Organometallics **1989**, *8*, 89–93

Many of the hydrogen atom positions were visible in a difference Fourier phased on the non-hydrogen atoms. Positions were calculated for all hydrogens assuming idealized geometry (with d(C–H) = 0.95 Å), and they were included as fixed atom contributors in the final cycles. A ψ scan indicated there was a significant absorption effect, and the data were thus corrected before the final cycles of refinement. A final difference Fourier was essentially featureless, with the largest peak being 1.3 e/Å^3 at the location of W(1).

$W_2(\mu\text{-}C_2Me)_2(O\text{-}i\text{-}Pr)_4$. Techniques identical with the above were used for handling and characterization of the crystal used and led to the assignment of the orthorhombic space group *Pnam* (alternate setting of *Pnma*, No. 62). An analytical absorption correction was applied to the data. Direct methods and Fourier techniques were again utilized, and hydrogen atoms were visible in a difference Fourier synthesis. For the final refinement, all non-hydrogen atoms were varied anisotropically, and hydrogen atoms were included as fixed atom contributors.

A final difference Fourier was featureless, the largest peak being 0.62 e/Å^3.

Acknowledgment. We thank the Department of Energy, Office of Basic Sciences Division for support. B.W.E. was the Indiana University SOHIO graduate fellow, 1985–1987.

Registry No. **1a** (*i*-Pr), 110456-68-3; **1a** (Et), 110433-53-9; **1a** (Me), 116563-29-2; **3a**, 110456-67-2; *syn*-**3b**, 116784-33-9; *anti*-**3b**, 116839-39-5; **3c**, 116784-34-0; **4** (Et), 110433-54-0; **4** (Me), 116840-29-0; **5**, 116784-35-1; $W_2(i\text{-}Bu)_2(NMe_2)_4$, 101860-16-6; EtC≡CEt, 928-49-4; MeC≡CMe, 627-21-4; ethylene, 74-85-1.

Supplementary Material Available: For $W_4(CEt)_2(MeCCMe)_4(O\text{-}i\text{-}Pr)_6$ and $W_2(\mu\text{-}C_2Me_2)_2(O\text{-}i\text{-}Pr)_4$, tables of anisotropic thermal parameters and complete listings of bond distances and angles (7 pages); listings of F_o and F_c values (11 pages). Ordering information is given on any current masthead page.

Metal Alkoxides: Models for Metal Oxides. 14.[1] Carbonylation of an Ethylidyne-Capped Tritungsten Alkoxide Cluster To Form $W_3(\mu\text{-}CMe)(O\text{-}i\text{-}Pr)_9(CO)_2$: Preparation, Properties, and Structure

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We have investigated the reactions between $W_3(\mu_3\text{-}CMe)(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$ and each of the alkynes (MeC≡CMe, PhC≡CH, HC≡CH, $CF_3C{\equiv}CCF_3$), ethylene, molecular hydrogen, and carbon monoxide (separately) at 1 atm and room temperature. The tritungsten ethylidyne capped cluster failed to show reactivity toward ethylene, H_2, and the alkynes MeC≡CMe and PhC≡CH. With HC≡CH and $CF_3C{\equiv}CCF_3$ polymerization of the alkyne occurred, but no detectable reaction with the tritungsten cluster was observed. However, carbon monoxide (2 equiv) was rapidly taken up to give, upon crystallization, black crystals of a compound of formula $W_3(CMe)(O\text{-}i\text{-}Pr)_9(CO)_2$. In the solid state an unusual structure is found involving a chain, or open triangle of W atoms (W–W–W = 150°), that may be best viewed as a d^1–d^1 alkylidyne-bridged moiety linked by three O-*i*-Pr ligands to a distorted octahedral d^4 *cis*-$W^{II}(CO)_2$ center: $(i\text{-}PrO)_3W(\mu\text{-}CMe)(\mu\text{-}O\text{-}i\text{-}Pr)W(O\text{-}i\text{-}Pr)(\mu\text{-}O\text{-}i\text{-}Pr)_3W(O\text{-}i\text{-}Pr)(CO)_2$. The W–W distance supported by the μ-CMe and μ-O-*i*-Pr ligands is 2.658 (1) Å comparable to that of the d^1–d^1 compound $(i\text{-}PrO)_2W(\mu\text{-}CSiMe)_2W(O\text{-}i\text{-}Pr)_2$. The other W-to-W distance is typical of a nonbonding distance. There is NMR evidence that the essential features of the solid-state structure are maintained in solution. NMR data for the ^{13}C-labeled compounds $W_3(^*CMe)(O\text{-}i\text{-}Pr)_9(CO)_2$ and $W_3(CMe)(O\text{-}i\text{-}Pr)_9(^*CO)_2$ reveal δ 313 ($J_{^{183}W-^{13}C}$ = 150 Hz) (24% intensity) for $W_2(\mu\text{-}^*CMe)$ and δ 267 and 264 with $J_{^{183}W-^{13}C}$ = ca. 190 Hz (15% intensity) and $J_{^{13}C-^{13}C}$ = 12.2 Hz. Crystal data for $W_3(CMe)(O\text{-}i\text{-}Pr)_9(CO)_2$ at −140 °C: α = 11.673 (4) Å, b = 18.640 (8) Å, c = 10.285 (3) Å, α = 102.38 (2)°, β = 103.04 (2)°, γ = 72.43 (2)°, Z = 2, d_{calcd} = 1.887 g cm^{-3}, and space group $P\bar{1}$.

Introduction

Ethylidyne ligands have been known to be present on the surface of various metals for a number of years now, and their formation can be monitored starting from a clean metal surface and ethylene.[2,3] Alkylidyne ligands are also well-known in carbonyl cluster chemistry, and the alkylidyne capped tricobalt nonacarbarbonyl compounds represent some of the earliest known and best studied examples of this class.[4,5] Our discovery of $W_3(\mu_3\text{-}CMe)(O\text{-}i\text{-}Pr)_9$[6] and related $W_3(\mu\text{-}CR)(OR')_9$ compounds[7] provided the first examples of μ_3-alkylidyne ligands supported entirely by oxygen donor ligands with coordinative unsaturation still present at the metal centers.[8] The square-based pyram-

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(2) E.g. on Pt surfaces, see: Somorjai, G. A. In *Chemistry in Two Dimensions: Surfaces*; Cornell University: Ithaca, NY, 1981; p 278.

(3) For a μ-vinylidene to μ-ethylidyne conversion see: Hills, M. M.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597.

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(8) Alkylidyne-capped compounds of formula $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(OAc)_6(H_2O)_3](anion)_x{\cdot}yH_2O$ have previously been obtained as products in the reactions between $Mo(CO)_6$ and carboxylic acids, RCOOH, where X, Y = O and/or alkylidyne: Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 234.

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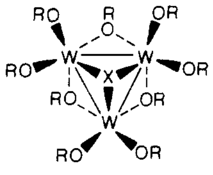
idal coordination about tungsten in these complexes is emphasized in the stick drawing I.



I, X = CMe

Previously we have reported[9] on reactions between $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9$ and each of L_2MCl_2 where L = PhCN and M = Pd and Pt which led to chlorine atom transfer and formation of $W_3(CMe)(O\text{-}i\text{-Pr})_9(Cl)_2$ along with M(0). A similar Cl atom transfer was achieved in reactions involving $HgCl_2$ and C_2Cl_6. These findings testify to the ease of oxidation of the $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9$ compound. [The original intention of the reactions involving $(PhCN)_2MCl_2$ where M = Pd or Pt was heterometallic cluster synthesis.]

We report here on reactions involving $W_3(\mu\text{-CMe})(O\text{-}i\text{-Pr})_9$ and alkynes, ethylene, dihydrogen, and carbon monoxide. These reactions were initiated in the hope of seeing carbon–carbon or carbon–hydrogen bond formation. Keister and co-workers[10] in studies of reactions of $Ru_3(\mu_3\text{-CR})(\mu\text{-H})_3(CO)_9$ with an alkyne, and subsequently H_2 have observed initial C–C bond formation and alkylidyne–alkyne coupling followed by hydrogenation of the C_3R_3 ligand.

Results and Discussion

Reactions. With Alkynes. Benzene-d_6 solutions of I and each of the alkynes, HC≡CH, MeC≡CMe, PhC≡CH, and $CF_3C{\equiv}CCF_3$, fail to react at room temperature. In the case of HC≡CH and $CF_3C{\equiv}CCF_3$, alkyne polymerization was observed, but $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9$ was unaffected as shown by ^1H NMR spectroscopy.

With Ethylene and H_2. When C_6D_6 solutions of $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9$ were exposed to ethylene and H_2 (separately, 1 atm at 22 °C), no apparent reaction occurred and only unreacted $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9$ was observed by ^1H NMR spectroscopy even after 2 weeks.

With Carbon Monoxide. When hydrocarbon solutions of $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9$ are exposed to CO at 22 °C, a rapid uptake of 2 equiv of CO occurs to give $W_3(CMe)(O\text{-}i\text{-Pr})_9(CO)_2$, according to eq 1.

$$\underset{\text{I}}{W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9} + 2CO \xrightarrow[\text{hexane}]{22\ °C} \underset{\text{II}}{W_3(CMe)(O\text{-}i\text{-Pr})_9(CO)_2} \quad (1)$$

No monocarbonyl intermediate(s) could be detected when only 1 equiv of CO was added to $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-Pr})_9$. The second uptake of CO is apparently more rapid than the first, and from labeling studies the dicarbonyl compound II is not labile toward loss of CO.

Spectroscopic Characterization of $W_3(CMe)(O\text{-}i\text{-Pr})_9(CO)_2$: NMR Studies. The ^1H and ^{13}C NMR spectra of II indicate the presence of nine types of O-*i*-Pr ligands each having diastereotopic methyl groups. This indicates a nonfluxional molecule is present in solution and further that the molecule has no molecular plane or other element of symmetry.

In addition to the alkoxide signals there were in the ^{13}C NMR spectrum three low-field signals at δ 313, 267, and 264 that are readily attributable to the alkylidyne and carbonyl carbon atoms. The specifically ^{13}C-labeled compounds $W_3(^{13}CMe)(O\text{-}i\text{-Pr})_9(CO)_2$ and $W_3(CMe)(O\text{-}i\text{-Pr})_9(^{13}CO)_2$ were employed to allow identification of the alkylidyne and carbonyl signals and the connectivity of these ligands to the three tungsten atoms by examination of the satellite signals arising from coupling to ^{183}W (I = 1/2, 14.5% natural abundance). See Figure 1.

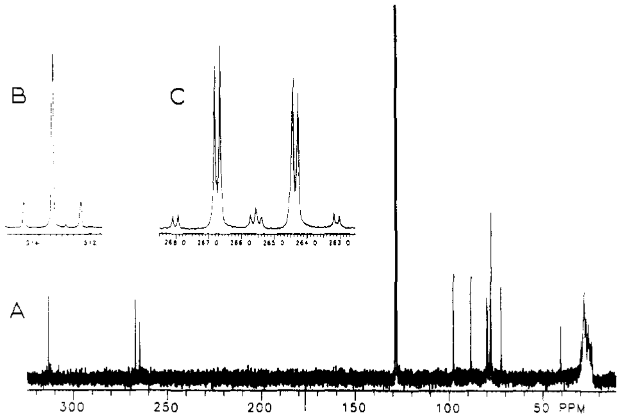


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of $W_3(CMe)(O\text{-}i\text{-Pr})_9(CO)_2$ in C_6D_6: (A) natural abundance; (B) $W_3(^{13}CMe)(O\text{-}i\text{-Pr})_9(CO)_2$; (C) $W_3(CMe)(O\text{-}i\text{-Pr})_9(^{13}CO)_2$.

The alkylidyne carbon signal at δ 313 shows $J_{^{183}W-^{13}C}$ = 150.3 Hz with satellites of 24% total intensity. This is indicative of the presence of a $W_2(\mu\text{-CMe})$ moiety in which the two tungsten atoms are in essentially equivalent environments. Significantly there is no alkylidyne–carbonyl coupling which implies that the CO ligands are not bonded to the $W_2(\mu\text{-CMe})$ moiety. The carbonyl signals, δ 267 and 264, show coupling to tungsten $J_{^{183}W-^{13}C}$ = 189.4 and 193.3 Hz, respectively, with a satellite intensity of 14%. This is indicative of terminal W–CO ligands, and the $J_{^{13}C-^{13}C}$ value of 12.2 Hz is clear evidence that both CO ligands are attached to the same tungsten atom.

Infrared Spectra. The IR spectrum of the natural abundance compound (KBr pellet) shows a pair of low energy CO stretching frequencies: $\nu(CO)$ = 1900 and 1760 cm^{-1} which shift to 1850 and 1720 cm^{-1} for $W_3(CMe)(O\text{-}i\text{-Pr})_9(^{13}CO)_2$. This is a clear indication of a *cis*-$W(CO)_2$ moiety, and the low values of $\nu(CO)$ are reminiscent of those seen in the d^4 *cis*-$Mo(CO)_2$ containing compound $Mo(O\text{-}t\text{-Bu})_2(py)_2(CO)_2$: $\nu(CO)$ = 1908 and 1768 cm^{-1}.[11]

Collectively the spectroscopic data provide us with the following suggestion with respect to structure. (1) There is a d^1–d^1 $W_2(\mu\text{-CMe})$ moiety and (2) a d^4 *cis*-$W(CO)_2$ group. (3) These two units are supported by alkoxide groups, both bridging and terminal, such that the molecule lacks any overall symmetry element in solution. In the presence of the π-donor RO ligands one might anticipate a pseudooctahedral coordination for the d^4 *cis*-$W(CO)_2$ moiety, but beyond this the complementary coordination for the $W_2(\mu\text{-CMe})$ moiety cannot be reliably predicted.

Solid-State and Molecular Structure. In the space group $P\bar{1}$, there is one molecule in the asymmetric unit. As predicted on spectroscopic grounds, there is an opened triangle of tungsten atoms, W(1)–W(2)–W(3) = 150°, with the W(1)–W(2) distance, 2.658 (1) Å, consistent with a d^1–d^1 distance supported by an alkylidyne and an alkoxide ligand, cf. W–W = 2.62 Å, $(i\text{-PrO})_4W_2(\mu\text{-CSiMe}_3)_2$.[12] The

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for $W_3(\mu\text{-CMe})(\text{O-}i\text{-Pr})_9(\text{CO})_2$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
W(1)	5740 (1)	2363 (1)	6090 (1)	34
W(2)	3562 (1)	2775 (1)	4561 (1)	21
W(3)	1587 (1)	2385 (1)	2156 (2)	55
O(4)	5138 (13)	2829 (9)	4327 (15)	20 (3)
C(5)	5592 (25)	3128 (16)	3368 (28)	33 (5)
C(6)	5427 (29)	3967 (19)	3856 (33)	46 (7)
C(7)	6904 (35)	2707 (22)	3284 (39)	62 (8)
C(8)	4167 (26)	2139 (17)	5964 (30)	38 (6)
C(9)	3753 (34)	1634 (22)	6604 (38)	58 (8)
O(10)	2434 (13)	3241 (8)	2726 (15)	18 (3)
C(11)	2184 (22)	3928 (14)	2396 (25)	25 (5)
C(12)	843 (34)	4436 (21)	2401 (38)	58 (8)
C(13)	2637 (40)	3954 (26)	1067 (46)	76 (10)
O(14)	3603 (15)	1915 (10)	2986 (17)	29 (3)
C(15)	4681 (40)	1100 (25)	2234 (46)	73 (10)
C(16)	4124 (55)	693 (35)	2968 (62)	110 (16)
C(17)	4420 (46)	1102 (29)	828 (53)	90 (13)
O(18)	1892 (18)	2584 (11)	4318 (20)	42 (4)
C(19)	1107 (35)	2795 (23)	5375 (40)	63 (9)
C(20)	145 (29)	3526 (19)	5148 (33)	47 (7)
C(21)	278 (49)	2108 (31)	4867 (56)	98 (14)
O(22)	5791 (17)	3324 (11)	7080 (20)	39 (4)
C(23)	6780 (31)	3556 (20)	8142 (36)	51 (7)
C(24)	6141 (33)	4255 (21)	9095 (38)	58 (8)
C(25)	7712 (39)	3690 (25)	7556 (44)	72 (10)
O(26)	6703 (16)	1529 (10)	5075 (18)	33 (4)
C(27)	7698 (30)	882 (19)	5464 (34)	47 (7)
C(28)A	7736 (54)	190 (35)	4245 (62)	41 (12)
C(29)A	8733 (54)	1010 (35)	6122 (62)	40 (12)
C(28)B	7302 (53)	393 (34)	5601 (60)	39 (12)
C(29)B	8422 (58)	716 (37)	4126 (66)	45 (13)
O(30)A	6782 (26)	2041 (17)	7625 (28)	13 (5)
C(31)A	6726 (41)	1797 (26)	8859 (47)	20 (8)
C(32)A	7976 (48)	1537 (31)	9670 (55)	32 (10)
C(33)	5539 (59)	2403 (37)	9659 (66)	126 (19)
O(30)B	6350 (29)	1787 (18)	7633 (31)	20 (6)
C(31)B	6029 (43)	1535 (28)	8711 (49)	23 (9)
C(32)B	7187 (54)	1222 (35)	9638 (62)	40 (12)
O(34)	3036 (14)	3765 (9)	5425 (15)	21 (3)
C(35)	3104 (23)	4333 (15)	6621 (27)	30 (5)
C(36)	2241 (24)	5085 (15)	6330 (28)	32 (5)
C(37)	2823 (29)	4033 (19)	7778 (33)	46 (7)
C(38)	−19 (45)	2877 (28)	1674 (50)	83 (12)
O(39)	−1162 (25)	3136 (16)	1311 (28)	70 (6)
C(40)A	622 (45)	1625 (29)	2399 (51)	26 (9)
O(41)A	28 (30)	1213 (20)	2388 (35)	29 (7)
C(40)B	1343 (71)	2604 (46)	−127 (85)	62 (18)
O(41)B	1121 (31)	2711 (20)	−1165 (37)	31 (7)
O(42)A	1940 (26)	1890 (16)	624 (29)	17 (5)
C(43)A	1272 (47)	1601 (30)	−476 (54)	31 (10)
C(44)A	2086 (52)	885 (33)	−1136 (60)	38 (12)
C(45)A	709 (55)	2217 (35)	−1420 (62)	39 (12)
O(42)B	1519 (27)	1399 (17)	1498 (31)	21 (6)
C(43)B	719 (47)	996 (30)	451 (54)	31 (10)
C(44)B	279 (48)	510 (31)	1202 (55)	32 (10)
C(45)B	1459 (54)	495 (35)	−619 (62)	41 (12)

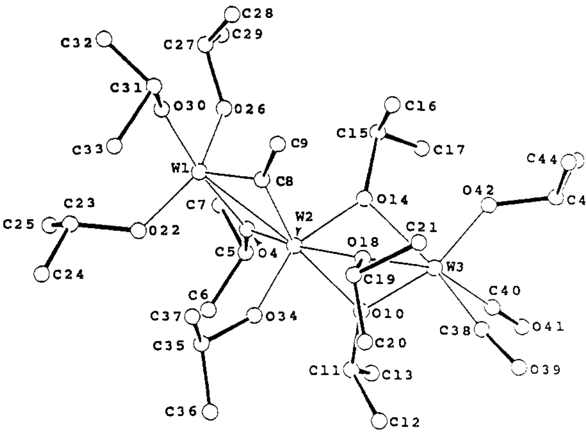

Figure 2. Ball-and-stick drawing of $W_3(\mu\text{-CMe})(\text{O-}i\text{-Pr})_9(\text{CO})_2$. Bond distances and angles are listed in Tables II and III, respectively.

Table II. Bond Distances (Å) for $W_3(\mu\text{-CMe})(\text{O-}i\text{-Pr})_9(\text{CO})_2$

A	B	dist	A	B	dist
W(1)	W(2)	2.6577 (18)	W(2)	C(8)	1.94 (3)
W(1)	O(4)	2.067 (15)	W(3)	O(10)	2.038 (15)
W(1)	O(22)	1.872 (20)	W(3)	O(14)	2.281 (17)
W(1)	O(26)	1.884 (18)	W(3)	O(18)	2.140 (20)
W(1)	O(30)A	1.853 (27)	W(3)	O(42)A	1.72 (3)
W(1)	O(30)B	1.98 (3)	W(3)	O(42)B	1.84 (3)
W(1)	C(8)	1.97 (3)	W(3)	C(38)	1.83 (5)
W(2)	W(3)	3.1031 (20)	W(3)	C(40)A	2.14 (5)
W(2)	O(4)	1.943 (15)	W(3)	C(40)B	2.41 (8)
W(2)	O(10)	2.223 (14)	O(39)	C(38)	1.27 (5)
W(2)	O(14)	2.018 (18)	O(41)A	C(40)A	1.18 (6)
W(2)	O(18)	2.038 (20)	O(41)A	C(44)B	1.59 (6)
W(2)	O(34)	1.852 (15)	O(41)B	C(40)B	1.09 (8)
			C(8)	C(9)	1.50 (5)

other W–W distance, W(2)–W(3) = 3.10 Å, is effectively a nonbonding distance and may be compared to the W-to-W distance found in the molecule $(i\text{-PrO})_4W(\mu\text{-O-}i\text{-Pr})_2W(\text{CO})_4$ which may be viewed as a W(VI)–$W(\text{O-}i\text{-Pr})_6$ molecule being coordinated by a pair of alkoxide ligands to a W(0)–$W(\text{CO})_4$ fragment.[13]

The local geometry about W(3) is that of a distorted octahedron while that about both W(1) and W(2) is a distorted trigonal bipyramid. The two fused trigonal bipyramids (tbps) share a common equatorial–axial edge involving the ethylidyne and isopropoxide ligands, respectively. The W–O(bridging and terminal) and W–C distances are well within anticipated ranges. Regrettably there are two crystallographic disorder problems. At W(1) there are two disordered O-*i*-Pr ligands while at W(3) there is one undisordered W–CO moiety, but two other groups, CO and O-*i*-Pr, are disordered over two positions. The disordering does not alter the fundamental aspects of the structure, namely, two d^1–d^1 fused tbps sharing a μ-CMe and μ-O-*i*-Pr ligand and an octahedral d^4 *cis*-$W(\text{CO})_2$ moiety joined by three bridging O-*i*-Pr ligands. The disorder is indicated in Table I by atoms A and B. One of the molecules is shown in Figure 2, and the disordering is shown in detail in the supplementary material. Listings of pertinent bond distances and bond angles are given in Tables II and III.

Concluding Remarks

The lack of reactivity of $W_3(\mu\text{-CMe})(\text{O-}i\text{-Pr})_9$ toward ethylene and alkynes may well reflect steric access to the metal centers. In the observed polymerization of C_2H_2 and $CF_3C{\equiv}CCF_3$ we cannot be sure that this is in fact induced by the tritungsten ethylidyne compound since each of these alkynes is very readily polymerized. The observed reaction with CO is quite interesting. Two metal–metal bonds are sacrificed to form a d^4 *cis*-$W(\text{CO})_2$ center allowing maximum W d_π-to-CO π^* back-bonding. To our knowledge this type of reaction is not typical of carbonyl cluster chemistry, though CO uptake or loss is often accompanied by skeletal atom rearrangements that may even involve C–C bond formation and rupture.[14,15]

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Table III. Bond Angles (deg) for $W_3(\mu\text{-CMe})(O\text{-}i\text{-}Pr)_9(CO)_2$

A	B	C	angle
W(2)	W(1)	O(4)	46.5 (4)
W(2)	W(1)	O(22)	98.1 (6)
W(2)	W(1)	O(26)	107.5 (5)
W(2)	W(1)	O(30)A	153.9 (9)
W(2)	W(1)	O(30)B	133.1 (10)
W(2)	W(1)	C(8)	46.7 (8)
O(4)	W(1)	O(22)	90.1 (7)
O(4)	W(1)	O(26)	86.1 (7)
O(4)	W(1)	O(30)A	159.0 (11)
O(4)	W(1)	O(30)B	172.7 (10)
O(4)	W(1)	C(8)	92.0 (9)
O(22)	W(1)	O(26)	140.1 (8)
O(22)	W(1)	O(30)A	82.1 (11)
O(22)	W(1)	O(30)B	97.1 (11)
O(22)	W(1)	C(8)	112.7 (10)
O(26)	W(1)	O(30)A	87.4 (10)
O(26)	W(1)	O(30)B	87.4 (10)
O(26)	W(1)	C(8)	107.1 (10)
O(30)A	W(1)	O(30)B	23.5 (10)
O(30)A	W(1)	C(8)	109.0 (13)
O(30)B	W(1)	C(8)	86.6 (13)
W(1)	W(2)	W(3)	150.02 (6)
W(1)	W(2)	O(4)	50.5 (4)
W(1)	W(2)	O(10)	149.1 (4)
W(1)	W(2)	O(14)	103.5 (5)
W(1)	W(2)	O(18)	137.3 (6)
W(1)	W(2)	O(34)	99.2 (5)
W(1)	W(2)	C(8)	47.8 (9)
W(3)	W(2)	O(4)	122.9 (4)
W(3)	W(2)	O(10)	41.0 (4)
W(3)	W(2)	O(14)	47.3 (5)
W(3)	W(2)	O(18)	43.3 (6)
W(3)	W(2)	O(34)	110.8 (5)
W(3)	W(2)	C(8)	119.1 (9)
O(4)	W(2)	O(10)	98.6 (6)
O(4)	W(2)	O(14)	89.3 (7)
O(4)	W(2)	O(18)	165.7 (7)
O(4)	W(2)	O(34)	97.6 (6)
O(4)	W(2)	C(8)	97.0 (10)
O(10)	W(2)	O(14)	71.3 (6)
O(10)	W(2)	O(18)	72.6 (7)
O(10)	W(2)	O(34)	84.1 (6)
O(10)	W(2)	C(8)	159.9 (9)
O(14)	W(2)	O(18)	77.3 (8)
O(14)	W(2)	O(34)	155.2 (7)
O(14)	W(2)	C(8)	96.3 (10)
O(18)	W(2)	O(34)	92.7 (7)
O(18)	W(2)	C(8)	89.6 (10)
O(34)	W(2)	C(8)	106.4 (10)
W(2)	W(3)	O(10)	45.6 (4)
W(2)	W(3)	O(14)	40.5 (4)
W(2)	W(3)	O(18)	40.8 (5)
W(2)	W(3)	O(42)A	122.3 (9)
W(2)	W(3)	O(42)B	121.9 (9)
W(2)	W(3)	C(38)	131.6 (16)
W(2)	W(3)	C(40)A	117.2 (13)
W(2)	W(3)	C(40)B	126.2 (19)
O(10)	W(3)	O(14)	69.7 (6)
O(10)	W(3)	O(18)	74.3 (7)
O(10)	W(3)	O(42)A	108.6 (10)
O(10)	W(3)	O(42)B	154.2 (10)
O(10)	W(3)	C(38)	104.0 (16)
O(10)	W(3)	C(40)A	156.7 (14)
O(10)	W(3)	C(40)B	86.6 (19)
O(14)	W(3)	O(18)	69.8 (7)
O(14)	W(3)	O(42)A	85.6 (10)
O(14)	W(3)	O(42)B	88.0 (10)
O(14)	W(3)	C(38)	172.0 (16)
O(14)	W(3)	C(40)A	108.0 (14)
O(14)	W(3)	C(40)B	110.1 (19)
O(18)	W(3)	O(42)A	152.8 (11)
O(18)	W(3)	O(42)B	110.8 (11)
O(18)	W(3)	C(38)	104.2 (16)
O(18)	W(3)	C(40)A	83.1 (14)
O(18)	W(3)	C(40)B	159.8 (20)
O(42)A	W(3)	O(42)B	55.1 (13)
O(42)A	W(3)	C(38)	101.2 (18)
O(42)A	W(3)	C(40)A	94.1 (17)
O(42)A	W(3)	C(40)B	40.9 (21)
O(42)B	W(3)	C(38)	99.2 (18)
O(42)B	W(3)	C(40)A	42.3 (17)
O(42)B	W(3)	C(40)B	89.3 (21)
C(38)	W(3)	C(40)A	75.8 (20)
C(38)	W(3)	C(40)B	73.6 (24)
C(40)A	W(3)	C(40)B	115.0 (23)
W(1)	O(4)	W(2)	83.0 (6)
W(1)	O(4)	C(5)	140.8 (14)
W(2)	O(4)	C(5)	136.1 (14)
W(2)	O(10)	W(3)	93.4 (6)
W(2)	O(10)	C(11)	129.2 (13)
W(3)	O(10)	C(11)	134.9 (13)
W(2)	O(14)	W(3)	92.2 (7)
W(2)	O(14)	C(15)	139.9 (17)
W(3)	O(14)	C(15)	127.7 (17)
W(2)	O(18)	W(3)	95.8 (8)
W(2)	O(18)	C(19)	125.7 (20)
W(3)	O(18)	C(19)	135.5 (19)
W(1)	O(22)	C(23)	129.7 (18)
W(1)	O(26)	C(27)	132.3 (18)
W(1)	O(30)A	O(30)B	88 (3)
W(1)	O(30)A	C(31)A	138.9 (27)
O(30)B	O(30)A	C(31)A	58 (3)
W(1)	O(30)B	O(30)A	69 (3)
W(1)	O(30)B	C(31)A	148 (3)
W(1)	O(30)B	C(31)B	146.0 (28)
W(2)	O(34)	C(35)	149.8 (15)
W(3)	O(42)A	O(42)B	66.2 (15)
W(3)	O(42)A	C(40)B	94 (3)
W(3)	O(42)A	C(43)A	132 (3)
W(3)	O(42)B	O(42)A	58.7 (14)
W(3)	O(42)B	C(40)A	80.1 (25)
W(3)	O(42)B	C(43)B	138 (3)
W(1)	C(8)	W(2)	85.6 (12)
W(1)	C(8)	C(9)	134.5 (23)
W(2)	C(8)	C(9)	139.6 (23)
W(3)	C(38)	O(39)	173 (4)
W(3)	C(40)A	O(41)A	173 (4)
W(3)	C(40)A	O(42)B	57.6 (21)
W(3)	C(40)B	O(41)B	173 (6)
W(3)	C(40)B	O(42)A	45.3 (24)
W(3)	C(40)B	C(43)A	81 (3)
W(3)	C(40)B	C(45)A	129 (5)

Experimental Section

General Data. Dry, oxygen-free solvents and atmospheres were used throughout. Reactions were run and all manipulations done by using standard Schlenk and drybox techniques. The starting material $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-}Pr)_9$ was prepared as reported earlier.[6]

^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (^1H, 300 MHz; ^{13}C, 75.4 MHz) in benzene-d_6. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 283 spectrometer.

$W_3(\mu_2\text{-CMe})(O\text{-}i\text{-}Pr)_9(CO)_2$. $W_3(\mu_3\text{-CMe})(O\text{-}i\text{-}Pr)_9$ (0.765 g, 0.65 mmol) was dissolved in 30 mL of benzene in a 200-mL Schlenk flask. The flask was evacuated, backfilled with 1 atm of CO, and stirred at room temperature for 26 h. The volatiles were removed in vacuo, the residues were extracted with 10 mL hexane, a small amount of insoluble material was filtered off, and the volume of the filtrate was reduced to ca. 2 mL. Cooling the solution to −15 °C for 3 days provided 395 mg (52% yield) of II as black crystals. The ^{13}C-labeled $W_3(\mu_2\text{-CMe})(O\text{-}i\text{-}Pr)_9(^{13}CO)_2$ was prepared in the same way except that 2 equiv of ^{13}CO were added via a gas-tight syringe. $W_3(\mu\text{-}^{13}CMe)(O\text{-}i\text{-}Pr)_9$ was prepared from $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and $(t\text{-}BuO)_3W{\equiv}^{13}CMe$.

$W_3(O\text{-}i\text{-}Pr)_9(\mu_2\text{-CMe})(CO)_2$. ^1H NMR (300 MHz, C_6D_6, 22 °C): δ 5.92, 5.62, 5.57, 5.42, 5.26, 4.71, 4.53, 4.36, 4.19 (multiplets), 4.95 (1 H, s), a series of overlapping doublets are observed between 1.6 and 0.75 ppm for the isopropoxy methyl groups. $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 22 °C): δ 313.1 (J_{WC} = 150.3 Hz, I = 24%), 266.8 (J_{WC} = 189.4 Hz, I = 14%), 264.5 (J_{WC} = 193.3 Hz, I = 16%),

Table IV. Summary of Crystal Data

empirical formula	$C_{31}H_{66}O_{11}W_3$
color of crystal	black
cryst dimens (mm)	0.22 × 0.04 × 0.12
space group	$P\bar{1}$
cell dimens	
temp (°C)	−140
a (Å)	11.673 (4)
b (Å)	18.640 (8)
c (Å)	10.285 (3)
α (deg)	102.38 (2)
β (deg)	103.04 (2)
γ (deg)	72.43 (2)
Z (molecules/cell)	2
V (Å^3)	2052.50
d (g/cm^3)	1.887
wavelength (Å)	0.710 69
mol wt	1166.41
linear absorptn coeff (cm^{-1})	86.151
detector to sample dist (cm)	22.5
sample to source dist (cm)	23.5
takeoff angle (deg)	2.0
av ω scan width at half-height	0.25
scan speed (deg/min)	4.0
scan width (deg + dispersion)	1.8
individual bkgd (s)	8
aperture size (mm)	3.0 × 4.0
2θ range (deg)	6–45
total no. of reflections collected	5987
no. of unique intensities	5370
no. with $F > 0.0$	4976
no. with $F > 3.0\sigma(F)$	4685
$R(F)$	0.0985
$R_w(F)$	0.0966
goodness of fit for the last cycle	3.176
max δ/σ for last cycle	0.12

97.4, 97.3, 88.1, 79.5, 79.2, 77.7, 77.6, 77.5, 77.3, 71.8, 41.1, several overlapping peaks are observed between 30 and 23 ppm for the isopropoxy methyl groups.

W_3(O-*i*-Pr)$_9$(μ_2-CMe)(^{13}CO)$_2$. ^{1}H NMR: δ 266.8, 264.5 (J_{CC} = 12.2 Hz). IR (cm^{-1}, KBr): ν(CO) 1900, 1760; ν(^{13}CO) 1850, 1720. Anal. Calcd for $W_3C_{31}H_{66}O_{11}$: C, 31.93; H, 5.66. Found: C, 31.70; H, 5.56.

Reactions Involving Ethylene and Dihydrogen. With H_2. W_3(μ_3-CMe)(O-*i*-Pr)$_9$ was dissolved in C_6D_6 in a 5-mm NMR tube and exposed to 1 atm of H_2. Allowing this solution to stand at room temperature for 2 weeks, with ^{1}H NMR monitoring, resulted in no reaction with H_2.

With C_2H_4. W_3(μ_3-CMe)(O-*i*-Pr)$_9$ was dissolved in C_6D_6 in a 5-mm NMR tube, and 5 equiv of C_2H_4 was added by using a calibrated vacuum line. Allowing the solution to stand at room temperature for 2 weeks resulted in no reaction except slight thermal decomposition of the starting material as shown by ^{1}H NMR spectroscopy.

Reactions Involving Alkynes. W_3(μ_3-CMe)(O-*i*-Pr)$_9$ was dissolved in C_6D_6 in a 5-mm NMR tube and treated with 2–3 equiv of one of the alkynes $MeC\equiv CMe$, $PhC\equiv CH$, $HC\equiv CH$ or $CF_3C\equiv CCF_3$. Allowing the solution to stand at room temperature for several days resulted in no reaction for $MeC\equiv CMe$ and $PhC\equiv CH$ as shown by ^{1}H NMR spectroscopy. For reactions with $HC\equiv CH$ and $CF_3C\equiv CCF_3$, abundant precipitate formed within 12 h but ^{1}H NMR spectroscopy showed W_3(μ_3-CMe)(O-*i*-Pr)$_9$ to still be present.

Crystallography Studies. A listing of programs and procedures used at the Indiana University Molecular Structure Center have been previously given.[16] A summary of crystal data is given in Table IV.

A suitable small crystal was selected under inert-atmosphere conditions. The sample was transferred to the goniostat where it was cooled to −140 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry (other than a center) and no systematic extinctions. The reflections were indexed by using a triclinic lattice, and the choice of the centrosymmetric space group $P\bar{1}$ was confirmed by the subsequent solution and refinement of the structure. A total of 5987 reflections were collected, and, following the usual data processing and averaging of equivalent reflections, a unique set of 5370 reflections remained. The R for the averaging was 0.026 for 533 reflections observed more than once. Four standard reflections measured every 300 reflections showed no systematic trends.

The structure was solved by using the usual combination of direct methods and difference Fourier techniques. The three W atoms were located in the initial E map and the remaining atoms in successive difference maps. It quickly became obvious that several of the substituent groups were affected by disorder. Careful inspection of difference maps eventually resulted in the pattern of disorder indicated in the tables by atoms A and B. At W(1) the disorder involves two of the isopropoxy groups, and at W(3) we find one ordered CO group together with two disordered CO groups and two disordered isopropoxy groups. The complete pattern of disorder is described in the supplementary material, while the ball-and-stick diagram (Figure 2) is drawn omitting the disordered atom labeled B.

The full-matrix least-squares refinement was completed by using a partial occupancy parameter for each of the disordered atoms, anisotropic thermal parameters for the three W atoms and isotropic thermal parameters for the remaining atoms. No attempts were made at including hydrogen atoms. The final R was 0.098. The final difference map contains numerous peaks of about 1.5–3.0 e/Å^3. The top 12 peaks are within 1.5 Å of the W atoms, and several others are found in the vicinity of the disordered atoms.

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Registry No. I, 92054-28-9; II, 117203-01-7; W_3(μ-^{13}CMe)(O-*i*-Pr)$_9$, 117203-00-6; W_3(μ_2-CMe)(O-*i*-Pr)$_9$(^{13}CO)$_2$, 117226-17-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and bond distances and bond angles and ball-and-stick drawings showing the disordering of the ligands (20 pages); a listing of F_o and F_c values (13 pages). Ordering information is given on any current masthead page.

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(16) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.