Organometallics **1996,** *15,* 4357−4361

Articles

Coupling of Alkynyl Ligands at a Quadruply Bonded Molybdenum Dimer

Kevin D. John, Steven J. Geib, and Michael D. Hopkins*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received May 10, 1996[⊗]

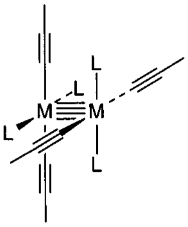
The complex $[Mo_2(C{\equiv}CSiMe_3)_3(\mu,\eta^2{:}\eta^2\text{-}HC{\equiv}CSiMe_3)\{\mu,\eta^1\text{-}C{=}C(SiMe_3)\text{-}\eta^2\text{-}C{\equiv}CSiMe_3\}(\mu\text{-}dmpm)_2][Li(dme)]$ ([**1**][Li(dme)]; dmpm = 1,2-bis(dimethylphosphino)methane, dme = 1,2-dimethoxyethane) was prepared in 32% yield from the reaction between $Mo_2Cl_4(dmpm)_2$, $LiCCSiMe_3$, and $HCCSiMe_3$ in dme. A single-crystal X-ray diffraction study of [**1**]$[Li(dme)_{0.5}(OEt_2)_{0.5}]$ revealed that **1** contains an alkynylvinylidene ligand derived from the head-to-tail coupling of two alkynyl ligands.

Introduction

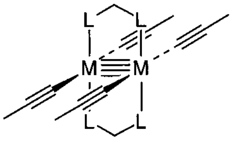
As part of our studies of conjugated transition-metal compounds, we previously reported the preparation of alkynyl-substituted, quadruply metal−metal-bonded complexes of the type $M_2(CCR)_4(PMe_3)_4$ (M = Mo, W; R = H, alkyl, Ph, $SiMe_3$).[1−4] In the course of efforts to extend this class of dimetallapolyynes to include derivatives with other ancillary ligands, we set out to prepare complexes of the type $Mo_2(CCR)_4(\mu\text{-dmpm})_2$ (dmpm = 1,2-bis(dimethylphosphino)methane). Our interest in these species derives from the fact that whereas the alkynyl ligands of $M_2(CCR)_4(PMe_3)_4$ complexes are spatially isolated from each other (D_{2d} symmetry, structure **A**) those of $M_2(CCR)_4(dmpm)_2$ complexes should lie in a single plane (D_{2h} symmetry, structure **B**); this lifts the degeneracy of the $\pi(M_2)$ orbitals and might influence the reactivity of the alkynyl ligands. We have discovered that when the procedure used for the synthesis of $Mo_2(CCSiMe_3)_4(PMe_3)_4$ is employed in the attempted synthesis of $Mo_2(CCSiMe_3)_4(dmpm)_2$ from $Mo_2Cl_4(dmpm)_2$ and $LiCCSiMe_3$, alkynyl-for-halide substitution is accompanied by head-to-tail coupling of alkynyl ligands to give a complex containing an alkynylvinylidene ligand. Herein we report the synthesis of $[Mo_2(C{\equiv}CSiMe_3)_3(\mu,\eta^2{:}\eta^2\text{-}HC{\equiv}CSiMe_3)\{\mu,\eta^1\text{-}C{=}C(SiMe_3)\text{-}\eta^2\text{-}C{\equiv}CSiMe_3\}(\mu\text{-dmpm})_2][Li(dme)]$ ([**1**][Li(dme)]; dme = 1,2-dimethoxyethane) and the X-ray crystal structure of [**1**]$[Li(dme)_{0.5}(OEt_2)_{0.5}]$.

Experimental Section

General Procedures. All manipulations were performed under inert atmosphere using standard glovebox and Schlenk techniques. Immediately prior to use, diethyl ether was distilled from sodium benzophenone ketyl, 1,2-dimethoxyethane (dme) was distilled from potassium, and pentane was distilled from calcium hydride. Benzene-d_6 and tetrahydrofuran (thf) were stirred over Na/K alloy (1:3), from which they were transferred *in vacuo* prior to use. Celite was dried under vacuum at 80 °C for 24 h. $Mo_2Cl_4(dmpm)_2$ was prepared according to the established procedure.[5] All other reagents were used as received.



A



B

Because of the thermal instability of [**1**][Li(dme)], samples for NMR spectroscopy were frozen immediately after preparation and thawed in the NMR spectrometer immediately prior to recording the spectrum. The solvents used for $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR samples were thf and dme, respectively, to which sufficient C_6D_6 was added to provide a signal lock.

Synthesis of [1][Li(dme)]. A 5.25:3.25 (mole basis) mixture of $LiCCSiMe_3$ and $HCCSiMe_3$ was prepared in 0 °C pentane (5 mL) from $HCCSiMe_3$ (0.42 g, 4.3 mmol) and *n*-BuLi (1.64 mL, 1.6 M in hexanes, 2.6 mmol), which was added dropwise over a 10 min period with stirring. The resulting suspension was stirred for 20 min, at which time dme (2 mL) was added to dissolve the precipitate. This solution was transferred via cannula to a stirred suspension of $Mo_2Cl_4(dmpm)_2$ (0.30 g, 0.5 mmol) in 0 °C dme (40 mL) over a 10 min period, resulting in a slow change in the color of the reaction mixture from blue to forest green. After 3 h, the volatile components were removed from the suspension under vacuum, with the temperature of the flask being maintained at 0 °C throughout. The remaining solid was extracted with pentane (40 mL) and the resulting slurry filtered through a Celite pad. Removal of the solvent under vacuum provided a dark green tar; this was dissolved in a minimum amount of dme and cooled to −40 °C, which resulted in the formation of forest-green microcrystals (0.18 g, 32% yield). Crystals grown in this fashion were of sufficient quality to allow measurement of their

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Stoner, T. C.; Dallinger, R. F.; Hopkins, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 5651−5653.

(2) Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 4201−4204.

(3) Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 409−411.

(4) Stoner, T. C.; Schaefer, W. P.; Marsh, R. E.; Hopkins, M. D. *J. Cluster Sci.* **1994**, *5*, 107−124.

(5) Cotton, F. A.; Falvello, L. R.; Harwood, W. S.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3949−3953.

S0276-7333(96)00351-2 CCC: $12.00

unit-cell parameters by single-crystal X-ray diffraction but diffracted too poorly to provide data from which the crystal structure could be deduced. Crystals of sufficient quality for the determination of the molecular structure by X-ray diffraction were grown from Et_2O. Use of this solvent leads to compositional disorder between Et_2O and dme in the crystal ([**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$], *vide infra*). Crystals of [**1**][Li(dme)] and [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] have identical lattice parameters.

^{1}H NMR (300.13 MHz, C_6D_6) for [**1**][Li(dme)]: δ 7.89 (m, 1 H, *H*CCSiMe$_3$), 2.95 (s, 6 H, OC*H*$_3$), 2.86 (s, 4 H, OC*H*$_2$), 1.29 (d, 3 H, $J = 3.99$ Hz, P*Me*), 1.19 (s, 9 H, Si*Me*$_3$), ~1.17 (partly obscured d, 3 H, P*Me*), ~1.07 (partly obscured d, 3 H, P*Me*), ~1.06 (partly obscured d, 3 H, P*Me*), 1.01 (d, 3 H, $J = 2.97$ Hz, P*Me*), 0.95 (s, 9 H, Si*Me*$_3$), ~0.93 (partly obscured d, 3 H, P*Me*), 0.67 (s, 9 H, Si*Me*$_3$), 0.61 (s, 9 H, Si*Me*$_3$), 0.55 (d, 3 H, $J = 4.29$ Hz, P*Me*), 0.35 (s, 9 H, Si*Me*$_3$), ~0.3 (partly obscured d, 3 H, P*Me*), 0.29 (s, 9 H, Si*Me*$_3$). The δ 0.9−1.3 region is too congested to allow PC*H*$_2$P resonances to be unambiguously identified; several weak, unassigned resonances are observed in this region. ^{13}C{^{1}H} NMR (125.7 MHz, thf/C_6D_6, −20 °C): δ 293.8 (br, η^1-*C*=C(SiMe$_3$)), 174.3 (br), 172.8 (br), 170.1 (br), 150.7, 135.5, 132.1 (t), 131.5, 109.6, 104.2, 95.0 (t), 72.2 (O*C*H$_2$, dme), 58.5 (*C*H$_3$O, dme), 41.9 (m, P*C*H$_2$), 40.3 (m, P*C*H$_2$), 17.7 (br m, P*C*H$_3$), 17.1 (m, P*C*H$_3$), 16.3 (m, P*C*H$_3$), 15.8 (m, P*C*H$_3$), 14.8 (m, P*C*H$_3$), 6.1 (Si*Me*$_3$), 3.5 (Si*Me*$_3$), 1.84 (Si*Me*$_3$), 1.75 (Si*Me*$_3$), 1.65 (Si*Me*$_3$), 0.77 (Si*Me*$_3$). The breadth and intensity of the δ 17.7 multiplet suggest it may consist of overlapping resonances. ^{31}P{^{1}H} NMR (202.4 MHz, dme/C_6D_6, −20 °C): δ 0.08 (ddd), −2.03 (ddd), −3.09 (ddd), −7.29 (ddd). IR, (ν(C≡C) region, neat): 1981 (sh), 1967 (br), 1938 cm^{-1} (br). Combustion analyses (C,H) were unsatisfactory, presumably because of the thermal instability of the compound.

Single-Crystal X-ray Diffraction Study of [1][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$]. Single-crystal X-ray diffraction experiments were performed with a Siemens P3 diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. X-ray diffraction data were refined using the Siemens SHELXTL PLUS (5.02) software package. Crystal data and refinement parameters for [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] are given in Table 1.

Block-shaped crystals of [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] were coated in Fluorolube under inert atmosphere and mounted on a glass fiber under a cold N_2 stream at −65 °C. On the basis of the unit cell parameters and photographic evidence, it was determined that the crystal was triclinic. Centrosymmetric $P\bar{1}$ was chosen on the basis of *E* values and the well-behaved solution and refinement of the structure. Lattice parameters were determined from a least-squares fit of the angular settings of 24 reflections in the range $20° \leq 2\theta \leq 25°$. The intensities of three representative reflections were measured every 197 reflections to check for decay of the crystal; decay was < 5%. An empirical absorption correction, based on azimuthal scans of six reflections, was applied. All data were corrected for Lorentz and polarization effects and for decay.

The molybdenum, phosphorus, silicon, and some carbon atoms of [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] were located using direct methods. Subsequent difference-Fourier syntheses provided positions for all other nonhydrogen atoms and for H(26). It was evident that the Li atom is coordinated by dme or diethyl ether and that there is significant compositional disorder at this "ether" site. The disorder was modeled by refining a free variable that described the population of the site by the oxygen atoms of dme (O(2) and O(3)) and diethyl ether (O(1)); the variable was constrained such that the total population was unity and that O(2) and O(3) had equal occupancies. Refinement of this variable revealed a 0.5:0.5 population by dme and diethyl ether, in rough agreement with that obtained from ^{1}H-NMR spectroscopy (Et_2O:dme ≅ 0.4:0.6). All hydrogen atoms except H(26) were placed in idealized positions by fixing the C−H distance to 0.96 Å and by assuming a staggered configuration. Nonhydrogen atoms were refined anisotropically, and H(26) was refined isotropically.

Table 1. Crystal Data and Data Collection and Refinement Parameters for [1][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$]

Crystal Data	
empirical formula	$C_{44}H_{93}LiMo_2O_{1.5}P_4Si_6$
formula wt	1137.42
cryst syst	triclinic
space group	$P\bar{1}$
Z	2
a, Å	12.202(5)
b, Å	14.301(4)
c, Å	18.955(7)
α, deg	100.10(2)
β, deg	96.29(2)
γ, deg	103.47(2)
V, Å^3	3127(2)
D_{calcd}, g cm^{-3}	1.208
μ(Mo Kα), mm^{-1}	0.647
F(000)	1200
crystal size, mm	0.15 × 0.36 × 0.47
Data Collection and Refinement	
T, K	208(2)
radiatn	Mo Kα (λ = 0.710 73 Å), graphite monochromated
2θ limits, deg	4−48
limiting indices	$0 \leq h \leq 13$, $-16 \leq k \leq 16$, $-21 \leq l \leq 21$
reflecns collected	10107
independent reflecns	9585 [$R_{int} = 0.0185$]
refinement method	full-matrix least-squares on F^2
data/restraints/param	9554/0/560
GOF on F^2	0.889
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0410$, $wR2 = 0.0939$
R indices (all data)	$R1 = 0.0642$, $wR2 = 0.1353$
largest diff. peak and hole	0.790, −0.638 e Å^{-3}

[a] $GOF = [\Sigma[w(F_o^2 - F_c^2)]^2/(n - p)]^{1/2}$. [b] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Results and Discussion

Our initial attempt to prepare $Mo_2(CCSiMe_3)_4(dmpm)_2$ from $Mo_2Cl_4(dmpm)_2$ and $LiCCSiMe_3$ employed the procedure used for the synthesis of $Mo_2(CCSiMe_3)_4(PMe_3)_4$. In this procedure, $Mo_2Cl_4(PMe_3)_4$ is reacted in dme with excess $LiCCSiMe_3$ (ca. 5.7 equiv), with the latter being prepared *in situ* from 5.7 equiv of *n*-BuLi and 5.8 equiv of $HCCSiMe_3$.[4] The excess alkyne does not have a deleterious effect on product formation—the yield is 94%—and ensures that all *n*-BuLi is consumed.

The reaction between $Mo_2Cl_4(dmpm)_2$ and 4.18 equiv of $LiCCSiMe_3$ (prepared in the above manner from 4.18 equiv of *n*-BuLi and 4.20 equiv of $HCCSiMe_3$) provides a small quantity of a microcrystalline product that is thermally unstable at room temperature. This product exhibits NMR spectra that are too complex to allow its composition to be unambiguously deduced but that nonetheless clearly indicate it is not the desired compound $Mo_2(CCSiMe_3)_4(dmpm)_2$. Specifically, six singlets of equal integrated intensity are observed in the ^{1}H-NMR spectrum in the range δ 0.30−1.19, which presumably can be assigned to $SiMe_3$ groups, and four complex multiplets of equal intensity are observed in the ^{31}P{^{1}H}-NMR spectrum; for $Mo_2(CCSiMe_3)_4(dmpm)_2$, each of these resonances should be a singlet. That the product contained alkynyl ligands was established by the presence of several bands in the 1900−2000 cm^{-1} region of the IR spectrum.

The composition of the product was determined to be [Mo$_2$(C≡CSiMe$_3$)$_3$(μ,η^2:η^2-HC≡CSiMe$_3$){μ,η^1-C=C(SiMe$_3$)-η^2-C≡CSiMe$_3$}(μ-dmpm)$_2$][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] ([**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$]) by a single-crystal X-ray diffraction study. The structure of [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] is shown

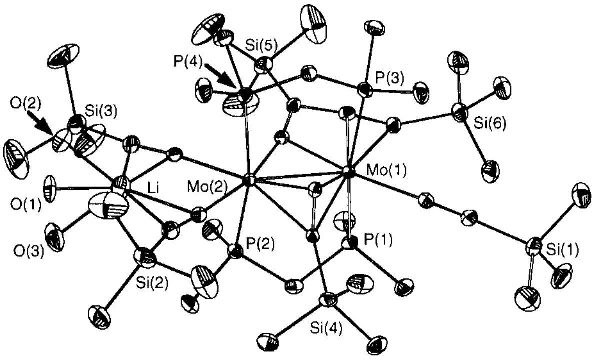


Figure 1. Molecular structure of [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$]. For clarity, the carbon and hydrogen atoms of dme and Et$_2$O and the hydrogen atoms of **1** have been omitted. Atoms are represented by thermal ellipsoids drawn at the 20% probability level. The occupancy by O(1) and by the O(2)/O(3) pair is 0.5 (see the Experimental Section).

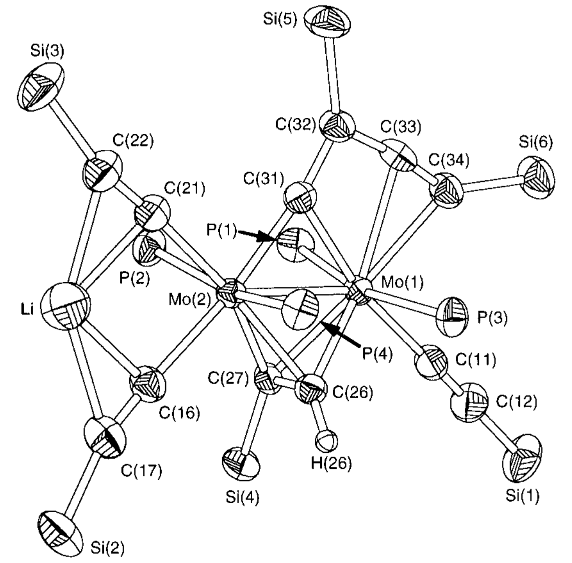


Figure 2. Molecular structure of the Mo$_2$C$_{12}$HLiP$_4$Si$_6$ core of [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$]. Nonhydrogen atoms are represented by thermal ellipsoids drawn at the 50% probability level. The hydrogen atom is represented by a sphere of arbitrary size.

in Figure 1 and that of the Mo$_2$C$_{12}$HLiP$_4$Si$_6$ core is depicted in Figure 2; bond distances and bond angles are given in Tables 2 and 3, respectively. The crystal structure reveals the compound to be a veritable museum of M(C≡C) bonding modes: it contains one terminal alkynyl ligand, two alkynyl ligands bonded end-on to molybdenum and side-on to lithium, an alkyne bound perpendicular to the Mo$_2$ bond, and an alkynylvinylidene ligand in which the alkynyl moiety is bonded to a single molybdenum atom roughly parallel to the Mo$_2$ bond and the vinylidene moiety bridges the two molybdenum centers. Thus, the reaction between Mo$_2$Cl$_4$(dmpm)$_2$ and LiCCSiMe$_3$ results in a product in which the [Mo$_2$(dmpm)$_2$]$^{4+}$ core is retained (counting the alkynylvinylidene ligand as a dianion) and alkynyl-for-chloride substitution has taken place, as expected, but that also incorporates the trace amount of HCCSiMe$_3$ in the reaction mixture.

Although the structure of [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] is complex, the metrical data for the individual linkages of which it is composed (Tables 2 and 3) can be straightforwardly interpreted, as can NMR resonances associated with these ligands. For the Mo$_2$(μ,η^2:η^2-HC≡CSiMe$_3$) unit, the Mo—C and C≡C bond distances and associated angles are within the normal ranges established for other M$_2$(μ,η^2:η^2-RC≡CR) compounds[6] and are similar to those for the compound [Mo$_2$(μ-HC≡CC$_6$H$_4$-4-Me)(μ-O$_2$CMe)(NH$_2$CH$_2$CH$_2$NH$_2$)$_4$]$^{3+}$,[7] which is the only previously reported compound derived from the addition of an alkyne across a Mo—Mo quadruple bond. One structural feature of note is that the bending of the alkyne ligand (∠[C(26)—C(27)—Si(4)] = 118.9(3)°) is much larger than usual (125—156°).[6] A space-filling model of the structure reveals this to be the result of significant steric repulsion between the alkyne SiMe$_3$ group and a dmpm ligand; this repulsion is manifested in the latter by the nonplanarity of the Mo$_2$P$_4$ unit (Figure 2). There is no crystallographic evidence for disorder of the alkyne ligand, that is, for the rotational isomer in which Si(4) is positioned near P(3) and P(4); the static orientation of this ligand is further supported by the observation of four ^{31}P{^{1}H}-NMR resonances. The low-field ^{1}H-NMR resonance of the terminal hydrogen atom (δ 7.89) is typical for a terminal alkyne ligand.[8]

Table 2. Selected Bond Distances for [1][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$]

nuclei	distance (Å)	nuclei	distance (Å)
Mo(1)—Mo(2)	2.5845(9)	C(16)—C(17)	1.231(7)
Mo(1)—C(11)	2.188(5)	C(16)—Li(1)	2.233(12)
Mo(1)—C(26)	2.112(5)	C(17)—Li(1)	2.395(13)
Mo(1)—C(27)	2.200(4)	C(17)—Si(2)	1.832(6)
Mo(1)—C(31)	2.173(5)	C(21)—C(22)	1.225(7)
Mo(1)—C(33)	2.434(5)	C(21)—Li(1)	2.260(13)
Mo(1)—C(34)	2.345(5)	C(22)—Li(1)	2.354(13)
Mo(1)—P(1)	2.521(2)	C(22)—Si(3)	1.840(6)
Mo(1)—P(3)	2.498(2)	C(26)—C(27)	1.358(7)
Mo(2)—C(16)	2.209(5)	C(26)—H(26)	1.03(4)
Mo(2)—C(21)	2.191(5)	C(27)—Si(4)	1.853(5)
Mo(2)—C(26)	2.177(5)	C(31)—C(32)	1.377(6)
Mo(2)—C(27)	2.243(4)	C(32)—C(33)	1.408(7)
Mo(2)—C(31)	2.033(5)	C(32)—Si(5)	1.853(5)
Mo(2)—P(2)	2.490(2)	C(33)—C(34)	1.261(7)
Mo(2)—P(4)	2.490(2)	C(34)—Si(6)	1.819(5)
Mo(2)···Li(1)	3.352(11)	Li(1)—O(1)	1.862(14)
C(11)—C(12)	1.212(7)	Li(1)—O(2)	2.09(2)
C(12)—Si(1)	1.811(5)	Li(1)—O(3)	2.10(2)

For the three alkynyl ligands, the Mo—C and C≡C bond distances and associated angles are consistent with expectation for transition-metal—alkynyl complexes.[3,9] The two C≡CSiMe$_3$ ligands coordinated to lithium are bent (∠[C(16)—C(17)—Si(2)] = 164.7(5)°, ∠[C(21)—C(22)—Si(3)] = 166.1(5)°) and their C≡C bond distances (d[C(16)—C(17)] = 1.231(7) Å, d[C(21)—C(22)] = 1.225(7) Å) may be slightly longer than that for the terminal alkynyl ligand (d[C(11)—C(12)] = 1.212(7) Å), although these latter differences are not statistically significant. A slight lengthening of the Li-coordinated C≡C bonds would be consistent with the fact that two of the C≡C stretching frequencies for [**1**][Li(dme)] (1967, 1938 cm^{-1}) are significantly lower for than that for Mo$_2$(CCSiMe$_3$)$_4$(PMe$_3$)$_4$ (1991 cm^{-1});[4] similar reductions in the frequency of ν(C≡C) upon coordination of lithium to

---

(6) Allen, F. H.; Garner, S. E. In *The Chemistry of Triple-Bonded Functional Groups, Supplement C2*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1994; Vol. 2, pp 109—151.

(7) Kerby, M. C.; Eichhorn, B. W.; Doviken, L.; Vollhardt, K. P. C. *Inorg. Chem.* **1991**, *30*, 156—158.

(8) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1—100.

(9) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79—154.

Table 3. Selected Bond Angles for $[\mathbf{1}][Li(dme)_{0.5}(OEt_2)_{0.5}]$

nuclei	angle (deg)	nuclei	angle (deg)
C(11)−Mo(1)−C(26)	91.0(2)	Mo(1)−Mo(2)···Li(1)	176.3(2)
C(11)−Mo(1)−C(27)	87.9(2)	P(2)−Mo(2)−P(4)	164.62(5)
C(11)−Mo(1)−C(31)	168.4(2)	C(16)−Li(1)−C(17)	30.6(2)
C(11)−Mo(1)−C(33)	117.2(2)	C(16)−Li(1)−C(21)	81.1(4)
C(11)−Mo(1)−C(34)	86.6(2)	C(16)−Li(1)−C(22)	111.7(5)
C(11)−Mo(1)−Mo(2)	141.79(13)	C(16)−Li(1)−Mo(2)	40.7(2)
C(11)−Mo(1)−P(1)	87.54(14)	C(16)−Li(1)−O(1)	136.7(7)
C(11)−Mo(1)−P(3)	87.82(14)	C(16)−Li(1)−O(2)	128.9(7)
C(26)−Mo(1)−C(31)	100.3(2)	C(16)−Li(1)−O(3)	121.2(7)
C(26)−Mo(1)−C(27)	36.6(2)	C(17)−Li(1)−C(21)	111.6(5)
C(26)−Mo(1)−C(33)	145.4(2)	C(17)−Li(1)−C(22)	142.3(5)
C(26)−Mo(1)−C(34)	158.5(2)	C(17)−Li(1)−Mo(2)	71.2(3)
C(26)−Mo(1)−Mo(2)	54.12(12)	C(17)−Li(1)−O(1)	106.1(6)
C(26)−Mo(1)−P(1)	117.72(14)	C(17)−Li(1)−O(2)	107.2(6)
C(26)−Mo(1)−P(3)	75.80(14)	C(17)−Li(1)−O(3)	98.6(6)
C(27)−Mo(1)−C(31)	102.7(2)	C(21)−Li(1)−C(22)	30.7(2)
C(27)−Mo(1)−C(33)	150.8(2)	C(21)−Li(1)−Mo(2)	40.4(2)
C(27)−Mo(1)−C(34)	163.9(2)	C(22)−Li(1)−Mo(2)	71.0(3)
C(27)−Mo(1)−Mo(2)	55.21(12)	C(21)−Li(1)−O(1)	142.0(7)
C(27)−Mo(1)−P(1)	81.11(13)	C(21)−Li(1)−O(2)	121.4(7)
C(27)−Mo(1)−P(3)	112.15(13)	C(21)−Li(1)−O(3)	134.5(7)
C(31)−Mo(1)−C(33)	51.4(2)	C(22)−Li(1)−O(1)	111.6(6)
C(31)−Mo(1)−C(34)	81.9(2)	C(22)−Li(1)−O(2)	101.2(6)
C(31)−Mo(1)−Mo(2)	49.68(12)	C(22)−Li(1)−O(3)	111.6(6)
C(31)−Mo(1)−P(1)	89.55(12)	O(2)−Li(1)−O(3)	77.3(7)
C(31)−Mo(1)−P(3)	92.34(12)	C(12)−C(11)−Mo(1)	178.6(4)
C(33)−Mo(1)−C(34)	30.5(2)	C(11)−C(12)−Si(1)	176.3(5)
C(33)−Mo(1)−Mo(2)	101.03(12)	C(17)−C(16)−Mo(2)	174.2(5)
C(33)−Mo(1)−P(1)	85.03(12)	C(17)−C(16)−Li(1)	82.0(5)
C(33)−Mo(1)−P(3)	85.15(13)	Li(1)−C(16)−Mo(2)	98.0(4)
C(34)−Mo(1)−Mo(2)	131.55(13)	C(16)−C(17)−Li(1)	67.4(4)
C(34)−Mo(1)−P(1)	83.52(13)	C(16)−C(17)−Si(2)	164.7(5)
C(34)−Mo(1)−P(3)	82.79(13)	Li(1)−C(17)−Si(2)	127.8(4)
Mo(2)−Mo(1)−P(1)	95.29(4)	C(22)−C(21)−Mo(2)	175.1(5)
Mo(2)−Mo(1)−P(3)	96.68(4)	C(22)−C(21)−Li(1)	78.9(5)
P(1)−Mo(1)−P(3)	165.77(5)	Li(1)−C(21)−Mo(2)	97.7(3)
C(16)−Mo(2)−C(21)	83.2(2)	C(21)−C(22)−Li(1)	70.4(4)
C(16)−Mo(2)−C(26)	86.1(2)	C(21)−C(22)−Si(3)	166.1(5)
C(16)−Mo(2)−C(27)	86.4(2)	Li(1)−C(22)−Si(3)	123.4(4)
C(16)−Mo(2)−C(31)	167.5(2)	C(27)−C(26)−Mo(1)	75.2(3)
C(16)−Mo(2)−Mo(1)	136.41(13)	C(27)−C(26)−Mo(2)	74.8(3)
C(16)−Mo(2)−P(2)	95.52(14)	Mo(1)−C(26)−H(26)	142(2)
C(16)−Mo(2)−P(4)	86.56(14)	Mo(2)−C(26)−H(26)	135(2)
C(21)−Mo(2)−C(26)	160.1(2)	Mo(1)−C(26)−Mo(2)	74.1(2)
C(21)−Mo(2)−C(27)	158.4(2)	C(26)−C(27)−Mo(1)	68.1(3)
C(21)−Mo(2)−C(31)	85.8(2)	C(26)−C(27)−Mo(2)	69.5(3)
C(21)−Mo(2)−Mo(1)	140.31(14)	C(26)−C(27)−Si(4)	118.9(3)
C(21)−Mo(2)−P(2)	80.72(13)	Mo(1)−C(27)−Mo(2)	71.13(13)
C(21)−Mo(2)−P(4)	84.41(13)	Mo(1)−C(27)−Si(4)	142.6(2)
C(26)−Mo(2)−C(27)	35.7(2)	Mo(2)−C(27)−Si(4)	146.1(2)
C(26)−Mo(2)−C(31)	102.7(2)	C(32)−C(31)−Mo(1)	115.5(3)
C(26)−Mo(2)−Mo(1)	51.79(12)	C(32)−C(31)−Mo(2)	168.6(4)
C(26)−Mo(2)−P(2)	117.12(13)	Mo(1)−C(31)−Mo(2)	75.8(2)
C(26)−Mo(2)−P(4)	78.20(13)	C(31)−C(32)−C(33)	92.3(4)
C(27)−Mo(2)−C(31)	105.9(2)	C(31)−C(32)−Si(5)	141.8(4)
C(27)−Mo(2)−Mo(1)	53.67(11)	C(33)−C(32)−Si(5)	125.8(4)
C(27)−Mo(2)−P(2)	81.48(12)	C(32)−C(33)−C(34)	171.7(5)
C(27)−Mo(2)−P(4)	113.88(12)	C(32)−C(33)−Mo(1)	100.8(3)
C(31)−Mo(2)−Mo(1)	54.57(13)	C(34)−C(33)−Mo(1)	70.9(3)
C(31)−Mo(2)−P(2)	88.46(14)	C(33)−C(34)−Mo(1)	78.6(3)
C(31)−Mo(2)−P(4)	86.53(14)	C(33)−C(34)−Si(6)	142.5(4)
Mo(1)−Mo(2)−P(2)	94.93(4)	Mo(1)−C(34)−Si(6)	138.8(3)
Mo(1)−Mo(2)−P(4)	94.00(4)		

alkynyl ligands have been reported for other anionic metal−alkynyl compounds.[10] The distances between lithium and the alkynyl α-carbon atoms (2.233(12), 2.260(13) Å) are shorter than those between lithium and the β-carbon atoms (2.395(13), 2.354(13) Å); qualitatively similar $M(C{\equiv}CR)_2(\mu\text{-}Li)$ structural motifs have been observed for the compounds $[YCp^*_2(C{\equiv}CBu^t)_2][Li(thf)]$[11] and $[Ti(C_5Me_4H)_2(C{\equiv}C{-}C{\equiv}CSiMe_3)_2][Li(thf)_2]$.[12]

The most interesting portion of the structure is the alkynylvinylidene ligand. The coordination of both the vinylidene and alkyne portions of the ligand results in significant strain in the C_4 backbone, as manifested by metal−carbon interactions that are highly asymmetric and bond distances and angles that deviate markedly from normal ranges. Specifically, the vinylidene fragment is semibridging, with stronger bonding to Mo(2) than to Mo(1) (d[Mo(2)−C(31)] = 2.033(5) Å, d[Mo(1)−C(31)] = 2.173(5) Å) and relatively little bending of the Mo(2)−C(31)−C(32) linkage (168.6(4)°). The ^{13}C-NMR resonance associated with the vinylidene α-carbon atom is observed at δ 293.8, which is comparable to the chemical shifts observed for other bridging vinylidene ligands.[13] The ligand is sharply bent at the vinylidene β-carbon atom (∠[C(31)−C(32)−C(33)] = 92.3(4)°), with the C═C bond distance (d[C(31)−C(32)] = 1.377(6) Å) lying toward the upper end of the range of distances established for $M_2(\mu\text{-}C{=}CRR')$ compounds (1.29−1.38 Å)[13] and the C−C bond between the alkynyl and vinylidene fragments (d[C(32)−C(33)] = 1.408(7) Å) being shorter than expected for a C(sp)−C(sp^2) single bond (1.44 Å); this presumably reflects the nonstandard hybridization of C(32). The alkyne portion of the ligand is weakly coordinated to Mo(1), as indicated by Mo−C bond distances (d[Mo(1)−C(34)] = 2.345(5) Å, d[Mo(1)−C(33)] = 2.434(5) Å) that are substantially longer than normal (2.00−2.15 Å).[8] The C≡C−Si unit of the alkyne is bent (142.5(4)°), as expected, but the C−C≡C unit is not (171.7(5)°).

A final structural question concerns the metal−metal bond order. If one views the structure of $[\mathbf{1}][Li(dme)_{0.5}(OEt_2)_{0.5}]$ as edge-sharing bioctahedral (counting the alkyne ligands as each occupying a single coordination site) the $d^4{-}d^4$ configuration results in a formal metal−metal double bond;[14,15] this prediction is consistent with the 18-electron rule and observed diamagnetism of the compound and with the Mo−Mo bond distance (2.5845(9) Å), which lies near the range for Mo═Mo bonds (2.45−2.55 Å).[16] Of course, the low symmetry of the compound and complex electronic characteristics of the carbon-based ligands demand that little quantitative significance be attached to this description of the bond order.

In light of the stoichiometry of **1** revealed by the crystal structure, we adjusted the ratio of the reactants $Mo_2Cl_4(dmpm)_2$, $LiCCSiMe_3$, and $HCCSiMe_3$ to improve the synthetic yield for [**1**][Li(dme)]. The yield is maximum (32%) when ca. 5 equiv of $LiCCSiMe_3$ and 3 equiv of $HCCSiMe_3$ (per equivalent of $Mo_2Cl_4(dmpm)_2$) are used, with lower yields being obtained for 5:1 (16%), 4:2 (25%), and 3:3 (12%) ratios of $LiCCSiMe_3$ to $HCCSiMe_3$.

An unresolved question concerns the mechanism by which the alkynylvinylidene ligand is formed. The fact

---

[10] Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1985**, *4*, 2062−2064.

[11] Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Olofson, J. M. *J. Organomet. Chem.* **1989**, *376*, 311−320.

[12] Varga, V.; Mach, K.; Hiller, J.; Thewalt, U. *J. Organomet. Chem.* **1996**, *506*, 109−112.

[13] Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257.

[14] Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555−4572.

[15] Cotton, F. A. *Polyhedron* **1987**, *6*, 667−677.

[16] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, 1993.

that this ligand is coordinated through the alkynyl fragment, despite the resulting strain in the C_4 backbone (and the presence of excess $HCCSiMe_3$ in the reaction mixture, which could take the place of this fragment in the coordination sphere of Mo(1)), suggests that the coupling occurs between coordinated alkynyl ligands. A related coupling has been reported by Akita *et al.*: photolysis of FeCp*(CO)$_2$(C≡CPh) in benzene results in formation of $Fe_2Cp^*_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}C\text{-}(Ph)C{\equiv}CPh\}$, the alkynylvinylidene ligand of which was proposed to form via head-to-tail coupling of alkynyl ligands through an intermediate containing one σ,η^1-C≡CPh ligand and one $\mu\text{-}\sigma,\eta^1;\pi,\eta^2$-C≡CPh ligand.[17]

In conclusion, we have discovered that the reactivity of the alkynyl ligands in complexes of the type $Mo_2(C{\equiv}CR)_4L_4$ ($L = PMe_3$, 1/2 dmpm) depends strongly on their spatial orientation, with the planar arrangement expected for compounds containing the $[Mo_2(dmpm)_2]^{4+}$ core resulting in an alkynyl coupling reaction during the attempted synthesis of $Mo_2(CCSiMe_3)_4(dmpm)_2$ that has not previously been observed for $Mo_2(CCR)_4(PMe_3)_4$ complexes. In this context, it is interesting to note Walton's observations that complexes containing the structurally related *trans*-$[Re_2(\mu\text{-}dppm)_2]^{4+}$ core (dppm = 1,2-bis(diphenylphosphino)methane) affect reductive nitrile−nitrile[18] and alkyne−carbonyl[19,20] coupling. Important features of the rhenium compounds in this regard are the geometry of the $[Re_2(dppm)_2]^{4+}$ fragment, which facilitates the side-by-side approach of unsaturated ligands in the plane perpendicular to the Re_2P_4 unit, and the "electron rich" metal−metal triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration), which, by virtue of the accessibility of formal ($\sigma^2\pi^4\delta^2\delta^{*1}$) and ($\sigma^2\pi^4\delta^2$) configurations, serves as an electron source for promoting reductive coupling.[18−20] It has not been established how sensitive such coupling reactions are to the M_2 electron configuration, as analogous reactivity studies of $[M_2(\mu\text{-}dppm)_2]^{n+}$ centers possessing other metal−metal bond orders have not yet been undertaken, but, in view of the result reported here for the reaction between $Mo_2Cl_4(dmpm)_2$ and $LiCCSiMe_3$, it is likely that a search for additional ligand−ligand coupling reactions of $Mo_2Cl_4(dmpm)_2$ and related compounds would be a worthwhile endeavor.

Acknowledgment. We thank Peter Magers for conducting preliminary experiments. This research was supported by National Science Foundation Grant No. CHE-9307013. Support to K.D.J. through a Lubrizol Graduate Fellowship and to M.D.H. through fellowships from the David and Lucile Packard and Alfred P. Sloan Foundations is gratefully acknowledged.

Supporting Information Available: A listing of atomic coordinates, anisotropic thermal parameters, bond lengths and bond angles, and hydrogen-atom coordinates and figures showing the atom numbering scheme, the unit cell, and crystal packing for [**1**][Li(dme)$_{0.5}$(OEt$_2$)$_{0.5}$] (17 pages). Ordering information is given on any current masthead page.

OM960351F

---

[17] Akita, M.; Sugimoto, S.; Terada, M.; Moro-oka, Y. *J. Organomet. Chem.* **1993**, *447*, 103−106.

[18] Esjornson, D.; Derringer, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2821−2829.

[19] Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 9319−9320.

[20] Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1994**, *13*, 1235−1242.