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# The Molybdenum–Molybdenum Triple Bond. 16.[1] Bis[(trimethylsilyl)methylidene]tetrakis(trimethylphosphine)dibromodimolybdenum($M\equiv M$). An Example of a Nonbridged Dinuclear Bis(carbene) Complex

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Hydrocarbon solutions of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4(M\equiv M)$ react rapidly with $PMe_3$ ($\geqslant$4 equiv) to yield $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4(M\equiv M)$, I, and $Me_4Si$ (2 equiv). I reacts further in hydrocarbon solvents to give $Mo_2Br_4(PMe_3)_4(M\overset{4}{-}M)$, II, and $MoBr(\equiv CSiMe_3)(PMe_3)_4$ along with $Me_4Si$ and *trans*-$Me_3SiCH=CHSiMe_3$. The mononuclear carbyne complex reacts with diphos ($Ph_2PCH_2CH_2PPh_2$) to give $MoBr(\equiv CSiMe_3)(diphos)_2$, III. Compounds I, II, and III have been characterized by NMR spectroscopy and single-crystal X-ray crystallography. I provides the first example of a nonbridged dinuclear bis(carbene) complex and the first example of the attachment of a divalent monodentate ligand to the $(Mo\equiv Mo)^{6+}$ unit. Pertinent bond distances (Å) and angles (deg) are as follows: Mo–Mo = 2.276 (1), Mo–Br = 2.636 (1), Mo–P = 2.534 (2) and 2.535 (2), Mo–C = 1.949 (5), Mo–Mo–C = 109.0 (2), Mo–Mo–Br = 116.54 (3), Mo–Mo–P = 101.54 (4) and 97.98 (4). Molecules of II belong to the symmetry group $C_{2v}$. There is a central $Mo_2Br_4P_4$ unit typical of that seen for compounds of formula $Mo_2X_4L_4(M\overset{4}{-}M)$: Mo–Mo = 2.131 (2) Å, Mo–Br = 2.553 (2) and 2.549 (1) Å, Mo–P = 2.554 (3) and 2.549 (3) Å; Mo–Mo–Br = 114 (1)°, and Mo–Mo–P = 102 (1)°. III contains a central $MoP_4(C)(Br)$ octahedral unit with the carbyne and bromide ligands occupying trans positions: Mo–C = 1.82 (1) Å, Mo–Br = 2.731 (3) Å, Mo–P = 2.50 (3) Å (averaged), and Br–Mo–C = 176.5 (1)°. Reactions between 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ and the monodentate phosphines proceed similarly to give $Mo_2Br_4L_4$ and $MoBr(\equiv CSiMe_3)L_4$ compounds, where L = $PMe_2Ph$ and $PEt_3$, via $Mo_2Br_2(=CHSiMe_3)_2L_4$ compounds which may be detected spectroscopically but not isolated because of their more rapid decomposition. The reaction between dmpm ($Me_2PCH_2PMe_2$) and 1,2-$Mo_2Br_2(CH_2SiMe_3)_4(M\equiv M)$ yields a thermally more stable compound $Mo_2Br_2(=CHSiMe_3)_2(dmpm)_2$ which, based on NMR spectroscopic data, is formulated as an analogue of I. Crystal data for I at −165 °C: $a$ = 20.461 (11) Å, $b$ = 9.918 (4) Å, $c$ = 20.468 (11) Å, $\beta$ = 120.67 (2)°, $Z$ = 4, $d_{calcd}$ = 1.540 g cm$^{-3}$, and space group $A2/a$. Crystal data for II at −171 °C: $a$ = 17.384 (7) Å, $b$ = 9.298 (3) Å, $c$ = 18.297 (7) Å, $\beta$ = 114.63 (2)°, $Z$ = 4, $d_{calcd}$ = 2.016 g cm$^{-3}$, and space group $A2/a$. Crystal data for III at −160 °C: $a$ = 16.133 (12) Å, $b$ = 16.571 (12) Å, $c$ = 10.546 (7) Å, $\alpha$ = 92.17 (3)°, $\beta$ = 103.13 (3)°, $\gamma$ = 95.47 (3)°, $Z$ = 2, $d_{calcd}$ = 1.400 g cm$^{-3}$, and space group $P\bar{1}$.

## Introduction

During the course of studies of metathetic reactions involving 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$, eq 1,[2] we attempted to prepare $\beta$-hydrogen-containing alkyl derivatives, e.g., X = $C_2H_5$. A rapid decomposition was noted even at low temperatures. This contrasts with the thermally stable 1,2-$Mo_2R_2(NMe_2)_4$ compounds (R = Et, Pr, Bu) which can be prepared in reactions analogous to (1) employing 1,2-$Mo_2Cl_2(NMe_2)_4$.[3]

$$\text{1,2-}Mo_2Br_2(CH_2SiMe_3)_4 + 2LiX \rightarrow \text{1,1- and 1,2-}Mo_2X_2(CH_2SiMe_3)_4 + 2LiBr \quad (1)^2$$

$$X = NMe_2,\ O\text{-}t\text{-}Bu,\ O\text{-}i\text{-}Pr,\ Me$$

We had anticipated that a compound of formula 1,2-$Mo_2Et_2(CH_2SiMe_3)_4$, if formed in the metathetic reaction 1, would be kinetically labile toward decomposition via an initial $\beta$-hydrogen abstraction step since metal d orbitals are available for M–H–C interactions. We have argued that the thermal stability and inertness toward $\beta$-hydrogen abstraction that is seen in the chemistry of 1,2-$Mo_2R_2(NMe_2)_4$ compounds arise because $Me_2N$ ligands are strong $\pi$-donor ligands and effectively interact with metal d orbitals that would otherwise be available for M–H–C interactions.[3] In an attempt to block or at least suppress decomposition by facile $\beta$-hydrogen abstraction, the metathetic reaction 1 was carried out in hexane at −78 °C in the presence of an excess of $PMe_3$. It was noted that 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ and $PMe_3$ reacted in hexane at −78 °C prior to the addition of ethyllithium. This paper describes our studies which were prompted by this observation. A preliminary report noting the formation of $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$ has appeared.[4]

## Results and Discussion

**Syntheses and Reactivity Patterns.** Addition of $PMe_3$ ($\geqslant$4 equiv) to a hexane or toluene solution of 1,2-$Mo_2Br_2(CH_2SiMe_3)_4$ causes an immediate color change from reddish orange to brown, even at −78 °C. When the reaction was carried out in a sealed NMR tube in toluene-$d_8$ as solvent, the formation of $Me_4Si$ (2 equiv) was detected. The possible formation of $Me_4Si$-$d_1$ was ruled out on the basis of $^2H$ NMR spectroscopy and GC/MS analyses of the volatile components in this reaction. This suggested that the hydrogen atom required to form $Me_4Si$ originated from the $\alpha$- or $\gamma$-carbon atom of the $Me_3SiCH_2$ ligands. The $^{31}P\{^1H\}$ NMR spectrum obtained on the NMR tube reaction mixture was more informative and is

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[1] Part 15. Chiu, H. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097.

[2] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 251.

[3] Chisholm, M. H.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *103*, 4046.

[4] Ahmed, K. J.; Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1983**, *105*, 6453.

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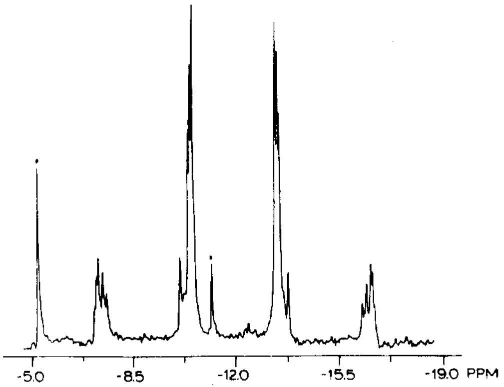


**Figure 1.** $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared (see text) sample of $Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$, in toluene-$d_8$, 16 °C at 40.5 MHz. Signals denoted by an asterisk correspond to $Mo_2Br_4(PMe_3)_4$ and $MoBr({\equiv}CSiMe_3)(PMe_3)_4$.

shown in Figure 1. The major product, ca. 85% based on $^{31}P$ signal intensities, has an AA'BB' spin system, and the two minor products show singlets in the ratio 2:1. With time the latter grow in intensity at the expense of the initially formed major product.

On a preparative scale, the major product can be isolated in 70% yield (based on eq 2) by extracting the crude solid product with hexane and subsequently crystallizing it at ca. −15 °C.

$$\mathrm{Mo_2Br_2(CH_2SiMe_3)_4 + 4PMe_3 \rightarrow \underset{I}{Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4} + 2Me_4Si} \quad (2)$$

Compound I is an air-sensitive, diamagnetic, amber crystalline solid. It is stable in the solid state at room temperature when stored sealed in vials either under nitrogen or in vacuo. In solution (hexane or toluene), it decomposes over a period of 1 week at room temperature and overnight at 65 °C, yielding green solutions. The decomposition of I in sealed NMR tubes has been followed by NMR spectroscopy. The $^1H$ NMR spectrum suggested the formation of $Me_4Si$ (2 equiv) and *trans*-$Me_3SiCH{=}CHSiMe_3$ (1 equiv). These volatile compounds were subsequently identified by mass spectroscopy and gas chromatography. From the decomposition of I in toluene-$d_8$, no $^2H$ incorporation into the organosilanes was observed. The $^{31}P\{^1H\}$ NMR spectrum of the decomposed solution of I showed only two singlets, one at $\delta$ −5 and the other at $\delta$ −11 (relative to $H_3PO_4$ external reference) in the integral ratio of 2:1, respectively. These are the two signals seen in the preparation of I in a sealed NMR tube as shown in Figure 1. There is no evidence for the liberation of $PMe_3$. Fractional crystallization from hexane gave a blue crystalline compound $Mo_2Br_4(PMe_3)_4$, which was subsequently identified as the compound having the $^{31}P$ signal at $\delta$ −11. We were unable to crystallize the other phosphorus-containing compound ($\delta(^{31}P)$ −5) or separate it completely from all traces of $Mo_2Br_4(PMe_3)_4$. However, by addition of diphos ($Ph_2PCH_2CH_2PPh_2$) the yellow crystalline compound $MoBr({\equiv}CSiMe_3)(diphos)_2$ was obtained and fully characterized. We believe this is formed by a simple substitution reaction and that the former compound is $MoBr({\equiv}CSiMe_3)(PMe_3)_4$. On the basis of NMR spectral data of the decomposition of I in sealed NMR tubes and the identification of the species present in solution, we would hope to be able to write a stoichiometric equation describing this process. However, this is not possible. The reactants and products shown in 3 come close in being balanced with respect to C, H, Br, and P. The fate of molybdenum is not clear. We have found that $Mo(arene)_2$ compounds are not formed. There is always a very small quantity of solid formed during the decomposition. Possibly this is molybdenum metal and accounts for the material imbalance in (3).

**Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $Mo_2Br_2(CHSiMe_3)_2(PMe_3)_4$ Molecule**

| atom | $10^4x$ | $10^4y$ | $10^4z$ | $10B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| Mo(1) | 7505.5 (2) | 304.5 (4) | 558.7 (2) | 10 |
| Br(2) | 6566.3 (3) | 1990.2 (5) | 662.2 (3) | 16 |
| P(3) | 6458 (1) | −1368 (1) | 280 (1) | 14 |
| C(4) | 6606 (4) | −3120 (6) | 123 (4) | 20 |
| C(5) | 5487 (3) | −1049 (7) | −474 (3) | 18 |
| C(6) | 6306 (4) | −1580 (7) | 1080 (4) | 20 |
| P(7) | 8451 (1) | 2202 (1) | 1206 (1) | 14 |
| C(8) | 9419 (3) | 1924 (7) | 1437 (4) | 17 |
| C(9) | 8562 (3) | 2545 (7) | 2132 (3) | 18 |
| C(10) | 8304 (4) | 3907 (5) | 839 (4) | 19 |
| C(11) | 8276 (3) | −958 (5) | 1257 (3) | 16 |
| Si(12) | 8586 (1) | −1363 (1) | 2266 (1) | 14 |
| C(13) | 8480 (4) | −3219 (6) | 2350 (4) | 20 |
| C(14) | 8066 (4) | −438 (7) | 2663 (4) | 22 |
| C(15) | 9617 (3) | −952 (7) | 2890 (4) | 23 |

**Table II. Selected Bond Distances (Å) and Angles (deg) in the $Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$ Molecule**

| Bond Distances | | | |
|---|---|---|---|
| Mo(1)–Mo(1) | 2.276 (1) | Mo(1)–C(11) | 1.949 (5) |
| Mo(1)–Br(2) | 2.636 (1) | P–C | 1.81 (1) (av) |
| Mo(1)–P(3) | 2.535 (2) | Si–C | 1.87 (1) (av) |
| Mo(1)–P(7) | 2.534 (2) | | |

| Bond Angles | | | |
|---|---|---|---|
| Mo(1)–Mo(1)–Br(2) | 116.54 (3) | P(3)–Mo(1)–P(7) | 159.39 (4) |
| Mo(1)–Mo(1)–P(3) | 101.54 (4) | P(3)–Mo(1)–C(11) | 91.12 (15) |
| Mo(1)–Mo(1)–P(7) | 97.98 (4) | P(7)–Mo(1)–C(11) | 88.71 (15) |
| Mo(1)–Mo(1)–C(11) | 109.09 (17) | Mo(1)–C(11)–Si(12) | 129.81 (32) |
| Br(2)–Mo(1)–P(3) | 82.28 (5) | Mo(1)–C(11)–H | 120 (3) |
| Br(2)–Mo(1)–P(7) | 83.14 (5) | Si(12)–C(11)–H | 110 (3) |
| Br(2)–Mo(1)–C(11) | 134.31 (17) | | |

$$\mathrm{3Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4 \rightarrow Mo_2Br_4(PMe_3)_4 + 2MoBr({\equiv}CSiMe_3)(PMe_3)_4 + 2Me_4Si + Me_3SiCH{=}CHSiMe_3} \quad (3)$$

Hydrocarbon solutions of $Mo_2Br_2(CH_2SiMe_3)_4$ also react with the monodentate phosphines $PMe_2Ph$ and $PEt_3$. The reaction apparently follows a similar path but is much more rapid in yielding $Mo_2Br_4L_4$ and $MoBr({\equiv}CSiMe_3)L_4$. Use of the chelating phosphine $Me_2PCH_2PMe_2$, dmpm, leads to the formation of $Mo_2Br_2({=}CHSiMe_3)_2(dmpm)_2$ and $Me_4Si$ (2 equiv) paralleling the reaction with $PMe_3$ (eq 2). The spectroscopic characterization of $Mo_2Br_2({=}CHSiMe_3)_2(dmpm)_2$, described later, firmly establishes this compound to be an analogue of I but having a different geometry because of the presence of the bridging dmpm ligands. The latter compound is quite notably more inert than I, and decomposition to $Mo_2Br_4(dmpm)_2$ and $MoBr({\equiv}CSiMe_3)(dmpm)_2$ has not been observed in hydrocarbon solutions.

**Solid-State Molecular Structures and Remarks on Bonding. $Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$, I.** Fractional coordinates and isotropic thermal parameters are given in Table I. Selected bond distances and angles are given in Table II, and an ORTEP view of the molecule giving the atom number scheme is shown in Figure 2. The molecule has crystallographically imposed $C_2$ symmetry. The central $Mo_2Br_2(C)_2P_4$ skeleton is virtually eclipsed as can be seen by the view of the molecule looking down the Mo–Mo bond shown in Figure 3.

The Mo—Mo distance of 2.276 (1) Å is comparable to distances seen for other $(Mo{\equiv}Mo)^{6+}$ containing compounds which generally fall in the range 2.20–2.30 Å.[5] The

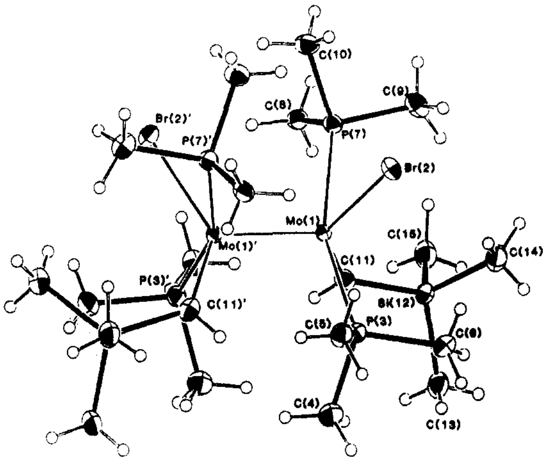


**Figure 2.** An ORTEP drawing of the $Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$ molecule showing the atom number scheme.

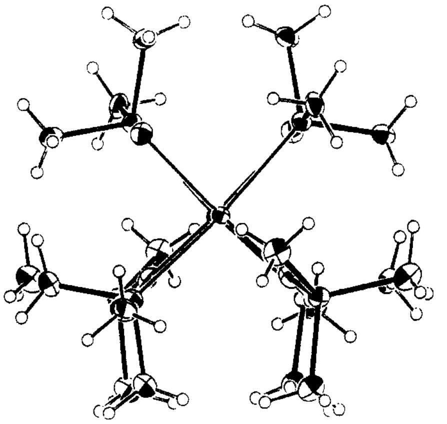


**Figure 3.** An ORTEP view of the $Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$ molecule looking down the Mo–Mo bond axis, showing the eclipsed geometry of the molecule.

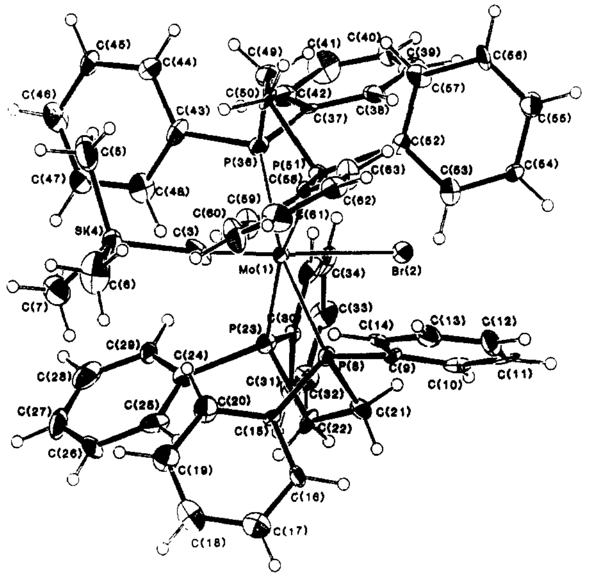
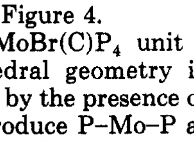


**Figure 4.** An ORTEP view of the $MoBr({\equiv}CSiMe_3)(Ph_2PCH_2CH_2PPh_2)_2$ molecule showing the almost linear Br–Mo–C–Si unit and giving the atom number scheme.

Mo═C distance of 1.949 (5) Å is most notably shorter than any $C_{sp^2}$ or $C_{sp^3}$ to Mo distance seen for alkyl or aryl groups bonded to the $(Mo{\equiv}Mo)^{6+}$ center. These fall in the range 2.14–2.19 Å.[3,6] The Mo═C distance, 1.95 (1) Å, is comparable to that seen for W═C in the mixed alkyl, alkylidene, alkylidyne compound $W({\equiv}CCMe_3)({=}CHCMe_3)(CH_2CMe_3)(dmpe)$, 1.942 (9) Å.[7] This distance is also typical of that seen for Mo–N bonds in $Mo_2X_2(NMe_2)_4$ compounds.[3,6] The latter are considered Mo–N double bonds as a result of $Me_2N$-to-Mo π-donation. The Mo–Br distance, 2.636 (1) Å, is roughly 0.1 Å longer than might have been expected, cf. Mo–Br = 2.553 (2) Å in II and W–Br = 2.482 (3) Å in $W_2Br_2(NMe_2)_4$.[8] The lengthening of the Mo–Br bond in I no doubt reflects the high trans influence[9] of the $Me_3SiCH$ ligand.

The bonding in I may be simply pictured as follows. Defining the *z* axis to be coincident with the M–M axis, each molybdenum atom may use atomic $d_{z^2}$, $d_{xz}$, and $d_{yz}$ orbitals to form one σ- and two π-bonds. The four metal ligand σ-bonds may use Mo atomic $d_{x^2-y^2}$, $p_x$, $p_y$, and s orbitals, and the $d_{xy}$ orbital will be used exclusively to form the Mo–C π-bond. Thus, as a result of forming a M–M triple bond, $\sigma^2\pi^4$, four metal–ligand σ-bonds and one metal–ligand π-bond, each metal attains a 16 valence shell of electrons as is seen in many $(M{\equiv}M)^{6+}$ containing compounds.[10] It should be noted that this picture predicts that the carbene carbon atom will orient its substituents, H and $SiMe_3$, along the M–M axis, as indeed is observed. The specific arrangement, proximal H and distal $Me_3Si$, is no doubt on steric grounds. The observed near eclipsed geometry for the $Mo_2Br_2(C)_2P_4$ unit is not required on electronic grounds but presumably arises from minimization of steric repulsions across the Mo—Mo bond, cf. the eclipsed geometry in $Re_2Cl_4(PR_3)_4$(*M≡M*) compounds.[11]

**$Mo_2Br_4(PMe_3)_4$, II.** Compound II has crystallographically imposed $C_2$ symmetry in the space group *A*2/*a*. The central $Mo_2Br_4P_4$ unit has virtual $D_{2d}$ symmetry as shown below. Since this structure is so similar to other well-characterized $(Mo\overset{4}{-}Mo)^{4+}$-containing compounds of formula $Mo_2X_4L_4$[5,12] details are made available in supplementary materials only. Pertinent bond distances are given in the abstract.



II

**$MoBr({\equiv}CSiMe_3)(diphos)_2$, III.** Compound III in the space group $P\bar{1}$ had toluene molecules of crystallization. Isotropic thermal parameters and fractional coordinates are given in Table III, and selected bond distances and angles are given in Table IV. An ORTEP view of the molecule giving the atom number scheme used in the tables is shown in Figure 4.

The central $MoBr(C)P_4$ unit is distorted from an idealized octahedral geometry in an understandable manner, namely, by the presence of two chelating diphos ligands which produce P–Mo–P angles of less than 90° within the five-membered ring and greater than 90° be-

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(5) For a recent listing of Mo–Mo distances in these and related compounds see: Cotton, F. A.; Walton, R. A. In "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(6) Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1983**, *105*, 163.

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(8) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Millar, M.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 320.

(9) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(10) Chisholm, M. H. *Faraday Symp. Chem. Soc.* **1980**, *14*, 194.

(11) Bennett, M. J.; Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 1563. See also discussion by: Cotton, F. A.; Walton, R. A. In "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; pp 184–186.

(12) E.g., $Mo_2Cl_4(PMe_3)_4$: Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kilthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

**Table III. Fractional Coordinates and Isotropic Thermal Parameters for $MoBr({\equiv}CSiMe)_3(diphos)_2$•Toluene**

| atom | $10^4x$ | $10^4y$ | $10^4z$ | $10B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| Mo(1) | 2857 (1) | 2847 (1) | 4528 (1) | 10 |
| Br(2) | 3681 (1) | 4385 (1) | 4916 (1) | 15 |
| C(3) | 2253 (7) | 1847 (7) | 4303 (11) | 18 |
| Si(4) | 1560 (2) | 855 (2) | 4174 (3) | 18 |
| C(5) | 1109 (9) | 713 (9) | 5626 (14) | 39 |
| C(6) | 2141 (9) | −69 (8) | 4028 (16) | 38 |
| C(7) | 678 (9) | 779 (8) | 2681 (13) | 28 |
| P(8) | 3981 (2) | 2681 (2) | 3260 (3) | 12 |
| C(9) | 5137 (7) | 2746 (6) | 3993 (10) | 12 |
| C(10) | 5675 (7) | 3463 (7) | 4075 (11) | 17 |
| C(11) | 6529 (7) | 3488 (7) | 4726 (11) | 17 |
| C(12) | 6851 (7) | 2815 (7) | 5304 (11) | 20 |
| C(13) | 6339 (8) | 2109 (7) | 5193 (11) | 21 |
| C(14) | 5477 (7) | 2070 (6) | 4568 (10) | 12 |
| C(15) | 3864 (7) | 1799 (6) | 2117 (10) | 10 |
| C(16) | 4461 (7) | 1747 (7) | 1338 (10) | 15 |
| C(17) | 4352 (8) | 1108 (7) | 402 (12) | 24 |
| C(18) | 3656 (8) | 531 (7) | 210 (13) | 26 |
| C(19) | 3070 (8) | 592 (7) | 956 (13) | 24 |
| C(20) | 3160 (8) | 1215 (7) | 1896 (12) | 22 |
| C(21) | 3922 (7) | 3506 (7) | 2126 (11) | 18 |
| C(22) | 3008 (7) | 3477 (7) | 1314 (11) | 16 |
| P(23) | 2195 (2) | 3386 (2) | 2335 (3) | 13 |
| C(24) | 1301 (7) | 2767 (7) | 1207 (11) | 16 |
| C(25) | 1427 (8) | 2108 (8) | 449 (11) | 22 |
| C(26) | 735 (8) | 1641 (8) | −397 (11) | 24 |
| C(27) | −95 (8) | 1831 (8) | −490 (13) | 29 |
| C(28) | −225 (8) | 2479 (9) | −296 (13) | 29 |
| C(29) | 465 (7) | 2934 (7) | 1111 (11) | 17 |
| C(30) | 1778 (6) | 4368 (7) | 2161 (10) | 12 |
| C(31) | 1521 (8) | 4684 (7) | 917 (11) | 19 |
| C(32) | 1139 (8) | 5396 (7) | 788 (11) | 20 |
| C(33) | 983 (8) | 5826 (7) | 1858 (13) | 24 |
| C(34) | 1219 (7) | 5517 (7) | 3072 (13) | 24 |
| C(35) | 1619 (7) | 4808 (7) | 3212 (12) | 19 |
| P(36) | 1934 (2) | 3247 (2) | 6028 (3) | 14 |
| C(37) | 1834 (7) | 4316 (7) | 6549 (10) | 16 |
| C(38) | 2580 (7) | 4795 (7) | 7254 (11) | 16 |
| C(39) | 2512 (8) | 5587 (8) | 7620 (11) | 24 |
| C(40) | 1745 (7) | 5929 (7) | 7381 (12) | 21 |
| C(41) | 1023 (8) | 5449 (7) | 6725 (13) | 27 |
| C(42) | 1066 (7) | 4642 (8) | 6302 (11) | 20 |
| C(43) | 788 (7) | 2845 (7) | 5611 (12) | 20 |
| C(44) | 310 (8) | 2742 (7) | 6549 (12) | 21 |
| C(45) | −543 (7) | 2457 (8) | 6162 (12) | 22 |
| C(46) | −934 (7) | 2271 (8) | 4881 (12) | 24 |
| C(47) | −462 (7) | 2351 (7) | 3934 (11) | 20 |
| C(48) | 398 (7) | 2643 (8) | 4309 (12) | 22 |
| C(49) | 2361 (8) | 2872 (8) | 7687 (11) | 25 |
| C(50) | 2978 (7) | 2232 (6) | 7681 (11) | 14 |
| P(51) | 3735 (2) | 2519 (2) | 6654 (3) | 13 |
| C(52) | 4528 (7) | 3269 (6) | 7673 (10) | 11 |
| C(53) | 5186 (7) | 3603 (7) | 7120 (11) | 17 |
| C(54) | 5843 (7) | 4141 (7) | 7846 (11) | 17 |
| C(55) | 5871 (8) | 4351 (8) | 9153 (11) | 24 |
| C(56) | 5231 (8) | 4041 (7) | 9700 (11) | 21 |
| C(57) | 4559 (7) | 3511 (7) | 8974 (11) | 17 |
| C(58) | 4347 (7) | 1616 (6) | 6782 (11) | 14 |
| C(59) | 3956 (8) | 921 (8) | 6018 (13) | 27 |
| C(60) | 4380 (9) | 225 (8) | 6130 (13) | 30 |
| C(61) | 5162 (8) | 206 (7) | 6966 (12) | 25 |
| C(62) | 5538 (7) | 900 (7) | 7698 (11) | 17 |
| C(63) | 5121 (7) | 1611 (7) | 7621 (12) | 19 |
| C(64)[a] | 7850 (8) | 1399 (8) | 469 (13) | 24 |
| C(65) | 7786 (8) | 1057 (8) | 1673 (15) | 34 |
| C(66) | 7260 (9) | 1372 (10) | 2390 (14) | 39 |
| C(67) | 6778 (9) | 2007 (11) | 1915 (16) | 46 |
| C(68) | 6839 (8) | 2345 (9) | 724 (14) | 36 |
| C(69) | 2620 (9) | 7965 (8) | 5 (14) | 32 |
| C(70) | 7450 (10) | 2384 (10) | −1272 (16) | 47 |

[a] Note C(64) through C(70) are toluene carbon atoms.

**Table IV. Selected Bond Distances (Å) and Angles (deg) for the $MoBr({\equiv}CSiMe)_3(diphos)_2$ Molecule**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Mo(1)–C(3) | 1.819 (12) | Mo(1)–P(36) | 2.517 (3) |
| Mo(1)–P(51) | 2.475 (3) | Mo(1)–P(23) | 2.550 (3) |
| Mo(1)–P(8) | 2.514 (3) | Mo(1)–Br(2) | 2.731 (2) |
| Bond Angles | | | |
| C(3)–Mo(1)–P(51) | 91.7 (1) | P(51)–Mo(1)–Br(2) | 89.0 (1) |
| C(3)–Mo(1)–P(8) | 102.8 (1) | P(8)–Mo(1)–P(36) | 168.6 (1) |
| C(3)–Mo(1)–P(36) | 87.8 (1) | P(8)–Mo(1)–P(23) | 77.6 (1) |
| C(3)–Mo(1)–P(23) | 98.4 (1) | P(8)–Mo(1)–Br(2) | 80.6 (1) |
| C(3)–Mo(1)–Br(2) | 176.5 (1) | P(36)–Mo(1)–P(23) | 105.1 (1) |
| P(51)–Mo(1)–P(8) | 96.0 (1) | P(36)–Mo(1)–Br(2) | 88.9 (1) |
| P(51)–Mo(1)–P(36) | 79.5 (1) | P(23)–Mo(1)–Br(2) | 81.2 (1) |
| P(51)–Mo(1)–P(23) | 169.0 (1) | Mo(1)–C(3)–Si(4) | 174.2 (7) |

tween P atoms of different ligands. On average, the C–Mo–P angles are larger than the Br–Mo–P angles, typical of the general phenomenon that multiple bonds take up more room on the surface of an atom than do single bonds.[13] The Mo—Br distance, 2.731 (2) Å, is exceedingly long reflecting the extremely high trans influence[9] of the $Me_3SiC{\equiv}$ ligand. The Mo—C distance, 1.819 (12) Å, is extremely short, cf. W≡C distances of 1.907 (2) Å in *trans*-$WI({\equiv}CPh)(CO)_4$[14] and 1.891 (25) Å in *trans*-$WMe({\equiv}CMe)(PMe_3)_4$.[15] In the Fischer compound the carbyne ligand competes with the carbonyl π-acceptor ligands for bonding to the metal $t_{2g}$ orbitals. In the Wilkinson compound the ethylidyne ligand is trans to a methyl ligand, and under this mutual high trans influence[9] both W–C bonds are longer than might otherwise have been expected. Thus the short Mo≡C distance in III is quite understandable.

**NMR Studies.** NMR data are recorded in the Experimental Section. The $^{13}C$ chemical shifts for the Mo≡C and Mo=C carbon atoms are in the anticipated range.[16,17] The $^1H$ chemical shifts for the $Me_3SiCH$ hydrogen atoms in II and $Mo_2Br_2({=}CHSiMe_3)_2(dmpm)_2$, IV, are extremely deshielded, δ 14–17, consistent with the observation that in the solid state the C—H bond is positioned directly over the Mo≡Mo bond.[18,19] Although we expect restricted rotation about the Mo–C(carbene) bond on electronic grounds, the NMR data establish only that in the ground state the C–H bond is directed over the M–M triple bond.

The $^{31}P\{^1H\}$ spectrum for I reveals an expected AA′BB′ spectrum, expected in terms of the observed solid state structure.[20] At low temperatures the $^{31}P\{^1H\}$ spectrum of $Mo_2Br_2({=}CHSiMe_3)_2(dmpm)_2$ appears as an A′ABB′ spectrum, but upon raising the temperature this collapses to a singlet. The $^1H$ NMR spectrum at low temperature shows four PMe signals, each being a doublet, $J_{PH}$ = 5–7 Hz. At higher temperatures these collapse to two doublets. These observations are consistent with the adoption of the structures shown in IVA and IVB. At low temperatures there is a slight twist of the bridging dmpm ligand as it crosses the Mo–Mo bond. The dihedral angle P–Mo–

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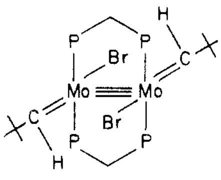
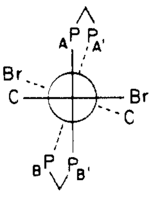
[20] The spectrum and coupling constants are similar to those observed in $Mo_2R_4(PR'_3)_2(PR''_3)_2(Mo\overset{4}{-}Mo)$ compounds: Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953.



IVa



IVB

Mo–P is not zero in the ground state as shown in IVB. However, at higher temperatures twisting about the Mo–Mo bond yields a time-averaged P–Mo–Mo–P dihedral angle of zero and the central skeleton has $C_{2h}$ symmetry as shown in IVA.

## Concluding Remarks

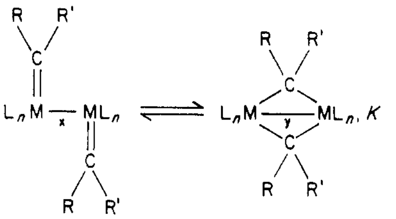
1. An interesting analogy with mononuclear chemistry is seen, both in reactivity and structure, when reaction 2 is compared with the $PMe_3$-promoted $\alpha$-abstraction reaction shown in eq 4.[17a] The structural analogy between I

$$\mathrm{W({\equiv}CCMe_3)(CH_2CMe_3)_3 + 2PMe_3 \rightarrow \underset{V}{W({\equiv}CCMe_3)({=}CHCMe_3)(CH_2CMe_3)(PMe_3)_2} + Me_4C} \qquad (4)^{17a}$$

and the dmpe analogue of V[7] is most striking. In both molecules, the metal atoms are in distorted square-based pyramidal geometries with the M≡X function occupying the apical position.

2. In I, the molybdenum atoms attain a share of 16 valence electrons and the $Me_3SiCH$ ligand is not of the "grossly distorted" type of alkylidene ligand commonly observed when an electron-deficient early transition metal shows incipient M—H and M≡C bond formation.[21] It is tempting to propose that the observed decomposition of I and formation of the $Me_3SiC{\equiv}$ containing complex proceeds via initial $PMe_3$ dissociation. This would make a metal d orbital available for an M–H–C interaction. Of particular note in this regard is the recent report by Rothwell and co-workers,[22] who noted the formation of the novel $\mu$-hydrido, $\mu$-alkylidyne complex $Mo_2(OAr)_2(CH_2SiMe_3)_2(\mu\text{-}H)(\mu\text{-}CSiMe_3)(py)_2$ in the reaction between 1,2-$Mo_2(OAr)_2(CH_2SiMe_3)_4$ and pyridine (Ar = 2,6-dimethylphenyl, py = pyridine). This compound, though only isolated in low yields, provides an example of where the $\alpha$-C–H bond of the $Me_3SiCH$ ligand has been converted to hydrido and carbyne ligands at a dinuclear metal center. In our work the course leading to the formation of $Mo_2Br_4(PMe_3)_4$ and $MoBr({\equiv}CSiMe_3)(PMe_3)_4$ is unclear but must surely involve a similar step in generating $Me_4Si$ and the $Mo{\equiv}CSiMe_3$ moiety.

3. In dinuclear chemistry carbene ligands generally occupy bridging positions. Indeed to our knowledge in dinuclear compounds containing two or more CRR′ ligands the latter are always found in the bridging positions though there is good evidence that bridge to terminal site exchange may be promoted by a relatively modest energy of activation.[23,24] The situation can be considered in terms of a generalized equilibrium shown in eq 5, where x and y represent M–M bond configuration.



(5)

In cases when the M–M bonding is little perturbed in (5) the formation of four metal–carbon $\sigma$-bonds in the dibridged carbene complex can be expected to be thermodynamically favored over the formation of two metal–carbon double bonds ($\sigma + \pi$) since the $\pi$-bond component is weaker than the $\sigma$-component. However, if M–M bonding is significantly different in the bridged and unbridged forms, this will also influence the position of equilibrium. In the present case the preference for the unbridged dinuclear bis(carbene) complex I can be understood as a consequence of the latter. Formation of a bridged carbene complex would destroy one of the $\pi$-components of the M–M triple bond. Furthermore the anticipated lengthening of the M–M bond would weaken the remaining $\sigma$- and $\pi$-components. We conclude that though M–C bond strengths will tend to favor bridging carbene complexes, the M–M bonding may, in certain instances, favor unbridged bis($\eta^1$-carbene) complexes. The situation parallels that for metal–amide and –alkoxide ligand which, as terminal ligands, are $\sigma$- and $\pi$-donors but may also form bridges. When steric factors permit, the bridging forms of the ligand are favored enthalpically by ca. 5–10 kcal mol$^{-1}$/bridge.[25] The occurrence of the unbridged bis(carbene) complex I is another example of the fascinating coordination chemistry surrounding the $(Mo{\equiv}Mo)^{6+}$ unit. The preference for the unbridged triple bond finds a parallel with the unbridged alkoxides of formula $Mo_2(OR)_6$ and $Mo_2(OR)_6L_2$, where L = a neutral donor ligand such as pyridine.[26] Ordinarily alkoxide bridged structures would be expected.

## Experimental Section

**Physical Techniques.** $^1H$ NMR spectra were recorded on Nicolet 360 and Varian Associates HR 220 spectrometers. $^{31}P$ NMR spectra were run on a Varian XL-100/Nicolet 1080 FT spectrometer. $^{13}C$ NMR spectra were recorded on a Nicolet 360-MHz spectrometer and a Bruker 270-MHz instrument. An HP 5992 GC/MS system was used to analyze the volatile products of the reaction. Infrared spectra were recorded on a Perkin-Elmer 283 instrument from Nujol mulls between CsI plates. Elemental analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, West Germany.

**Syntheses.** All the reactions were carried out under a dry and oxygen-free atmosphere of $N_2$, using standard Schlenk techniques. Samples were handled in a Vacuum Atmospheres Co. Dry Lab System. Hexane and toluene were eluted from molecular sieve columns and stored under $N_2$. Ether was refluxed with Na/benzophenone and also stored under $N_2$.

**$Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$(*Mo*≡*Mo*).** $Mo_2Br_2(CH_2SiMe_3)_4$[2] (0.94 g, 1.34 mmol) was dissolved in toluene (40 mL), and, with the use of a calibrated vacuum manifold, $PMe_3$ (5.36 mmol, 4 equiv) was condensed onto this solution frozen at −196 °C. The mixture was brought to −78 °C and stirred at that temperature for 15 min. Then it was slowly brought to room temperature and stirred for another 10 min after which the solvent was removed in vacuo and the residue was extracted with hexane (100 mL). A small quantity of insoluble material was removed by filtration, and the filtrate was reduced in volume and cooled to ca. −15 °C. The green-yellow microcrystalline precipitate so formed was collected and recrystallized from hexane slowly

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**Table V. Crystal Data Summary**[a]

| | I | II | III |
|---|---|---|---|
| empirical formula | $Mo_2C_{20}H_{56}Br_2P_4Si_2$ | $Mo_2C_{12}H_{36}Br_4P_4$ | $MoC_{56}H_{57}BrP_4Si\cdot C_7H_8$ |
| color of Cyst | yellow–brown | red/green | yellow |
| crystal dimens, mm | 0.20 × 0.24 × 0.28 | 0.21 × 0.23 × 0.18 | 0.08 × 0.09 × 0.12 |
| space group | *A*2/*a* | *A*2/A | $P\bar{1}$ |
| cell dimens | | | |
| temp, (°C) | −165 | −171 | −160 |
| *a*, Å | 20.461 (11) | 17.384 (7) | 16.133 (12) |
| *b*, A | 9.918 (4) | 9.298 (3) | 16.571 (12) |
| *c*, A | 20.468 (11) | 18.297 (7) | 10.546 (7) |
| $\alpha$, deg | | | 92.17 (3) |
| $\beta$, deg | 120.67 (2) | 114.63 (2) | 103.13 (3) |
| $\gamma$, deg | | | 95.47 (3) |
| *Z* (molecules/cell) | 4 | 4 | 2 |
| vol, Å$^3$ | 3572.31 | 2688.35 | 2727.91 |
| Density (gm/cm$^3$) | 1.540 | 2.016 | 1.400 |
| wavelength, Å | 0.71069 | 0.71069 | 0.71069 |
| mol wt | 828.42 | 815.81 | 1150.03 |
| linear abs coeff, cm$^{-1}$ | 31.543 | 70.349 | 11.352 |
| detector to sample dist, cm | 22.5 | 22.5 | 22.5 |
| sample to source dist, cm | 23.5 | 23.5 | 23.5 |
| av $\omega$ scan width at half height | 0.25 | 0.25 | 0.25 |
| scan speed, deg/min | 10.0 | 4.0 | 4.0 |
| scan width, deg, + dispersion | 1.8 | 2.0 | 2.0 |
| individual bkgd, s | 3 | 4 | 10 |
| aperture size, mm | 3.0 × 4.0 | 3.0 × 4.0 | 3.0 × 4.0 |
| $\theta$ range, deg | 5–40 | 6–45 | 6–45 |
| total no. of reflctns collected | 2802 | 2509 | 7456 |
| no. of unique intensities | 1674 | 1749 | 7168 |
| no. with $F > 2.33\sigma(R)$ | 1581 | 1468 | 4985 |
| $R(F)$ | 0.023 | 0.051 | 0.075 |
| $R_w(F)$ | 0.027 | 0.042 | 0.068 |
| goodness of fit for the last cycle | 1.074 | 2.259 | 0.981 |
| max $\Delta/\sigma$ for last cycle | 0.07 | 0.05 | 0.05 |

[a] I is $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$, II is $Mo_2Br_4(PMe_3)_4$, and III is $MoBr(\equiv CSiMe_3)(Ph_2PCH_2CH_2PPh_2)_2$·toluene.

(cooling from 50 to 18 °C) yielding amber crystals of $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$ (0.77 g, ca. 70% yield based on **2**).

NMR data obtained from solutions in toluene-$d_8$ at +16 °C ($\delta$ in ppm relative to $Me_4Si$ for $^1H$ and $^{13}C$ and $H_3PO_4$ for $^{31}P$): $^1H$ 0.80 (s, $Me_3Si$), 1.45 (d, $J$ = 7 Hz), 1.55 (d, $J$ = 7 Hz, PMe), 14.1 (virtual triplet, $J$ = 6.4 Hz, $=CHSiMe_3$); $^{13}C\{^1H\}$ 3.5 ($SiMe_3$), 17.5 (d, $J$ = 23 Hz), 19.5 (d, $J$ = 25 Hz, $PMe_3$), 283 ($CHSiMe_3$); $^{31}P\{^1H\}$ −8, −14 (AA′BB′ spin pattern, $J_{AB} \approx 140$ Hz). Infrared data: 1418 (m), 1290 (s), 1280, (s), 1270 (s), 1255 (w), 1238 (w), 1230 (s), 950 (vs), 940 (vs), 850 (sb), 820 (s), 785 (w), 750 (w), 730 (w), 722 (m), 715 (m), 680 (w), 670 (w), 660 (w), 620 (w), 415 (w), 325 (wb), 270 (wb) cm$^{-1}$.

Anal. Calcd for $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$: C, 29.00; H, 6.81; Br, 19.29. Found: C, 29.09; H, 6.83; Br, 19.30.

**$Mo_2Br_4(PMe_3)_4(Mo\overset{4}{-}Mo)$.** $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$ (0.8 g) was dissolved in toluene (20 mL), and the solution was stirred for 10 h at 65 °C during which time the color changed from brown to dark green. This green solution was reduced in volume and cooled to ca. −15 °C resulting in the formation of dark blue crystals: $Mo_2Br_4(PMe_3)_4$ (0.15 g, 25% based on (3)).

NMR data obtained from toluene-$d_8$ solutions at +16 °C: $^1H$ $\delta$ 1.4 (t, $^2J + {}^4J_{P-H}$ = 6.5 Hz, $^{13}C\{^1H\}$ $\delta$ 13.7 (t, $^1J + {}^3J_{P-C}$ = 25 Hz); $^{31}P$ $\delta$ −11.1 (s).

**$MoBr(\equiv CSiMe_3)(Ph_2PCH_2CH_2PPh_2)_2$·Toluene.** $Mo_2Br_2(CH_2SiMe_3)_4$ (0.9 g, 1.3 mmol) was dissolved in toluene, and $PMe_2Ph$ (0.75 mL, 4 equiv) was added via a microliter syringe. The mixture was stirred for 4.5 h at room temperature (during this time the final products in the reaction are formed completely). The volatile components were then removed in vacuo, and the residual green solids were extracted with hexane. This allowed separation of $MoBr(\equiv CSiMe_3)(PMe_2Ph)_4$ from $Mo_2Br_4(PMe_2Ph)_4$, the latter being sparingly soluble in hexane. $Ph_2PCH_2CH_2PPh_2$ (0.35 g) was then added to the filtered hexane extract and stirred for 36 h at room temperature to precipitate $MoBr(\equiv CSiMe_3)(Ph_2PCH_2CH_2PPh_2)_2$ as a yellow solid. This was recrystallized from toluene (by cooling a concentrated solution from +20 to ca. −15 °C) as yellow plates (with a greenish tinge). $MoBr(\equiv CSiMe_3)(diphos)_2$ (0.68 g, ca. 70% yield based on (2) and (3)).

NMR data obtained from toluene-$d_8$ solutions at 16 °C: $^1H$ $\delta$ −0.55 (s, $SiMe_3$), 2.21 and 2.95 (br m, $CH_2CH_2$), 6.1–7.2 (Ph); $^{13}C\{^1H\}$ 2.19 (s, $SiMe_3$), 32.7 (m, $CH_2CH_2$), 134–141 (Ph), 321.2 ($CSiMe_3$); $^{31}P$ $\delta$ 62.5 (s).

Infrared data: 3040 (w), 1440 (s), 1260 (m), 1232 (w, d), 1150 (w, br), 1095 (m), 1085 (m), 1060 (s), 1025 (w), 872 (w, d), 830 (m), 810 (m), 745 (m), 740 (s), 725 (m), 690 (s), 650 (m), 630 (w), 525 (s), 518 (s), 510 (m), 498 (m), 412 (w, d) cm$^{-1}$.

Anal. Calcd for $MoBr(\equiv CSiMe_3)(Ph_2PCH_2CH_2PPh_2)_2\cdot C_7H_8$: C, 65.5; H, 5.70; Br, 6.95. Found: C, 65.4; H, 5.63; Br, 6.87.

$MoBr(\equiv CSiMe_3)(diphos)_2$ may be prepared in an analogous manner from the reaction between either $PEt_3$ or $PMe_3$ with $Mo_2Br_2(CH_2SiMe_3)_4$, followed by addition of diphos.

**$Mo_2Br_2(=CHSiMe_3)_2(Me_2PCH_2PMe_2)_2$.** $Mo_2Br_2(CH_2SiMe_3)_4$ (0.37 g, 0.5 mmol) was suspended in hexane (8 mL) and cooled to 0 °C. $Me_2PCH_2PMe_2$ (1.0 mmol) was added to the suspension slowly via a microliter syringe over a period of 5 min with constant stirring. The reaction mixture was then brought to room temperature and stirring continued for another 10 min. This was then filtered and the filtrate discarded. The residual solid was washed with hexane and extracted with toluene (100 mL) which was then reduced in volume to ca. 40 mL and cooled to ca. −15 °C, yielding light tan crystals of $Mo_2Br_2(=CHSiMe_3)_2(Me_2PCH_2PMe_2)_2$ (199.1 mg, 50% yield).

NMR data obtained from toluene-$d_8$ solution at −50 °C: $^1H$ $\delta$ 0.16 (s, $SiMe_3$), 0.70 (d, $J_{PH}$ = 5.1 Hz), 1.09 (d, $J_{PH}$ = 5.1 Hz), 1.30 (d, $J_{PH}$ = 7.6 Hz), 5.16 (d, $J_{PH}$ = 7.9 Hz, $PMe_2$), 2.74 (br, part of $CH_aH_b$), 16.70 (m, $CHSiMe_3$); $^{31}P$ $\delta$ −4.8 (m), and −7.5 (m, AA′BB′ spin pattern, $PMe_2$). IR data: 1365 (s), 950 (m, br), 932 (s), 855 (m, br), 821 (w, br), 723 (w) cm$^{-1}$.

Anal. Calcd for $Mo_2Br_2(=CHSiMe_3)_2(Me_2PCH_2PMe_2)_2$: C, 27.11; H, 6.02; Br, 20.05. Found: C, 26.99; H, 6.10; Br, 20.11.

**Crystallographic Studies.** General operating procedures and listings of programs have been given previously.[27] Crystal data for the three compounds studied in this work are given in Table V.

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[27] Huffman, J. C.; Lewis, L.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755. Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

**$Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$.** A suitable sample was cleaved from a larger well-formed crystal and transferred to the goniostat by using standard inert-atmosphere handling techniques employed at the IUMSC. The sample was characterized by using a standard reciprocal lattice search technique and found to be monoclinic of space group *A*2/*a*. All measurements were performed at –165 °C.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. All hydrogens were located in a difference Fourier phased on the non-hydrogen isotropic parameters. Final refinement included isotropic hydrogen and anisotropic non-hydrogen thermal parameters.

A final difference Fourier was featureless, the largest peak being 0.45 e/Å$^3$.

The structure lies on a crystallographic twofold axis as shown in one of the ORTEP views. In general the structure is considered well determined, as evidenced by the low residuals, low estimated standard deviations, and well-defined hydrogen positions.

Only one hydrogen atom was located in the difference Fourier synthesis near C(11), and it refined to a position as expected for Mo=CH—Si.

**$Mo_2Br_4(PMe_3)_4$.** A suitable sample was cleaved from a large needle and transferred to the goniostat using standard inert-atmosphere handling techniques employed at the IUMSC. The crystal was characterized at –171 °C by using a reciprocal lattice search technique and found to be monoclinic of space group *A*2/*a* (nonstandard setting of *C*2/*c*).

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques, and all hydrogen atoms were clearly discernible in a difference Fourier phased on the non-hydrogen parameters. Final full-matrix least squares included isotropic hydrogen parameters and anisotropic thermal parameters for non-hydrogen atoms as well as positional parameters and an overall scale factor.

The structure lies on a crystallographic twofold axis and has near *mm* symmetry as well. A final difference Fourier synthesis was essentially featureless, the largest peak being 0.65 e/Å$^3$.

**$MoBr(\equiv CSiMe_3)(Ph_2PCH_2CH_2PPh_2)_2\cdot$Toluene.** A suitable sample was cleaved from a larger crystal and transferred to the goniostat by using standard inert-atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space at –160 °C revealed no systematic absences or symmetry, indicating a triclinic lattice.

The structure was solved by direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen contributors and were included in the final cycles as fixed atom contributors in idealized positions.

A final difference Fourier was featureless, the largest peak being 0.85 e/Å$^3$.

The asymmetric unit contains a molecule of toluene in addition to the complex. The closest approach between the complex and the solvent molecule is 3.5 Å.

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**Registry No.** I, 83214-27-1; II, 89707-70-0; III, 96413-40-0; III·toluene, 96413-41-1; IV, 96413-43-3; $Mo_2Br_4(PMe_2Ph)_4$, 96413-42-2; $Mo_2Br_4(PEt_3)_4$, 59752-94-2; $MoBr(\equiv SiMe_3)(PEt_3)_4$, 96413-44-4; $MoBr(\equiv cSiMe_3)(PMe_3)_4$, 96413-45-5; $Mo_2Br_2(CH_2SiMe_3)_4$, 75059-90-4; $PMe_3$, 594-09-2; $PMe_2Ph$, 672-66-2; $Ph_2PCH_2CH_2PPh_2$, 1663-45-2; $PEt_3$, 554-70-1; $Me_2PCH_2PMe_2$, 64065-08-3; Mo, 7439-98-7.

**Supplementary Material Available:** Complete listings of bond distances and angles, isotropic thermal parameters for H atoms, anisotropic thermal parameters for non-hydrogen atoms, and structure factor amplitudes (52 pages). Ordering information is given on any current masthead page. The complete structural reports are available from the Indiana University Chemistry Library, in microfiche form only and at a cost of $2.50 per report. Request MSC Report Nos. 82088, 82027, and 83064 for $Mo_2Br_2({=}CHSiMe_3)_2(PMe_3)_4$, $Mo_2Br_4(PMe_3)_4$, and $MoBr(\equiv CSiMe_3)(diphos)_2\cdot$toluene.

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# Two Compounds Containing a Divanadium Tetrabenzoate Frame and Cyclopentadienyl or Pentamethylcyclopentadienyl Ligands

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Two compounds $(\eta^5\text{-}C_5H_5)_2V_2(C_6H_5CO_2)_4$, 1, and $(\eta^5\text{-}C_5Me_5)_2V_2(C_6H_5CO_2)_4$, **2**, have been prepared from vanadocene and decamethylvanadocene, respectively, and characterized by single-crystal X-ray crystallography. The data are as follows. For **1**: $P\bar{1}$; $a$ = 10.640 (2) Å, $b$ = 10.774 (3) Å, $c$ = 8.510 (2) Å, $\alpha$ = 112.83 (2)°, $\beta$ = 101.41 (2)°, $\gamma$ = 69.43 (2)°, $V$ = 839.6 (6) Å$^3$, $Z$ = 1, $R_1$ = 0.0477, $R_2$ = 0.0547. For **2**: *C*2/*c*; $a$ = 11.576 (3) Å, $b$ = 16.721 (2) Å, $c$ = 21.452 (2) Å, $\beta$ = 90.45 (3)°, $V$ = 4152 (3) Å$^3$, $Z$ = 4, $R_1$ = 0.0733, $R_2$ = 0.0885. The V–V′ distances of 3.636 (1) Å for **1** and 3.652 (2) Å for **2** suggest that little if any direct bonding occurs between two vanadium atoms. The presence of pentamethylcyclopentadienyl ligands in the axial positions in **2** causes a twist of the four carboxylate bridges with torsional angles for the two independent O–V–V′–O′ units equal to 5.9° and 10.9°. In the cyclopentadienyl derivative **1** the corresponding torsional angles are each 2.6°.

## Introduction

Vanadocene, $(\eta^5\text{-}C_5H_5)_2V$, represents an interesting starting material for entry into low-valent nonaqueous vanadium organometallic chemistry.[1] Of particular interest to us was the reaction of vanadocene with carboxylic acids in benzene leading to products of empirical formula $CpV(RCO_2)_2$, as reported by Razuvaev, Latyaeva, Lineva, and Zelenev in 1974.[2] Such compounds were prepared for three carboxylic acids, R = H, $CH_3$, and $C_6H_5$, and their composition was postulated to be monomeric on the basis of elemental analyses, IR spectra, and chemical reactions with EtONa and HCl.

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(1) See, for example: Connelly, N. G. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 672.

(2) Razuvaev, G. A.; Latyaeva, V. N.; Lineva, A. G.; Zelenev, S. V. *Dokl. Chem.* 1974, *216*, 355.

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