regarding these reagents.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters and hydrogen-atom coordinates (5 pages); a table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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(28) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

(29) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

(30) Huttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1976–1977**, *15*, 133.

(31) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.