

# Metal Alkoxides: Models for Metal Oxides. 7.<sup>1</sup> Trinuclear and Tetranuclear Alkylidyne Clusters of Tungsten Supported by Alkoxide Ligands

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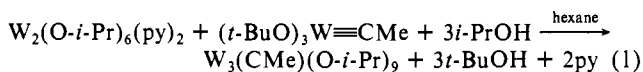
**Abstract:** The ethylidyne capped triangulo compound  $W_3(\mu_3\text{-CMe})(\mu_2\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$  is formed competitively with  $W_2(\text{O-}i\text{-Pr})_6(\mu\text{-C}_4\text{Me}_4)(\text{C}_2\text{Me}_2)$  in the reaction between  $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$  and 1 equiv of  $\text{MeC}\equiv\text{CMe}$  and is the major and sole isolable product in the reaction between  $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$  and  $(t\text{-BuO})_3\text{W}\equiv\text{CMe}$  carried out in hexane/*i*-PrOH. Similarly,  $(t\text{-BuO})_3\text{W}\equiv\text{CMe}$  and  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$  react in hexane/*i*-PrOH to give  $\text{Mo}_2\text{W}(\text{CMe})(\text{O-}i\text{-Pr})_9$ , which is isomorphous with the tungsten compound. The  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  molecule has virtual  $C_{3v}$  symmetry: each tungsten atom is in a square based pyramidal geometry with the W-C bond in the apical position. Pertinent averaged bond distances (Å) are W-W = 2.74 (1), W-C = 2.06 (1), W-O = 1.91 (1) (terminal OR), and W-O = 2.04 (2) (bridging OR). Variable-temperature <sup>1</sup>H NMR studies on the  $W_3$  and  $\text{Mo}_2\text{W}$  compounds indicate that a similar structure is maintained in solution and that site exchange between the terminal *O-}i\text{-Pr}* ligands involves a pseudorotation mechanism. No evidence is found for bridge ⇌ terminal exchange on the NMR time scale. The reaction between  $(\text{Me}_3\text{SiCH}_2)_4\text{W}_2(\mu\text{-CSiMe}_3)_2$  and excess EtOH in hexane yields  $W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$  and  $\text{Me}_4\text{Si}$ . In the solid state, there are discrete centrosymmetric  $W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$  molecules. The four tungsten atoms form a zigzag chain, W-W-W = 141.64 (2)°, with alternating short, 2.516 (1) Å, and long, 3.513 (1) Å, distances corresponding formally to W-W single and nonbonding distances, respectively. The molecule may be viewed as a dimer [ $W_2(\mu\text{-CSiMe}_3)(\text{OEt})_7$ ]<sub>2</sub> with the two halves being joined by a pair of alkoxy bridges. Each tungsten is in a distorted octahedral geometry, and the  $W_4\text{C}_2\text{O}_{14}$  core represents the fusing together of two confacial bioctahedra along a common edge. The  $\mu\text{-CSiMe}_3$  ligand occupies one site of the face shared by two tungsten atoms. The W-C distances are notably asymmetric, 1.922 (7) and 2.087 (7) Å, representing formally W-W double and single bond distances. The tetranuclearity is maintained in benzene solution, and bridge ⇌ terminal OEt site exchange is rapid on the NMR time scale. These are the first trinuclear and tetranuclear alkylidyne clusters of tungsten supported exclusively by alkoxide ligands. Comparisons with related molecules are made.

In this series of papers we are seeking to explore the structural analogies between metal oxides and metal alkoxides and to develop organometallic chemistry supported by alkoxide ligands.<sup>2</sup> We describe here our preparation and characterization of trinuclear and tetranuclear alkylidyne complexes of tungsten supported by alkoxide ligands, namely  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  and  $W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$ , and the mixed-metal compound  $\text{Mo}_2\text{W}(\text{CMe})(\text{O-}i\text{-Pr})_9$ . These are the first trinuclear and tetranuclear alkylidyne clusters supported exclusively by alkoxide ligands.

## Syntheses

$W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  was first discovered as a minor product in the reaction between  $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$  and  $\text{MeC}\equiv\text{CMe}$ . Since it was established<sup>3</sup> that with 3 or more equiv of  $\text{MeC}\equiv\text{CMe}$  the major product was  $W_2(\text{O-}i\text{-Pr})_6(\mu\text{-C}_4\text{Me}_4)(\text{C}_2\text{Me}_2)$ , the origin of the trinuclear compound was of considerable interest. A plausible route involved the comproportionation of  $W(\text{CMe})(\text{O-}i\text{-Pr})_3$  and  $W_2(\text{O-}i\text{-Pr})_6$ , given that the ethylidyne complex  $W(\text{CMe})(\text{O-}i\text{-Pr})_3$  was formed<sup>4</sup> either competitively with an alkyne adduct or by an equilibrium of the type proposed<sup>5</sup> previously for  $W_2(\text{O-}t\text{-Bu})_6(\mu\text{-C}_2\text{H}_2)(\text{py})$  and  $(t\text{-BuO})_3\text{W}\equiv\text{CMe}$ .

Consistent with this line of reasoning, we find that the reaction shown in eq 1 leads to the formation of  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  in ca. 60% isolated crystalline yield and by <sup>1</sup>H NMR spectroscopy is essentially quantitative.



(1) Part 6: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

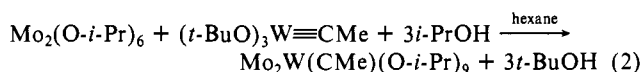
(2) Chisholm, M. H. *ACS Symp. Ser.* **1983**, *211*, 243.

(3) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806.

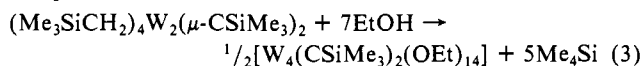
(4)  $W_2(\text{O-}i\text{-Bu})_6$  has been shown to react with  $\text{MeC}\equiv\text{CMe}$  to give  $(t\text{-BuO})_3\text{W}\equiv\text{CMe}$ : Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(5) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

The reaction shown in eq 1 represents the combined reactions of alcoholysis and comproportionation. The detailed order of these is not known. The comproportionation of the  $W\equiv\text{CMe}$  and  $W\equiv\text{W}$  moieties has a direct parallel with the formation of oxo-capped alkoxides:  $\text{MO}(\text{O-}i\text{-Pr})_4 + (i\text{-PrO})_3\text{M}\equiv\text{M}(\text{O-}i\text{-Pr})_3 \rightarrow \text{M}_3\text{O}(\text{O-}i\text{-Pr})_{10}$ , where M = Mo and W.<sup>6</sup> An extension of reaction 1 to include other alkylidyne and alkoxide ligands seems likely and is being investigated. An indication of the generality of the comproportionation is seen in the successful synthesis of the mixed-metal alkylidyne-capped trinuclear complex by the reaction shown in eq 2.



$W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$  is formed in the reaction between  $[(\text{Me}_3\text{SiCH}_2)_2\text{W}(\mu\text{-CSiMe}_3)]_2$  and an excess of ethanol according to eq 3.



The generality of eq 3 is limited by the nature of the alcohol. Bulky and less acidic alcohols such as *t*-BuOH and *i*-PrOH give  $(\text{RO})_4\text{W}_2(\mu\text{-CSiMe}_3)_2$  compounds by alcoholysis of only the  $\text{Me}_3\text{SiCH}_2$  ligands.<sup>7</sup> In view of the recent synthesis of  $(t\text{-BuO})_4\text{W}_2(\mu\text{-CPh})_2$ ,<sup>8</sup> an extension of the alcoholysis reaction, eq 3, can be envisaged to include the  $\mu\text{-CPh}$  ligand.

**Physicochemical Properties.**  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  is a dark green-brown crystalline compound while  $W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$  is red. Both compounds are air-sensitive and must be handled in dry and oxygen-free atmospheres and solvents. The compounds are soluble in hydrocarbon solvents. A cryoscopic molecular

(6) (a) Chisholm, M. H.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 1021. (b) Chisholm, M. H.; Huffman, J. C.; Kober, E. M. *Inorg. Chem.*, in press.

(7) Chisholm, M. H.; Heppert, J. A., results to be published.

(8) Cotton, F. A.; Schwotzer, W.; Shamshoun, E. S. *Organometallics* **1983**, *2*, 1167.

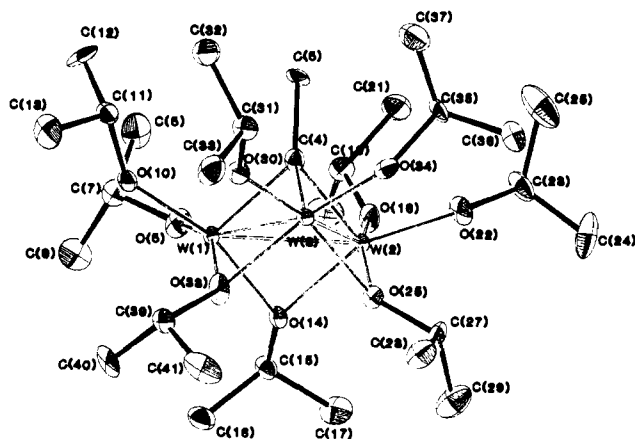


Figure 1. An ORTEP view of the  $W_3(\mu_3\text{-CMe})(\mu_2\text{-O-}i\text{-Pr})_3(\text{O-}i\text{-Pr})_6$  molecule showing the atom numbering scheme used in the tables.

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

atom	$10^4x$	$10^4y$	$10^4z$	$10B_{iso}$
W(1)	6821.2 (3)	2418.2 (5)	6633.5 (4)	10
W(2)	7685.5 (3)	347.9 (5)	3994.6 (4)	10
W(3)	7398.8 (3)	-251.9 (5)	6162.3 (4)	9
C(4)	8014 (7)	889 (12)	5612 (11)	14
C(5)	8829 (7)	934 (12)	5612 (12)	15
O(6)	6874 (5)	3965 (9)	6337 (8)	21
C(7)	6821 (8)	5283 (13)	7139 (13)	19
C(8)	7615 (9)	5440 (14)	6473 (15)	28
C(9)	6052 (9)	6336 (14)	7311 (15)	27
O(10)	6776 (5)	3336 (8)	8410 (8)	15
C(11)	7244 (7)	3210 (13)	9193 (12)	18
C(12)	7701 (9)	4140 (15)	9249 (15)	29
C(13)	6630 (9)	3541 (16)	10616 (13)	31
O(14)	6523 (5)	1892 (8)	4995 (7)	12
C(15)	6054 (7)	2738 (12)	4575 (12)	15
C(16)	5154 (8)	3535 (14)	5701 (13)	23
C(17)	6096 (8)	1859 (15)	3203 (13)	24
O(18)	8117 (5)	1268 (8)	3036 (7)	15
C(19)	8491 (7)	2218 (13)	3120 (12)	17
C(20)	8083 (9)	3221 (15)	2703 (15)	27
C(21)	9424 (8)	1495 (15)	2237 (14)	26
O(22)	8586 (5)	-1377 (9)	2569 (8)	19
C(23)	9246 (8)	-1844 (14)	1251 (13)	22
C(24)	9161 (11)	-2963 (16)	205 (14)	39
C(25)	10089 (9)	-2352 (17)	1249 (16)	38
O(26)	7110 (5)	-834 (8)	4552 (7)	11
C(27)	7112 (8)	-2108 (12)	3674 (12)	17
C(28)	6720 (9)	-2667 (14)	4581 (14)	25
C(29)	6645 (10)	-1834 (15)	2873 (15)	29
O(30)	7318 (5)	12 (8)	7951 (8)	16
C(31)	7693 (7)	-786 (13)	8495 (13)	18
C(32)	8178 (8)	-112 (14)	9189 (13)	21
C(33)	6997 (9)	-921 (15)	9516 (13)	26
O(34)	8291 (5)	-2002 (8)	5337 (8)	15
C(35)	9172 (7)	-2695 (12)	4494 (12)	15
C(36)	9349 (8)	-4137 (14)	3471 (14)	26
C(37)	9654 (8)	-2744 (15)	5358 (14)	28
O(38)	6224 (5)	1322 (8)	7241 (7)	13
C(39)	5522 (7)	1682 (13)	8495 (12)	17
C(40)	4860 (8)	3029 (14)	8926 (12)	23
C(41)	5236 (8)	534 (16)	8253 (15)	31

weight determination in benzene confirmed that  $W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$ , which as shown later may be viewed as the dimer  $[W_2(\text{CSiMe}_3)(\text{OEt})_7]_2$ , remains associated in solution.

#### Solid-State Molecular Structures

$W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$ . An ORTEP view of the molecule is shown in Figure 1. Atomic positional parameters are given in Table I, and listings of selected bond distances and angles are given in Tables II and III, respectively.

The local coordination geometry about each tungsten atom corresponds to that of a square-based pyramid in which the

Table II. Bond Distances ( $\text{\AA}$ ) for the  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  Molecule

A	B	distance
W(1)	W(2)	2.732 (2)
W(1)	W(3)	2.742 (1)
W(1)	O(6)	1.929 (9)
W(1)	O(10)	1.905 (8)
W(1)	O(14)	2.048 (8)
W(1)	O(38)	2.023 (7)
W(1)	C(4)	2.059 (11)
W(2)	W(3)	2.748 (1)
W(2)	O(14)	2.031 (8)
W(2)	O(18)	1.910 (8)
W(2)	O(22)	1.929 (8)
W(2)	O(26)	2.063 (7)
W(2)	C(4)	2.062 (12)
W(3)	O(26)	2.012 (8)
W(3)	O(30)	1.925 (7)
W(3)	O(34)	1.900 (8)
W(3)	O(38)	2.056 (8)
W(3)	C(4)	2.062 (11)
O(6)	C(7)	1.420 (15)
O(10)	C(11)	1.432 (14)
O(14)	C(15)	1.431 (14)
O(18)	C(19)	1.412 (14)
O(22)	C(23)	1.430 (15)
O(26)	C(27)	1.447 (14)
O(30)	C(31)	1.423 (15)
O(34)	C(35)	1.424 (14)
O(38)	C(39)	1.448 (14)
C-C ( <i>i-Pr</i> )		1.51 (1) (av)

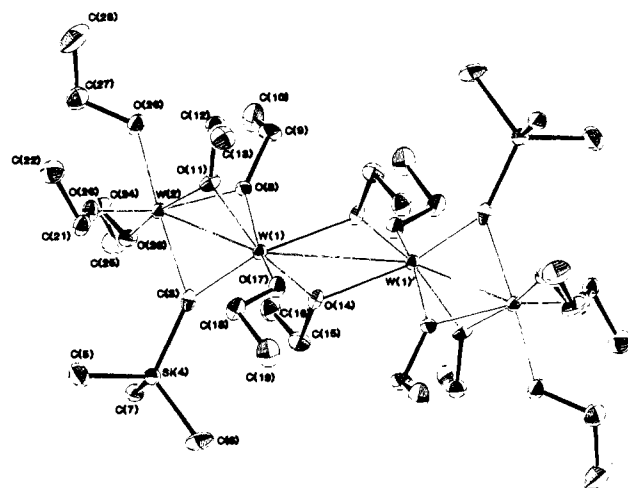


Figure 2. An ORTEP view of the centrosymmetric  $W_4(\mu\text{-CSiMe}_3)_2(\text{OEt})_{14}$  molecule giving the atom numbering scheme used in the tables.

$\mu_3\text{-CMe}$  ligand occupies the apical position. The presence of three  $\mu_2\text{-OR}$  groups constitute for each tungsten a cis-pair of basal sites with two terminal OR groups completing the square. The molecule has virtual  $C_{3v}$  symmetry.

The W-O distances associated with the terminal alkoxide ligands fall in the range 1.90 to 1.93  $\text{\AA}$ , typical of distances wherein the alkoxide ligand is acting as a  $\sigma$  and  $\pi$  donor to tungsten.<sup>9</sup> The W-O distances of the  $\mu_2\text{-OR}$  ligands, 2.02 to 2.06  $\text{\AA}$ , are typical of W-O distances for  $\mu_2\text{-OR}$  ligands and are essentially what is expected for  $\sigma$  bonds.<sup>9</sup> The three W-C distances to the capping alkylidene carbon atom are equivalent at 2.06 (1)  $\text{\AA}$ , comparable to the Mo-C distances seen in ethylidyne-capped  $\text{Mo}_3$  clusters such as  $\text{Mo}_3(\text{CMe})_2(\text{OAc})_6(\text{H}_2\text{O})_3^{2+}$  salts.<sup>10,11</sup>

The W-W distances, 2.74 (1)  $\text{\AA}$  (averaged), are notably longer than those in the oxo-capped compound  $W_3\text{O}(\text{O-}i\text{-Pr})_{10}$ <sup>6</sup> and in compounds containing a central  $\text{Mo}_3(\mu_3\text{-O})(\mu_2\text{-O})_3^{4+}$  core such as  $\text{Zn}_2\text{Mo}_3\text{O}_8$  and the Mo(4+) aquo ion, which have M-M dis-

(9) Chisholm, M. H. *Polyhedron* 1983, 2, 681.

(10) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* 1981, 103, 243.

(11) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* 1981, 103, 5779.

Table III. Selected Bond Angles (deg) for the  $W_3(\text{CMe})(\text{O}-i\text{-Pr})_9$  Molecule

A	B	C	angle
W(2)	W(1)	W(3)	60.28 (3)
W(2)	W(1)	O(6)	100.60 (25)
W(2)	W(1)	O(10)	149.37 (23)
W(2)	W(1)	O(14)	47.69 (21)
W(2)	W(1)	O(38)	91.77 (22)
W(2)	W(1)	C(4)	48.5 (3)
W(3)	W(1)	O(6)	155.88 (26)
W(3)	W(1)	O(10)	100.91 (25)
W(3)	W(1)	O(14)	91.01 (22)
W(3)	W(1)	O(38)	48.27 (22)
W(3)	W(1)	C(4)	48.3 (3)
O(6)	W(1)	O(10)	89.1 (4)
O(6)	W(1)	O(14)	84.7 (3)
O(6)	W(1)	O(38)	154.4 (3)
O(6)	W(1)	C(4)	108.5 (4)
O(10)	W(1)	O(14)	162.9 (3)
O(10)	W(1)	O(38)	91.5 (3)
O(10)	W(1)	C(4)	100.8 (4)
O(14)	W(1)	O(38)	87.4 (3)
O(14)	W(1)	C(4)	96.2 (4)
O(38)	W(1)	C(4)	96.6 (4)
O(14)	W(2)	O(18)	91.2 (3)
O(14)	W(2)	O(22)	157.1 (3)
O(14)	W(2)	O(26)	86.8 (3)
O(14)	Wn2)	C(4)	96.6 (4)
O(18)	W(2)	O(22)	90.0 (3)
O(18)	W(2)	O(26)	162.5 (3)
O(18)	W(2)	C(4)	102.5 (4)
O(22)	W(2)	O(26)	85.2 (3)
O(22)	W(2)	C(4)	105.5 (4)
O(26)	W(2)	C(4)	95.0 (4)
O(26)	W(3)	O(30)	155.2 (3)
O(26)	W(3)	O(34)	90.8 (3)
O(26)	W(3)	O(38)	87.1 (3)
O(26)	W(3)	C(4)	96.5 (4)
O(30)	W(3)	O(34)	90.1 (3)
O(30)	W(3)	O(38)	84.6 (3)
O(30)	W(3)	C(4)	107.5 (4)
O(34)	W(3)	O(38)	162.3 (3)
O(34)	W(3)	C(4)	102.3 (4)
O(38)	W(3)	C(4)	95.4 (4)
W(1)	O(6)	C(7)	135.8 (7)
W(1)	O(10)	C(11)	141.2 (7)
W(1)	O(14)	W(2)	84.1 (3)
W(1)	O(14)	C(15)	130.2 (7)
W(2)	O(14)	C(15)	132.6 (6)
W(2)	O(18)	C(19)	142.9 (7)
W(2)	O(22)	C(23)	136.2 (8)
W(2)	O(26)	W(3)	84.8 (3)
W(2)	O(26)	C(27)	128.6 (7)
W(3)	O(26)	C(27)	133.6 (7)
W(3)	O(30)	C(31)	136.4 (7)
W(3)	O(34)	C(35)	140.6 (7)
W(1)	O(38)	W(3)	84.5 (3)
W(1)	O(38)	C(39)	132.5 (7)
W(3)	O(38)	C(39)	131.4 (7)
W(1)	C(4)	W(2)	83.0 (4)
W(1)	C(4)	W(3)	83.4 (4)
W(1)	C(4)	C(5)	130.6 (8)
W(2)	C(4)	W(3)	83.6 (4)
W(2)	C(4)	C(5)	129.3 (8)
W(3)	C(4)	C(5)	129.7 (8)

tances of 2.51–2.54 Å.<sup>12</sup> However, a number of other triangulo-capped compounds of Mo(IV) and W(IV) have M–M distances in the range 2.73 to 2.76 Å,<sup>12</sup> and based on distance, electron counting, and symmetry we formulate the existence of 3 W–W bonds in the new compound.

$W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$ . An ORTEP view of the centrosymmetric molecule is shown in Figure 2. Atomic positional parameters are given in Table IV and selected bond distances and angles are

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for the  $W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$  Molecule

atom	$10^4x$	$10^4y$	$10^4z$	$10B_{\text{iso}}$
W(1)	351.2 (2)	4497.3 (1)	6111.5 (2)	9
W(2)	-344.1 (3)	4375.1 (2)	7649.6 (2)	10
C(3)	1397 (7)	4715 (4)	7419 (5)	14
Si(4)	2955 (2)	5051 (1)	8240 (1)	14
C(5)	3506 (9)	4357 (5)	9263 (6)	27
C(6)	4276 (7)	5142 (5)	7622 (7)	23
C(7)	2705 (7)	5988 (5)	8773 (6)	18
O(8)	-1332 (4)	4898 (3)	6340 (3)	14
C(9)	-2654 (7)	4910 (4)	5799 (6)	18
C(10)	-3373 (8)	5511 (5)	6181 (6)	27
O(11)	-491 (5)	3561 (3)	6566 (4)	14
C(12)	-1372 (7)	2935 (4)	6212 (6)	17
C(13)	-650 (8)	2270 (5)	5970 (6)	22
O(14)	653 (5)	5486 (3)	5533 (3)	12
C(15)	1152 (7)	6185 (4)	6046 (6)	17
C(16)	225 (8)	6551 (5)	6530 (6)	19
O(17)	1546 (5)	3848 (3)	5753 (4)	15
C(18)	2468 (7)	3323 (4)	6343 (6)	17
C(19)	3524 (8)	3155 (5)	5866 (6)	27
O(20)	305 (5)	3595 (3)	8576 (4)	15
C(21)	1089 (7)	2942 (4)	8592 (5)	16
C(22)	405 (8)	2241 (5)	8799 (6)	23
O(23)	-293 (4)	5275 (3)	8410 (4)	14
C(24)	-1157 (8)	5602 (4)	8893 (6)	19
C(25)	-1009 (8)	6454 (5)	8882 (7)	25
O(26)	-2091 (5)	4137 (3)	7790 (4)	17
C(27)	-2424 (8)	3905 (5)	8632 (6)	24
C(28)	-3313 (11)	3230 (6)	8408 (8)	38

Table V. Selected Bond Distances (Å) for the  $W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$  Molecule

A	B	distance
W(1)	W(1)'	3.513 (1)
W(1)	W(2)	2.516 (1)
W(1)	O(8)	2.061 (5)
W(1)	O(11)	2.070 (5)
W(1)	O(14)	1.988 (5)
W(1)	O(14)'	2.283 (5)
W(1)	O(17)	1.899 (5)
W(1)	C(3)	1.922 (7)
W(2)	O(8)	2.081 (5)
W(2)	O(11)	2.076 (5)
W(2)	O(20)	1.893 (5)
W(2)	O(23)	1.908 (5)
W(2)	O(26)	1.999 (5)
W(2)	C(3)	2.087 (7)
Si(4)	C(3)	1.854 (8)
Si(4)	C(5)	1.863 (9)
Si(4)	C(6)	1.884 (8)
Si(4)	C(7)	1.864 (8)
O(8)	C(9)	1.420 (8)
O(11)	C(12)	1.450 (8)
O(14)	C(15)	1.453 (8)
O(17)	C(18)	1.440 (8)
O(20)	C(21)	1.423 (9)
O(23)	C(24)	1.429 (8)
O(26)	C(27)	1.405 (9)
C–C (OEt)		1.51 (1) (av)

given in Tables V and VI, respectively.

There is a chain of four tungsten atoms with alternating short, 2.51 (1) Å, and long, 3.51 (1) Å, W-to-W distances. The W–W–W angle in the  $W_4$  chain is 141°. Each tungsten atom is in a distorted octahedral environment being coordinated to five oxygen atoms and the carbon atom of the bridging  $\text{Me}_3\text{SiC}$  ligand. The internal tungsten atoms W(1) and W(1)' are coordinated to only one terminal alkoxide ligand. These are connected to the external tungsten atoms through the agency of a pair of  $\mu_2$ -OR ligands and the bridging  $\text{Me}_3\text{SiC}$  ligand and to each other by a pair of  $\mu$ -OR ligands. The molecule may be viewed as a dimer [ $W_2(\text{CSiMe}_3)(\text{OEt})_7$ ]<sub>2</sub>: two confacial bioctahedra are fused along a common edge.

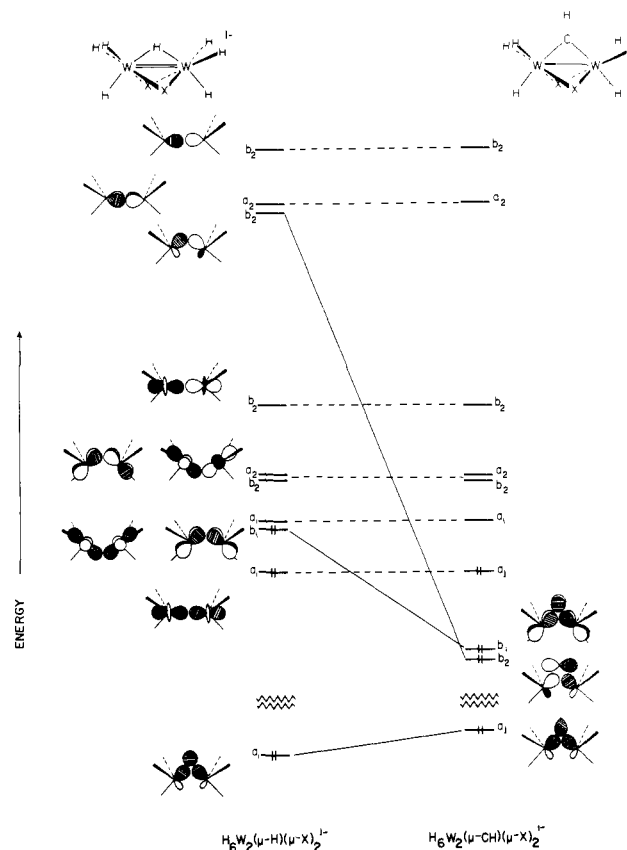
(12) Muller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 875.

**Table VI.** Selected Bond Angles (deg) for the  $W_4(CSiMe_3)_2(OEt)_{14}$  Molecule

A	B	C	angle
W(1)'	W(1)	W(2)	141.62 (2)
W(2)	W(1)	O(8)	52.97 (13)
W(2)	W(1)	O(11)	52.76 (13)
W(2)	W(1)	O(14)	136.02 (12)
W(2)	W(1)	O(17)	125.15 (15)
W(2)	W(1)	C(3)	54.13 (21)
O(8)	W(1)	O(11)	74.72 (19)
O(8)	W(1)	O(14)	91.27 (19)
O(8)	W(1)	O(17)	161.09 (20)
O(8)	W(1)	C(3)	94.78 (25)
O(11)	W(1)	O(14)	164.06 (19)
O(11)	W(1)	O(17)	89.93 (20)
O(11)	W(1)	C(3)	92.67 (25)
O(14)	W(1)	O(14)'	69.54 (21)
O(14)	W(1)	O(17)	102.14 (20)
O(14)	W(1)	C(3)	96.10 (24)
O(17)	W(1)	C(3)	96.96 (26)
W(1)	W(2)	O(8)	52.23 (13)
W(1)	W(2)	O(11)	52.54 (13)
W(1)	W(2)	O(20)	121.60 (15)
W(1)	W(2)	O(23)	117.00 (15)
W(1)	W(2)	O(26)	128.90 (15)
W(1)	W(2)	C(3)	48.28 (19)
O(8)	W(2)	O(11)	74.17 (19)
O(8)	W(2)	O(20)	159.73 (21)
O(8)	W(2)	O(23)	93.81 (20)
O(8)	W(2)	O(26)	85.52 (19)
O(8)	W(2)	C(3)	89.44 (22)
O(11)	W(2)	O(20)	87.33 (21)
O(11)	W(2)	O(23)	167.40 (20)
O(11)	W(2)	O(26)	93.09 (20)
O(11)	W(2)	C(3)	87.92 (23)
O(20)	W(2)	O(23)	105.10 (22)
O(20)	W(2)	O(26)	87.33 (21)
O(20)	W(2)	C(3)	98.25 (24)
O(23)	W(2)	O(26)	89.65 (20)
O(23)	W(2)	C(3)	88.20 (24)
O(26)	W(2)	C(3)	174.37 (23)
C(3)	Si(4)	C(5)	108.5 (4)
C(3)	Si(4)	C(6)	114.0 (4)
C(3)	Si(4)	C(7)	109.0 (4)
C(5)	Si(4)	C(6)	107.6 (5)
C(5)	Si(4)	C(7)	108.2 (4)
C(6)	Si(4)	C(7)	109.3 (4)
W(1)	O(8)	W(2)	74.80 (16)
W(1)	O(8)	C(9)	136.0 (4)
W(2)	O(8)	C(9)	132.5 (4)
W(1)	O(11)	W(2)	74.71 (16)
W(1)	O(11)	C(12)	143.0 (5)
W(2)	O(11)	C(12)	133.3 (4)
W(1)	O(14)	W(1)	110.46 (21)
W(1)	O(14)	C(15)	127.7 (4)
W(1)	O(17)	C(18)	129.8 (4)
W(2)	O(20)	C(21)	134.2 (4)
W(2)	O(23)	C(24)	133.5 (4)
W(2)	O(26)	C(27)	128.5 (5)
W(1)	C(3)	W(2)	77.6 (3)
W(1)	C(3)	Si(4)	148.6 (4)
W(2)	C(3)	Si(4)	133.7 (4)

If a terminal RO ligand is counted as  $-1$ , a bridging OR ligand as  $-1/2$ , and the bridging  $Me_3SiC$  ligand as  $-1/2$  per metal, then the formal oxidation state of the outer tungsten atoms, W(2) and W(2)', is  $+5 1/2$  while that of the inner tungsten atoms, W(1) and W(1)', is  $+4 1/2$ . This difference is internally compensated by the bridging trimethylsilyldyne forming shorter bonds to W(1) than to W(2). Indeed, the W(1)-C(3) and W(2)-C(3) distances of 1.988 (5) and 2.087 (7) Å may formally be considered as W-C double and single bonds, respectively.

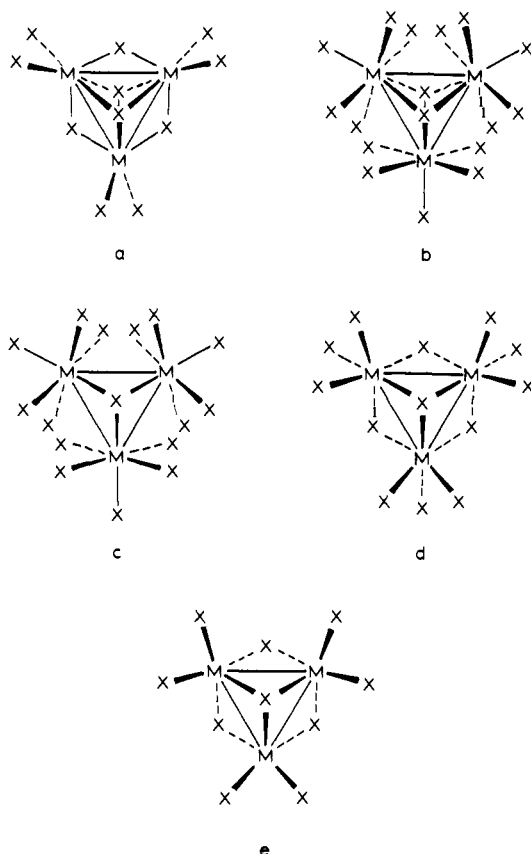
The  $W_4$  unit has four electrons available for M-M bonding and these are used to form two single bonds between W(1) and W(2) and W(1)' and W(2)'. The W(1)-to-W(1)' distance of 3.51 (1) Å is clearly a nonbonding distance. The W(1)-W(2) distance of 2.51 (1) Å is short for a W-W single-bond distance; indeed,



**Figure 3.** Qualitative molecular orbital diagram outlining the orbital correspondences between  $H_6W_2(\mu-H)(\mu-X)_2^-$  and  $H_6W_2(\mu-CH)(\mu-X)_2^-$  ( $X = OH$ ). The  $H_6W_2(\mu-H)(\mu-X)_2^-$  and  $H_6W_2(\mu-CH)(\mu-X)_2^-$  species were chosen as simple models for one of the dinuclear confacial bioctahedral units in  $W_4(\mu-H)_2(O-i-Pr)_{14}$  and  $W_4(\mu-CSiMe_3)_2(OEt)_{14}$ , respectively. A qualitative relationship between formal metal-metal triple bonds of configuration  $\sigma^2\pi^4$  and bonding in the  $H_6W_2(\mu-H)(\mu-X)_2^-$  moiety can be drawn by considering the metal-metal bonding  $a_1$  and  $b_1$  orbitals to contribute a  $\sigma^2\pi^2$  component to W-W bonding, while the metal-hydrogen bonding  $a_1$  orbital which is primarily hydrogen in character contributes a  $\pi^2$  component to metal-metal bonding. Correspondences between these orbitals and orbitals of similar appearance in the  $H_6W_2(\mu-CH)(\mu-X)_2^-$  molecule are shown by solid lines. A new  $b_2$  orbital which is primarily carbon in character and is metal-carbon bonding also appears in the bonding set. This orbital is antibonding with respect to its metal-metal interaction and, consequently, contributes a  $\pi^{*2}$  component to W-W bonding. The net metal-metal bonding in  $H_6W_2(\mu-CH)(\mu-X)_2^-$  can therefore be modeled by a " $\sigma^2\pi^2$ " configuration. (The general MO diagram for dinuclear systems in a confacial bioctahedral coordination environment and the effects of  $\pi$ -donor ligands on these systems were obtained from R. H. Summerville and R. Hoffmann (*J. Am. Chem. Soc.* **1979**, *101*, 3821-3831). An extended Hückel calculation using weighted Hij's (see: Hoffmann, *R. J. Chem. Phys.* **1963**, *39*, 1397-1412 and references therein) was used to confirm the proposed ordering and character of MO's for the  $H_6W_2(\mu-CH)(\mu-X)_2^-$  moiety. An idealized octahedral coordination geometry was assumed for the  $WH_3$  fragments while bridging groups were placed equidistant from each W center with average bond angles and distances obtained from the X-ray structure. Bond distances and angles include W-H = 1.75 Å, W-C = 2.00 Å, W-O = 2.09 Å, C-H = 1.09 Å, O-H = 0.96 Å, W-C-W = 78°, W-O-W = 74°, W-C-H = 141°, and W-O-H = 143°. Parameters for H, O, and C used in the calculations are standard for extended Hückel, while W parameters were obtained from the work of Summerville and Hoffmann.)

it is close to a typical W=W bond distance.<sup>13</sup> In this regard it should be noted that W-to-C bonding will be mixed with M-M bonding. In an extreme view one may consider the confacial bioctahedron as a  $d^3-d^3$  ditungsten unit with a  $CR^+$  unit occupying one of the bridging positions. This emphasizes the interactions

(13) For a comparison of W-W distances in dinuclear alkoxides and assignments of M-M bond order see ref 9.



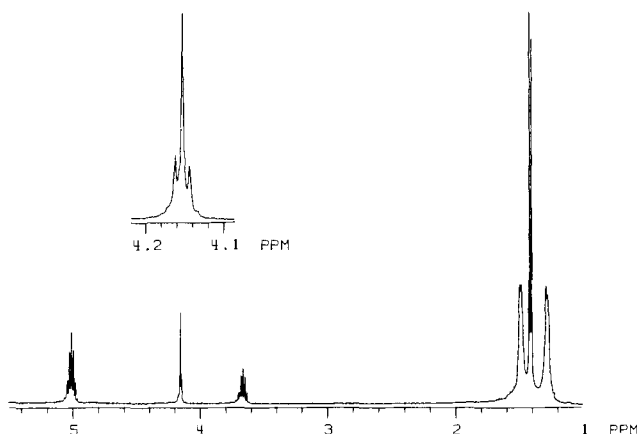
**Figure 4.** Prototypical representations of the bicapped and hemicapped triangular structures now known for molybdenum and/or tungsten. (a) The  $M_3X_{11}$  unit found in  $M_3(\mu_3-O)(\mu_3-OR)(\mu_2-OR)_3(OR)_6$  compounds. (b) The  $M_3X_{17}$  unit in  $M_3(\mu_3-O)_2(O_2CR)_6(H_2O)_3^{2+}$  ions. (c) The  $M_3X_{16}$  unit in the  $W_3(\mu_3-O)(O_2CR)_6(H_2O)_3^{2+}$  ion. (d) The  $M_3X_{13}$  unit found in the aquated  $Mo_3(\mu_3-O)(\mu_2-O)_3^{4+}$  containing ion and (e) the  $M_3X_{10}$  unit seen in  $W_3(\mu_3-CMe)(\mu_2-O-i-Pr)_3(O-i-Pr)_6$ . These representations show how the metal atoms are bonded to either 7 (b), 6 (a, c and d) or 5 (e) ligand atoms. The present structure (e) is seen to be related to (d) by the removal of the ligands trans to the capping  $\mu_3-X$  group.

between M-M  $\sigma$ ,  $\pi$ , and  $\delta$  bonding and M-C  $\sigma$  and  $\pi$  bonding and is shown schematically in Figure 3. This is the first time that an alkyidyne ligand has been found to occupy a bridging site in a confacial bioctahedron.

The W-O distances associated with the terminal OR ligands are shorter by  $>0.1$  Å than those of the  $\mu_2$ -OR ligands consistent with  $\sigma + \pi$  character of the former. Most notable, however, are the relatively long distances of W-O bonds that are trans to the W-C bonds. This leads to a very marked asymmetry in W-O distances of the central bridge: W(1)-O(14) = 1.988 (5) Å vs. W(1)-O(14)' = 2.283 (5) Å.

**Comparisons with Related Structures.** There is now a large group of triangulo complexes of Mo and W having either one or two capping groups with 6 electrons available for M-M bonding.<sup>11,13</sup> These contain metal atoms that are either 6 or 7 coordinate with respect to ligand-to-metal bonding and have  $M_3X_{17}$ ,  $M_3X_{16}$ ,  $M_3X_{13}$ , or  $M_3X_{11}$  central skeletons, where X = a ligand atom directly bonded to M. The compound  $W_3(CMe)(O-i-Pr)_9$  provides a new structural type being the first member of an  $M_3X_{10}$  group. These structural types are shown in Figure 4. The  $M_3X_{10}$  structure is closely related to the  $M_3X_{13}$  unit with each metal atom in the former being five coordinate rather than six coordinate and lacking a ligand trans to the  $\mu_3-X$  position.

The  $W_4(CSiMe_3)_2(OEt)_{14}$  structure is directly analogous to that found for  $W_4(H)_2(O-i-Pr)_{14}$ <sup>15</sup> with the  $\mu$ -CSiMe<sub>3</sub> ligand in the



**Figure 5.**  $^1H$  NMR spectrum of  $W_3(CMe)(O-i-Pr)_9$  dissolved in benzene- $d_6$  recorded at 21 °C, 360 MHz. The ethylidyne proton resonance is shown in the inset at scale expansion. Coupling to  $^{183}W$ ,  $I = 1/2$ , 14.5% natural abundance, produces an apparent 1:4:1 triplet,  $J_{183W-H} = 7.1$  Hz.

former occupying the site of  $\mu$ -H in the latter molecule. Both molecules may be viewed as dimers,  $[W_2(\mu-X)(OR)_7]_2$ , but for X = H there is formally a W-W double bond since the average oxidation state of tungsten is +4 whereas for X = CSiMe<sub>3</sub> there is formally a W-W single bond since the average oxidation state of tungsten is +5. The short W-W distances differ little: 2.45 Å (X = H) and 2.51 Å (X = CSiMe<sub>3</sub>). In both cases there is a mixing of M- $\mu$ -X bonding and M-M bonding. This is well documented in metal hydride chemistry where an M-H-M unit is often portrayed as a protonated metal-metal bond. Both molecules can be viewed as derivatives of  $d^3$ - $d^3$  confacial bioctahedra in which either  $H^+$  or  $RC^+$  occupies one of the bridging positions resulting in formally M-M double and single bonds when the bridging ligands are reduced to  $H^-$  and  $RC^3-$ , respectively.

#### $^1H$ NMR Studies

**$W_3(CMe)(O-i-Pr)_9$ .** The  $^1H$  NMR spectrum of  $W_3(CMe)(O-i-Pr)_9$  recorded in benzene- $d_6$  at 21 °C and 360 MHz is shown in Figure 5. There are two septets in the integral ratio 2:1 assignable to terminal and bridging  $OCHMe_2$  protons, respectively. In the methyl region of the spectrum there is a sharp doublet flanked by two doublets which are broad. Upon lowering the temperature the broadened doublets sharpen to give at -10 °C three sharp doublets of equal intensity. Upon raising the temperature the two doublets which appear broad at 21 °C broaden further, collapse into the base line, and then at +60 °C start to coalesce. Decomposition becomes rapid above this temperature. These are the only changes observed.

These observations lead us to the following conclusions.

(1) The low-temperature-limiting spectrum is entirely consistent with that anticipated from the molecular structure found in the solid state which has six chemically equivalent terminal *O-i-Pr* ligands and three equivalent bridging ones. The methyl groups of the terminal ligands are diastereotopic.

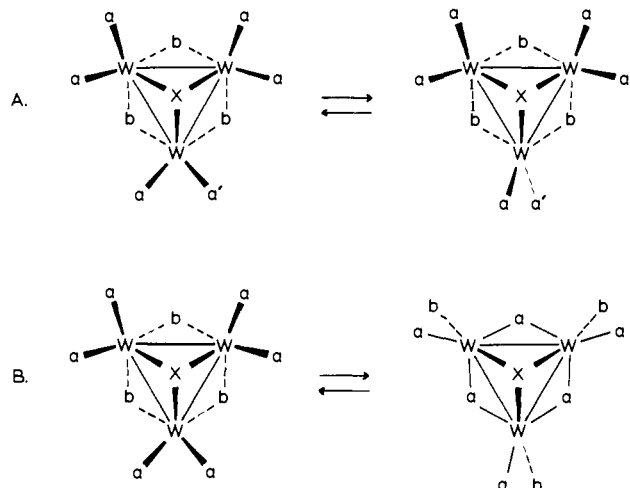
(2) Upon raising the temperature site exchange between the bridging and terminal ligands does not occur but some dynamic process leads to the loss of the diastereotopic character of the methyl groups of the terminal *O-i-Pr* ligands.

Assuming that this selective exchange process is intramolecular (all evidence is consistent with this assumption) two processes could be envisaged to explain the observed spectra. A pseudorotation about each tungsten atom could exchange the terminal *O-i-Pr* ligand positions by way of a square-based pyramid  $\rightleftharpoons$  trigonal bipyramid  $\rightleftharpoons$  square-based pyramid interconversion. In this way each terminal *O-i-Pr* ligand would pass through a molecular plane of symmetry. Alternatively, the six terminal *O-i-Pr* ligands could exchange sites by forming and opening bridges in a concerted manner. This could be viewed as a "merry-go-round" akin to that

(14) Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1983**, *104*, 5394 and ref 1-10 cited therein.

(15) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. *J. Am. Chem. Soc.* **1981**, *103*, 779.

Scheme I. Two Plausible Dynamic Processes Leading to the Loss of the Diastereotopic Nature of the Methyl Groups of the Terminal *O-i-Pr* Ligands in the  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  Molecule<sup>a</sup>



<sup>a</sup> In A, shown at the top, the two terminal *O-i-Pr* ligands at any one tungsten center pass through a molecular plane of symmetry by a twisting motion. In B, bridges open and close as in a merry-go-round or carousel-like manner. The *O-i-Pr* ligands denoted by a and b are not exchanged because b remain distal to the capping X ligand. The latter mechanism can be ruled out for the mixed metal compound  $\text{Mo}_2\text{W}(\text{CMe})(\text{O-}i\text{-Pr})_9$  on the basis of the VT <sup>1</sup>H NMR spectra (see text).

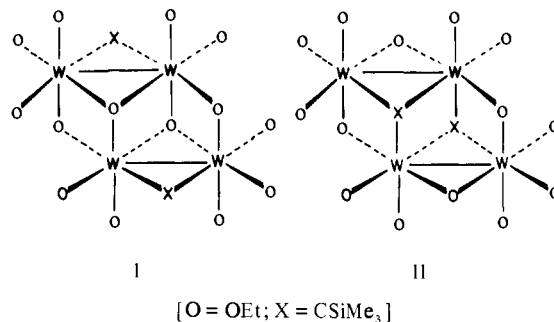
observed in some CO ligand site exchange processes in transition-metal carbonyl chemistry.<sup>16</sup> These processes are represented diagrammatically in Scheme I. The essential feature in the latter process is that alkoxy ligands which are proximal with respect to the capping ethylidyne ligand remain proximal and those that are distal remain distal even though bridges open and close.

With regard to the site-exchange mechanism, the <sup>1</sup>H NMR spectra of the  $\text{Mo}_2\text{W}(\text{CMe})(\text{O-}i\text{-Pr})_9$  molecule are informative since it may be viewed as an isotopomer of the tritungsten compound.

$\text{Mo}_2\text{W}(\text{CMe})(\text{O-}i\text{-Pr})_9$ . The low-temperature-limiting spectrum recorded at  $-45^\circ\text{C}$  at 360 MHz in toluene-*d*<sub>8</sub> is in agreement with expectations based upon substituting two tungsten atoms by molybdenum atoms in the  $W_3(\text{CMe})(\text{O-}i\text{-Pr})_9$  structure. The molecule has only one mirror plane of symmetry, resulting in two types of bridging *O-i-Pr* ligands,  $2\text{MoW}(\mu\text{-O-}i\text{-Pr}):1\text{Mo}_2(\mu\text{-O-}i\text{-Pr})$ , and three types of terminal *O-i-Pr* ligands in the ratio 2:2:2. With the exception of the unique bridging *O-i-Pr* ligand which bridges the two molybdenum atoms, the methyl groups of the isopropoxide ligands are diastereotopic. Five septets are observed in the methyne region of the spectrum in the integral ratio 2:2:2:2:1 and nine doublets of equal intensity are seen in the methyl region. An absolute assignment of the observed spectrum is not possible, but the signal due to the methyne proton of the  $\text{Mo}_2(\mu\text{-O-}i\text{-Pr})$  moiety is easily identified, being of relative intensity one, and its neighboring septet of intensity two, which is well upfield of all the other septets, can reliably be assigned to the methyne protons of the two *O-i-Pr* ligands spanning the Mo–W bonds. Upon raising the temperature these signals are invariant, indicating that the bridging groups remain bridging and do not open and close on the NMR time scale. The three methyne septets at lower field, which are assignable to terminal *O-i-Pr* ligands, collapse to two septets of relative intensity 4:2 from which we conclude that *O-i-Pr* ligands bound to molybdenum remain bound to molybdenum and those bound to tungsten remain bound to tungsten. The NMR evidence mitigates against the “merry-go-round” mechanism and shows that bridge-terminal site exchange cannot be invoked to explain the observed dynamic exchange process. The pseudoro-

tation mechanism appears to be the only viable low-energy process.

$W_4(\text{CSiMe}_3)_2(\text{OEt})_{14}$ . The <sup>1</sup>H NMR spectrum recorded at  $-70^\circ\text{C}$ , 360 MHz in toluene-*d*<sub>8</sub>, shows one  $\text{SiMe}_3$  signal and seven partially overlapping triplets of equal intensity assignable to the  $\text{OCH}_2\text{CH}_3$  protons. The methylene protons appear in the region 4–5 ppm as seven partially resolved multiplets, each being part of an anticipated  $\text{ABX}_3$  spectrum. The low-temperature spectrum is therefore consistent with the centrosymmetric structure found in the solid state. However, the spectrum could also be reconciled with the centrosymmetric structures shown in 1 and 11 below.<sup>17</sup>



Upon raising the temperature the methylene signals collapse to a quartet and methyl signals to a triplet at  $+45^\circ\text{C}$ . Evidently bridge-terminal OEt exchange becomes rapid and an intramolecular mechanism of the type previously proposed<sup>15</sup> for the fluxional and structurally related  $W_4(\mu\text{-H})_2(\text{O-}i\text{-Pr})_{14}$  molecule could be operative.

### Concluding Remarks

The ability of alkylidyne ligands to act as bridging groups between two and three metal atoms supported by alkoxide ligands and metal–metal bonds leads us to speculate that similar local environments might exist in reactive metal oxide surfaces. Evidence for the formation of  $\mu_3$ -alkylidyne ligands in the reactions between alkynes and metal surfaces has been presented.<sup>18,19</sup> Similar reactions can be envisaged for metal oxide surfaces.

Further studies aimed at extending the range of these trinuclear and tetranuclear alkylidyne/alkoxide clusters and elucidating the reactivity of the M–C bonds are underway.

### Experimental Section

The preparations of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$ ,  $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$ , and  $[(t\text{-BuO})_3\text{W}\equiv\text{CMe}]_2$  have been described.<sup>4,20,21</sup> All manipulations were carried out under vacuum or inert atmospheres. Dry and oxygen-free solvents were used in all preparations.

<sup>1</sup>H NMR spectra were recorded on a Nicolet NT-360 360-MHz spectrometer in dry and oxygen-free benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub>. Chemical shifts are reported relative to the residual protons of  $\text{C}_6\text{D}_6$  set at  $\delta$  7.15 or the  $\text{CHD}_2$  quintet of  $\text{C}_7\text{D}_8$  set at  $\delta$  2.09. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between CsI plates. Elemental analyses were performed by the Bernhardt Analytical Laboratory of Germany. Electronic absorption spectra were obtained with a Hitachi 330 recording spectrophotometer. Samples were run vs. a solvent blank with 1-cm or 1-mm quartz cells.

$W_3(\text{O-}i\text{-Pr})_9(\text{CMe})$ . Two procedures allowed isolation of pure crystalline product. Method B is the better method.

**Method A:** To  $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$  (0.500 g, 0.568 mmol) dissolved in hexanes (10 mL) was added  $\text{C}_2\text{Me}_2$  (0.57 mmol) in hexanes (12 mL) dropwise with stirring. The flask and addition funnel were closed off to  $\text{N}_2$  flow during the addition. The addition was complete in 3 h, and the reaction was further stirred for 1 h. The volume of the solution was then reduced to 2–3 mL and cooled at  $-20^\circ\text{C}$  for 24 h. This produced dark green crystals which were isolated by filtration and dried in vacuo (yield 0.160 g, 38% based on W).

**Method B:** In a  $\text{N}_2$ -filled glovebox  $W_2(\text{O-}i\text{-Pr})_6(\text{py})_2$  (0.400 g, 0.454 mmol) was dissolved in hexanes/*i*-PrOH (10 mL/2 mL). To the solution was added  $[(t\text{-BuO})_3\text{W}\equiv\text{CMe}]_2$  (0.195 g, 0.227 mmol) in hexanes (2–3

(16) For example, see: Cotton, F. A.; Wilkinson, G. In “Advanced Inorganic Chemistry”; 4th ed.; Wiley: New York, 1980; Figure 28.23, p 1228, and accompanying discussion.

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Table VII. Summary of Crystal Data

	W <sub>3</sub> (CMe)(O- <i>i</i> -Pr) <sub>9</sub>	W <sub>4</sub> (CSiMe <sub>3</sub> ) <sub>2</sub> (OEt) <sub>14</sub>
empirical formula	W <sub>3</sub> C <sub>29</sub> H <sub>66</sub> O <sub>9</sub>	C <sub>35</sub> H <sub>88</sub> O <sub>14</sub> Si <sub>2</sub> W <sub>4</sub>
color of crystal	black/brown	red
crystal dimensions (mm)	0.16 × 0.16 × 0.16	0.24 × 0.20 × 0.20
space group	P $\bar{1}$	P2 <sub>1</sub> /n
cell dimensions		
temp, °C	-159	-155
<i>a</i> , Å	18.255 (6)	10.812 (3)
<i>b</i> , Å	11.396 (3)	17.576 (6)
<i>c</i> , Å	11.500 (3)	14.225 (4)
α, deg	110.55 (2)	106.42 (2)
β, deg	72.56 (2)	
γ, deg	75.16 (2)	
Z, molecules/cell	2	2
volume, Å <sup>3</sup>	1954.46	2592.83
calcd density, g/cm <sup>3</sup>	1.887	1.968
wavelength, Å	0.71069	0.71069
molecular weight	1110.39	1536.65
linear absorption coeff, cm <sup>-1</sup>	90.388	91.341
max. absorption	0.0890	
min. absorption	0.2910	
detector to sample distance, cm	22.5	22.5
sample to source distance, cm	23.5	23.5
av ω scan width at half height	0.25	0.25
scan speed, deg/min	4.0	6.0
scan width, deg + dispersion	2.0	1.8
individual background, s	8	8
aperture size, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6-45	6-50
total no. of reflections collected	5243	8244
no. of unique intensities	5147	4573
no. with <i>F</i> > 0.0		4350
no. of <i>F</i> > 3σ( <i>F</i> )	4755	3854
<i>R</i> ( <i>F</i> )	0.0449	0.0289
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.0474	0.0312
goodness of fit for the last cycle	1.334	0.669
max. δ/σ for last cycle.	0.05	0.05

mL) with a disposable pipet. The color of the solution changed from dark red to dark green immediately. The reaction mixture was stirred for 2 h, the volatiles were removed, and the solid residue was redissolved in hexanes (2-3 mL). It was necessary to warm the hexanes slightly (30-40 °C) to dissolve all of the solid. Cooling at -20 °C for 3 days produced dark green crystals which were isolated by filtration and dried in vacuo (yield 0.270 g, 54%). <sup>1</sup>H NMR spectra of a stripped reaction mixture showed the reaction is >90% for formation of the W<sub>3</sub>(CMe) species with Method B. Anal. Calcd for W<sub>3</sub>O<sub>9</sub>C<sub>29</sub>H<sub>66</sub>: C, 31.37; H, 5.99; N, 0.00. Found: C, 31.15; H, 5.80; N, <0.05.

<sup>1</sup>H NMR (-10 °C, toluene-*d*<sub>6</sub>): δ (OCHMe<sub>2</sub>) 1.27 (18 H), 1.41 (18 H), and 1.49 (18 H) (d, *J*<sub>HH</sub> = 6 Hz); δ (OCHMe<sub>2</sub>) 3.63 (3 H) and 5.00 (6 H) (sept, *J*<sub>HH</sub> = 6 Hz); δ (CMe) 4.14 (3 H, s, <sup>3</sup>*J*<sub>WH</sub> = 7.12 Hz). IR (cm<sup>-1</sup>): 1334 (m), 1322 (m), 1262 (w), 1161 (s), 1121 (s), 1010 (s), 991 (s), 979 (s), 954 (s), 848 (s), 612 (m), 596 (s), 581 (m), 550 (m), 481 (w), 455 (w), 428 (w), 305 (w).

UV-vis (hexanes): (λ<sub>max</sub>, nm (ε, L M<sup>-1</sup> cm<sup>-1</sup>)) 743 (450), 486 (1200), 390 (3700), 295 (11 000), 232 (50 000), 228 (54 000) and 226 (50 000).

Mo<sub>2</sub>W(O-*i*-Pr)<sub>9</sub>(CMe). This compound was prepared by a procedure analogous to the Method B preparation of W<sub>3</sub>(O-*i*-Pr)<sub>9</sub>(CMe). Dark brown crystals were collected in 62% yield. Anal. Calcd for Mo<sub>2</sub>WO<sub>9</sub>C<sub>29</sub>H<sub>66</sub>: C, 37.27; H, 7.12; N, 0.00. Found: C, 36.99; H, 6.88; N, <0.03.

<sup>1</sup>H NMR (-45 °C, toluene-*d*<sub>6</sub>): δ (OCHMe<sub>2</sub>) 1.24 (6 H), 1.31 (6 H), 1.33 (6 H), 1.39 (6 H), 1.42 (6 H), 1.44 (6 H), 1.45 (6 H), 1.54 (6 H), and 1.58 (6 H) (d, *J*<sub>HH</sub> = 6 Hz); δ (OCHMe<sub>2</sub>) 3.55 (2 H), 3.69 (1 H), 4.88 (2 H), 5.05 (2 H), and 5.16 (2 H) (sept, *J*<sub>HH</sub> = 6 Hz); δ (CMe) 4.04 (3 H, s). At 21 °C coupling to <sup>183</sup>W is observed for the ethylidyne protons: *J*<sub>WH</sub> = 5.7 Hz.

IR (cm<sup>-1</sup>): 1317 (m), 1160 (m), 1118 (s), 1001 (m), 980 (s), 958 (s), 846 (m), 609 (m), 595 (m), 580 (m), 554 (w), 456 (w), 430 (w), 215 (w).

W<sub>4</sub>(CSiMe<sub>3</sub>)<sub>2</sub>(OEt)<sub>14</sub>. W<sub>2</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub><sup>22</sup> (0.50 mmol) was dissolved in hexanes (10 mL) and ethanol (5.0 mmol) was added to

the solution via syringe. After allowing the mixture to stand at ambient temperature for 12 h, the solvent was removed in vacuo, and the resulting solid residues were dissolved in hexanes (10 mL). Filtration yielded a red-brown supernatant liquid and no perceptible solid residue. Drastic reduction of the solvent volume followed by refrigeration at -20 °C produced large dark-red crystals identified as W<sub>4</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub>(OEt)<sub>14</sub> by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy, X-ray crystallography, and elemental analysis. Yield 0.26 g, 68%. Anal. Calcd for W<sub>4</sub>O<sub>14</sub>Si<sub>2</sub>C<sub>36</sub>H<sub>88</sub>: C, 28.06; H, 5.76. Found: C, 28.01; H, 5.65.

<sup>1</sup>H NMR spectrum (-70 °C, toluene-*d*<sub>6</sub>): δ 4.92, 4.86, 4.70, 4.65, 4.50, 4.38, and 4.01 (2 H, m, OCH<sub>2</sub>CH<sub>3</sub>); 1.72, 1.56, 1.44, 1.39, 1.38, 1.29, and 1.24 (3 H, t, OCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz), 0.61 (9 H, s, μ-CSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (21 °C, CD<sub>2</sub>Cl<sub>2</sub>): δ 71.3 (OCH<sub>2</sub>C-H<sub>3</sub>), 18.8 (OCH<sub>2</sub>CH<sub>3</sub>), 3.58 (μ-CSiMe<sub>3</sub>).

IR spectrum (Nujol) (cm<sup>-1</sup>): 1375 (s), 1240 (m), 1149 (m), 1110 (s), 1094 (s), 1050 (vs, b), 1032 (vs, b), 914 (s), 904 (s), 877 (s), 836 (s), 751 (m), 682 (w), 624 (m), 608 (w), 573 (m), 546 (m), 513 (s), 472 (m), 411 (w), 368 (w), 329 (w), 321 (w).

A solution molecular weight range of 1500-1700 g/m was determined for W<sub>4</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub>(OEt)<sub>14</sub> via freezing point depression in benzene.

**Crystallographic Studies.** General operating procedures and listings of programs have been reported.<sup>6a</sup> Crystal data for the two compounds are summarized in Table VII. Preliminary examination of the mixed-metal compound Mo<sub>2</sub>W(CMe)(O-*i*-Pr)<sub>9</sub> indicated it was isomorphous with W<sub>3</sub>(CMe)(O-*i*-Pr)<sub>9</sub>. The mixed-metal compound is undoubtedly disordered with respect to the location of the metal atoms so no data were taken other than the cell parameters. For Mo<sub>2</sub>W(CMe)(O-*i*-Pr)<sub>9</sub>, *a* = 18.191 (8) Å, *b* = 11.391 (5) Å, *c* = 11.501 (5) Å, α = 110.79 (2)°, β = 72.65 (2)°, γ = 75.31 (2)°.

W<sub>3</sub>(CMe)(O-*i*-Pr)<sub>9</sub>. A suitable crystal was cleaved from a large "clump" of crystals and was transferred to the goniostat under a N<sub>2</sub> atmosphere.

Data were located in the usual manner and the three metal atoms located in a map phased by direct methods. All remaining non-hydrogen atoms were located in a subsequent difference Fourier. Nearly all hydrogen atoms were visible in a difference map phased on the non-hydrogen coordinates, but attempts to refine them isotropically failed, with several failing to converge. For this reason all hydrogens were placed in fixed idealized positions [d(C-H) = 0.95 Å] for the final cycles of refinement.

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Data were corrected for absorption, although the correction may be poorly defined due to the very irregular shape of the fragment utilized. A final difference Fourier revealed several peaks of density 1.0 to 2.1 e/Å<sup>3</sup> within 1.0 Å of the three metal atoms but was otherwise featureless.

**W<sub>4</sub>(CSiMe<sub>3</sub>)<sub>2</sub>(OEt)<sub>14</sub>.** A suitable small crystal was selected and transferred to the goniostat, where it was cooled to -155 °C. The crystal was characterized in the usual manner. A systematic search of a limited hemisphere of reciprocal space yielded a set of diffraction maxima which exhibited monoclinic symmetry and had systematic extinctions corresponding to the unique space group *P*<sub>2</sub><sub>1</sub>/*n*.

The structure was solved by locating the two W atoms with direct methods, and the remainder of the non-hydrogen atoms were located in two successive difference Fourier phases with the W atoms. The structure was refined by full-matrix least-squares with use of anisotropic thermal parameters on all atoms, and the hydrogen atoms were then located in a difference Fourier. Final refinements were completed with use of isotropic thermal parameters on the hydrogen atoms.

A final difference Fourier was essentially featureless, and a few peaks of ca. 0.8-1.0 e/Å<sup>3</sup> were located in proximity to the W atoms.

The molecule contains a crystallographic center of inversion.

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**Note Added in Proof.** We have recently found that W<sub>4</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub>(OEt)<sub>14</sub> crystallizes from hexane in a second monoclinic form. Crystal data at -160 °C are as follows: *a* = 14.207 (8) Å, *b* = 10.821 (5) Å, *c* = 17.391 (11) Å, β = 97.69 (3)°, *Z* = 2, *d*<sub>calcd</sub> = 1.926 g cm<sup>-3</sup> in the space group *P*<sub>2</sub><sub>1</sub>/*c*. All molecular dimensions are within 3σ. The two molecular structures are essentially superimposable.

**Registry No.** W<sub>3</sub>(O-*i*-Pr)<sub>9</sub>(CMe), 94499-61-3; W<sub>4</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub>(OEt)<sub>14</sub>, 94517-67-6; Mo<sub>2</sub>W(CMe)(O-*i*-Pr)<sub>9</sub>, 94499-62-4; W<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(μ-C<sub>4</sub>Me<sub>4</sub>)(C<sub>2</sub>Me<sub>2</sub>), 87654-13-5; W<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(Py)<sub>2</sub>, 70178-75-5; (*t*-BuO)<sub>3</sub>W≡CMe, 82209-23-2; Mo<sub>2</sub>(O-*i*-Pr)<sub>6</sub>, 62521-20-4; W<sub>2</sub>(μ-CSiMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>, 59654-41-0; C<sub>2</sub>Me<sub>2</sub>, 503-17-3.

**Supplementary Material Available:** Complete listings of bond lengths and bond angles, anisotropic thermal parameters, and structure factor amplitudes (81 pages). Ordering information is given on any masthead page. The complete structural reports are available from the Indiana University Chemistry Library in microfiche form only at \$2.50 per report. Request MSC Report No. 84041 and 84047 for W<sub>3</sub>(CMe)(O-*i*-Pr)<sub>9</sub> and W<sub>4</sub>(CSiMe<sub>3</sub>)<sub>2</sub>(OEt)<sub>14</sub>, respectively.

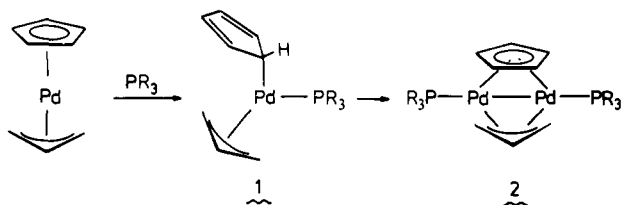
## Interconversion of η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>, η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub>, and Ionic "η<sup>0</sup>"-C<sub>5</sub>H<sub>5</sub> Rhenium Compounds—X-ray Crystal Structure of [Re(NO)(CH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>]<sup>+</sup>[C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received July 30, 1984

**Abstract:** The reaction of (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(CH<sub>3</sub>)(PMe<sub>3</sub>) (6) and PMe<sub>3</sub> produced (η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(CH<sub>3</sub>)(PMe<sub>3</sub>)<sub>3</sub> (10). The reaction is reversible with *K*<sub>eq</sub> = 0.4 M<sup>-2</sup> at 4 °C in THF-*d*<sub>6</sub>. Upon heating at 48 °C in THF in the presence of high concentrations of PMe<sub>3</sub>, the equilibrium mixture of 6 and 10 was converted to [Re(NO)(CH<sub>3</sub>)(PMe<sub>3</sub>)<sub>4</sub>]<sup>+</sup>[C<sub>5</sub>H<sub>5</sub>]<sup>-</sup> (9), which precipitates from solution. When 9 was heated in THF at 81 °C in the absence of added PMe<sub>3</sub>, it was reconverted to 6 and free PMe<sub>3</sub>. The structure of 9 was determined by X-ray crystallography: monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c*, with unit cell constants *a* = 12.893 (2) Å, *b* = 13.622 (2) Å, *c* = 15.068 (2) Å, β = 97.47 (2)°, and *Z* = 4.

The reactions of trialkylphosphines with η<sup>5</sup>-cyclopentadienyl transition-metal complexes result in a variety of interesting cyclopentadienyl ligand transformations. Werner reported that the reaction of (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Pd(2-RC<sub>3</sub>H<sub>4</sub>) with P(*i*-Pr)<sub>3</sub> produced an η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub> mono(phosphine) adduct 1 which reacted further to give the novel binuclear complex 2 in which the C<sub>5</sub>H<sub>5</sub> ring spans two metals.<sup>1</sup>

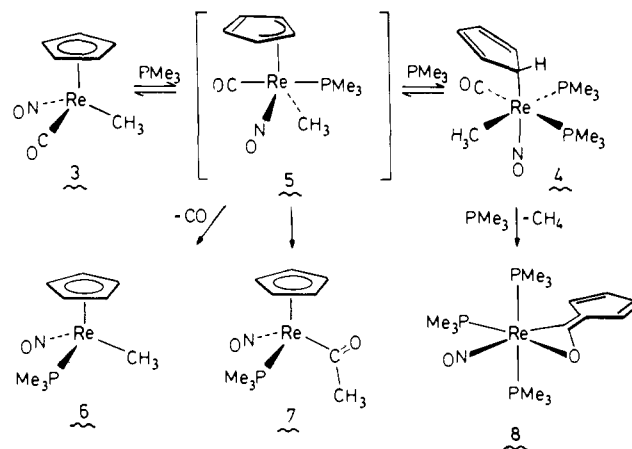


We have previously reported evidence for cyclopentadiene ring slippage (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> ⇌ η<sup>3</sup>-C<sub>5</sub>H<sub>5</sub> ⇌ η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub>) during phosphine substitution reactions at coordinatively saturated metal centers.<sup>2</sup>

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Scheme I



Thus, (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Re(NO)(CH<sub>3</sub>)(CO) (3) reacted rapidly and reversibly with 2 equiv of PMe<sub>3</sub> at 25 °C to give the η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub> bis(phosphine) adduct 4 via a proposed η<sup>3</sup>-C<sub>5</sub>H<sub>5</sub> mono(phosphine) intermediate 5. When benzene-*d*<sub>6</sub> solutions of 4 were heated to 90 °C an equilibrium mixture of 3 and 4 was slowly converted to a 4:1 (50%) mixture of phosphine-substituted methyl and acetyl complexes, 6 and 7, probably via the same η<sup>3</sup>-C<sub>5</sub>H<sub>5</sub> intermediate