exchange between the 1- and 2-positions of the μ-C(Me)C-(Me)CSiMe$_3$ ligand is occurring on the NMR time scale (see Figure 2). From the coalescence temperature of +55 °C, $\Delta G^{\ddagger}$ ca. 15 Kcal mol^{-1} can be estimated. The exchange process does not involve a scrambling of the CSiMe$_3$ group nor does it involve the CH$_2$SiMe$_3$ ligands. Though some changes in the ^{1}H spectra do occur with changing temperature all changes other than the CMe scrambling can be understood in terms of chemical shift variations with temperature. Thus, though 1,2-CMe site exchange is quite rapid on the NMR time scale, the asymmetry imposed by the C(Me)C(Me)CSiMe$_3$ ligand straddling the W–W bond is retained.

The slow formation of II from I (R = Me) appears to preclude a fluxional process involving II $\rightleftharpoons$ I. This, taken together with the likelihood that a rapid reversible insertion of the alkyne moiety would scramble the CSiMe$_3$ groups, leads us to propose an alternate mechanism involving the interconversion of the μ-1,3-dimetallaallyl ligand with a μ-metallacyclopropenyl ligand as shown in Scheme I. Here by a series of 60° twists and bond openings and closings it is possible to achieve scrambling of all (1, 2, and 3) carbon sites. This would allow for formation of the μ-C(H)CSiMe$_3$C(H) ligand without invoking an acetylene metathesis-like reaction in which a C$_2$ unit was extruded from the μ-C$_3$ ligand. Also, if for steric or electronic reasons the μ-C-(R)C(R)CSiMe$_3$ ligand has a marked preference for the CSiMe$_3$ group in the 3-position, then only a facile 1 $\rightleftharpoons$ 2 site exchange of CR groups would occur.

Interestingly, (Me$_3$SiCH$_2$)$_4$Ta$_2$(μ-CSiMe$_3$)$_2$,[6] which is a structural analogue of the tungsten derivative but is a d^0–d^0 dimer, does not react with alkynes at ambient temperatures. Many questions are raised by these observations, and further studies are in progress.[7]

Supplementary Material Available: Fractional coordinates and isotropic thermal parameters for the (Me$_3$SiCH$_2$)$_4$W(μ-C$_3$Ph$_2$SiMe$_3$)(μ-CSiMe$_3$) molecule (1 page). Ordering information is given on any current masthead page.

(6) Mowat, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1120–1124.

(7) We thank the National Science Foundation for financial support.

Quadruple Bonds between Molybdenum Atoms Supported by Alkoxide Ligands. Structural Effects and Reactivity Patterns

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We wish to report the preparation of a series of compounds of formula Mo$_2$(OR)$_4$L$_4$($M\overset{4}{-}M$) and structural type I. These are

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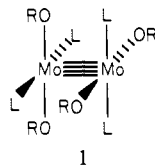
the first compounds containing the (Mo$\overset{4}{-}$Mo)$^{4+}$ unit supported by alkoxy ligands and show interesting structural parameters and reactivity patterns not previously observed in the chemistry of compounds containing Mo–Mo quadruple bonds.[1]

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

Alcoholysis reactions[2] of 1,2-Mo$_2$-i-Bu$_2$(NMe$_2$)$_4$ in hexane reveal a marked dependence on steric factors of the alcohol. Reaction employing t-BuOH yields Mo$_2$-t-Bu(O-t-Bu)$_5$, isobutane, and dimethylamine (4 equiv), whereas with t-BuCH$_2$OH, the purple crystalline compound Mo$_2$(OCH$_2$-t-Bu)$_4$(HNMe$_2$)$_4$($M\overset{4}{-}M$) is obtained with liberation of 1 equiv of isobutylene and isobutane. Reactions employing i-PrOH yield purple solutions that contain a mixture of species, including Mo$_x$(O-i-Pr)$_4$(HNMe$_2$)$_4$ as determined by ^{1}H NMR spectroscopy. This purple solution is reactive toward ethylene to give Mo$_2$Et(O-i-Pr)$_5$($M\equiv M$) and toward neutral donor ligands to give Mo$_2$(O-i-Pr)$_4$L$_4$($M\overset{4}{-}M$) compounds where L = py, H$_2$NMe, and PMe$_3$. Rather interestingly, in the presence of excess i-PrOH, the solvent complex Mo$_2$(O-i-Pr)$_4$(HO-i-Pr)$_4$ crystallizes from the reaction mixture [Mo$_2$-i-Bu$_2$(NMe$_2$)$_4$ + i-PrOH] at –20 °C. The latter compound is unstable at room temperature, slowly decomposing to Mo$_2$(O-i-Pr)$_6$ along with other as yet uncharacterized products. However, when freshly prepared, it may be used to synthesize new (Mo$\overset{4}{-}$Mo)$^{4+}$ containing compounds. With CO$_2$ and acacH (2,4-pentanedione), Mo$_2$(O-i-Pr)$_4$(HO-i-Pr)$_4$ reacts in hydrocarbon solvents to give Mo$_2$(O$_2$CO-i-Pr)$_4$ and Mo$_2$(acac)$_4$, respectively. Addition of HNMe$_2$ (4 equiv) and ethylene affords Mo$_2$Et(O-i-Pr)$_5$ with a return to the (Mo$\equiv$Mo)$^{6+}$ unit, but addition of H$_2$NMe and ethylene yields only the substituted product Mo$_2$-(O-i-Pr)$_4$(H$_2$NMe)$_4$. Except for the thermally unstable compound Mo$_2$(O-i-Pr)$_4$(HO-i-Pr)$_4$, satisfactory elemental analyses have been obtained for the new compounds reported.

These reactions may be understood in the following manner. Alcoholyses of Mo$_2$R'$_2$(NMe$_2$)$_4$ compounds (R' = a β-hydrogen containing alkyl) proceed by β-hydrogen atom transfer and reductive elimination to give alkene, alkane, and "Mo$_2$(OR)$_4$", as was suggested earlier on the basis of labeling experiments.[3] The "Mo$_2$(OR)$_4$" species may be trapped and isolated as an Mo$_2$-(OR)$_4$L$_4$ compound *only* if steric factors are favorable, otherwise an oxidative-addition reaction will regenerate the (Mo$\equiv$Mo)$^{6+}$ unit: "Mo$_2$(OR)$_4$" + ROH + alkene $\rightarrow$ Mo$_2$R'(OR)$_5$. The importance of steric factors in stabilizing Mo$_2$(OR)$_4$L$_4$ compounds is evident from the reaction of Mo$_2$(O-i-Pr)$_4$(HO-i-Pr)$_4$ with HNMe$_2$ and H$_2$NMe in the presence of ethylene, which lead to Mo$_2$Et(O-i-Pr)$_5$($M\equiv M$) and Mo$_2$(O-i-Pr)$_4$(H$_2$NMe)$_4$($M\overset{4}{-}M$), respectively. This leads us to suggest that the oxidative-addition step involves reaction of a coordinatively unsaturated (Mo$\overset{4}{-}$Mo)$^{4+}$ speceis such as Mo$_2$(O-i-Pr)$_4$(HNMe$_2$)$_3$.

A comparison of pertinent structural parameters[4] for Mo$_2$-(OCH$_2$-t-Bu)$_4$(HNMe$_2$)$_4$, Mo$_2$(OCH$_2$-t-Bu)$_4$(PMe$_3$)$_4$, Mo$_2$(O-i-

(2) All reactions and manipulations were carried out in dry and oxygen-free solvents (hexane or toluene) and atmospheres (N$_2$).

(3) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075.

(4) Crystal data: (1) for Mo$_2$(O-i-Pr)$_4$(py)$_4$ at –167 °C, space group $P\bar{1}$, a = 18.254 (6) Å, b = 10.327 (2) Å, c = 10.076 (2) Å, α = 70.92 (1)°, β = 103.08 (1)°, γ = 104.38 (1)°, Z = 2, d_{calcd} = 1.44 g cm^{-3}. 4492 unique reflections, 3765 having F > 2.33σ(F) were used in full least squares refinements, including isotropic hydrogen atom positions. Final residual are R_F = 0.031 and R_{wF} = 0.033; (2) for Mo$_2$(OCH$_2$-t-Bu)$_4$(HNMe$_2$)$_4$ at –160 °C, space group $I4cm$, a = 22.064 (5) Å, b = 22.064 (5) Å, c = 16.985 (4) Å, Z = 8, d_{calcd} = 1.16 g cm^{-3}. Of 1480 unique reflections, 1433 having F > 2.33σ(F) were used in the refinement. Hydrogen atoms were located in a difference Fourier and were placed in idealized calculated positions for the final three cycles. Final residuals are R_F = 0.063 and R_{wF} = 0.065; (3) for Mo$_2$(OCH$_2$-t-Bu)$_4$(PMe$_3$)$_4$ at –160 °C, space group Pa, a = 19.441 (10) Å, b = 11.619 (5) Å, c = 9.906 (4) Å, β = 106.41 (2)°, Z = 2, d_{calcd} = 1.31 g cm^{-3}. Of the 2828 unique reflections, the 2463 having F > 2.33σ(F) were used in the least-squares refinement. At the present stage of refinement, hydrogen atoms have not been included. Current residuals are R_F = 0.062 and R_{wF} = 0.063; (4) for Mo$_2$(O-i-Pr)$_4$(HO-i-Pr)$_4$ at –162 °C: probable space group based on extinctions $P4/nmm$ with a = 12.810 (5) Å, c = 9.869 (5) Å, Z = 2, d_{calcd} = 1.37 g cm^{-3}. The total number of reflections collected was 2287, of which 637 were unique and 599 had F > 2.33σ(F). The molecule was found to be disordered about the crystallographic fourfold axis. Hydrogen atom positions were calculated and were used as fixed atom contributors in the least-squares refinement. Current residuals are R_F = 0.083 and R_{wF} = 0.100. While each end of the molecule appears different, this may be an artifact of the disorder. Attempts to place the molecule in lower symmetry space groups yielded equivalent results.

Table I. Comparison of M–M, M–O, and M–N/P Distances in Some Dimolybdenum (M≡M) and (M≣M) Compounds Supported by O, N, and P Donor Ligands

compound[a]	M–M bond order	M–M, Å	M–O, Å (av)	M–N/P, Å (av)	ref
$Mo_2(OCH_2\text{-}t\text{-}Bu)_6$	3	2.222 (2)	1.88 (1)		b
$Mo_2(O\text{-}i\text{-}Pr)_6(py)_2$	3	2.250 (2)	1.93 (1)	2.32 (1)	c
$Mo_2(O\text{-}i\text{-}Pr)_4(mhp)_2$	3	2.206 (1)	1.91 (1) OR, 2.04 (1) mhp	2.27 (1)	d
$Mo_2(O\text{-}i\text{-}Pr)_4(py)_4$	4	2.195 (1)	2.03 (1)	2.27 (1)	e
$Mo_2(OCH_2\text{-}t\text{-}Bu)_4(PMe_3)_4$	4	2.209 (1)	2.03 (2)	2.54 (2)	e
$Mo_2(mhp)_4$	4	2.065 (1)	2.09 (1)	2.17 (1)	f
$Mo_2(OCH_2\text{-}t\text{-}Bu)_4(HNMe_2)_4$	4	2.133 (2)	2.08 (1)	2.27 (2)	e
$Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$	4	2.110 (3)	2.09 (1) OR, 2.17 (1) HOR		e
$Mo_2(O_2CMe)_4$	4	2.093 (1)	2.11 (2)		g

[a] mhp is the anion of 2-hydroxy-6-methylpyridine; py = pyridine. [b] Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801. [c] Leonelli, J. Ph.D. Thesis, Indiana University, 1982. [d] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Inorg. Chem.* **1981**, *20*, 2215. [e] This work. [f] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725. [g] Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2768.

Pr)$_4$(py)$_4$, and Mo$_2$(O-*i*-Pr)$_4$(HO-*i*-Pr)$_4$ with those for some related (Mo≡Mo)$^{6+}$ and (Mo$\underline{}$Mo)$^{4+}$ containing compounds is given in Table I. The following points are worthy of note: (1) The Mo–Mo distances in Mo$_2$(OCH$_2$-*t*-Bu)$_4$(PMe$_3$)$_4$ (2.209 (2) Å) and Mo$_2$(O-*i*-Pr)$_4$(py)$_4$ (2.196 (1) Å) are the longest reported for Mo–Mo quadruple bonds. (2) The Mo–OR distances in the (Mo$\underline{}$Mo)$^{4+}$ containing compounds are more than 0.1 Å longer than those found in (Mo≡Mo)$^{6+}$ containing compounds. (3) The compounds Mo$_2$(OR)$_4$L$_4$(*M*$\underline{}$*M*), where L = HNMe$_2$ and *i*-PrOH, contain hydrogen bonds across the Mo–Mo bond of the type depicted by II.[5] This results in (i) a shorter Mo–Mo distance,

$$\left(\begin{array}{c} R \\ \diagdown \\ O\cdots H \diagdown \\ | \quad\quad L \\ Mo \equiv Mo \end{array} \right)_4$$

II
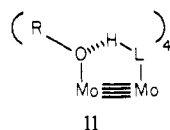
(ii) longer Mo–OR distances, and (iii) smaller RO–Mo–Mo angles, relative to the Mo$_2$(OR)$_4$L$_4$ compounds where L = py and PMe$_3$.[6]

Qualitatively, these structural features may be understood in terms of the mutual influence of the alkoxide π-donor ligand and the Mo–Mo quadruple bond. In the (Mo≡Mo)$^{6+}$ containing compounds, either one or both of the in-plane Mo atomic orbitals (d$_{x^2-y^2}$, d$_{xy}$) are available for RO-to-Mo π-bond formation. In (Mo$\underline{}$Mo)$^{4+}$ containing compounds, there are formally no vacant Mo d atomic orbitals to form π-bonds with the RO ligands. Four d orbitals are used to form the Mo–Mo quadruple bond, σ^{2}π^{4}δ^2 (d$_{z^2}$, d$_{xz}$, d$_{yz}$, and d$_{xy}$), and one (d$_{x^2-y^2}$) is used in combination with s, p$_x$, and p$_y$ to form Mo–OR/L σ-bonds. The filled oxygen p atomic orbitals will mix with the empty Mo–Mo δ* and π* molecular orbitals, thereby weakening and lengthening the Mo–Mo bond. The introduction of hydrogen bonds across the Mo–Mo bond, as shown in II, serves to neutralize the π-donor properties of the RO ligand, thus lengthening and shortening the Mo–OR and Mo–Mo distances, respectively.

Both the reactivity patterns and the physicochemical properties of these new compounds of type I are under investigation.[7]

Supplementary Material Available: Listings of atomic positional parameters for Mo$_2$(O-*i*-Pr)$_4$(py)$_4$, Mo$_2$(O-*i*-Pr)$_4$(HO-*i*-Pr)$_4$, Mo$_2$(OCH$_2$-*t*-Bu)$_4$(PMe$_3$)$_4$, and Mo$_2$(OCH$_2$-*t*-Bu)$_4$(HNMe$_2$)$_4$ (4 pages). Ordering information is given on any current masthead page.

(5) This type of RO---HOR bonding was seen in W$_2$Cl$_4$(OR)$_4$(HOR)$_2$ compounds and has been noted to give rise to both symmetric and asymmetric hydrogen bridges: Cotton, F. A.; Falvello, L. R.; Fredrick, M. F.; DeMarco, D.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 3088. In the present case the bridging hydrogens were located in the Fourier difference map for Mo$_2$-(OCH$_2$-*t*-Bu)$_4$(HNMe$_2$)$_4$ but not for Mo$_2$(O-*i*-Pr)$_4$(HO-*i*-Pr)$_4$. In the ^{1}H NMR spectra the bridging hydrogen appears at low field consistent with its position over the M–M multiple bond: Mo$_2$(O-*i*-Pr)$_4$(HO-*i*-Pr)$_4$ δ(OH–O) = 13.1 ppm and Mo$_2$(OCH$_2$-*t*-Bu)$_4$(HNMe$_2$)$_4$ δ(O–HN) = 6.9 ppm.

(6) Compare Mo–Mo–O angles (averaged) in Mo$_2$(OCH$_2$-*t*-Bu)$_4$L$_4$ which are 101° and 110° when L = HNMe$_2$ and PMe$_3$, respectively.

Asymmetric Acylation Reactions of Chiral Imide Enolates. The First Direct Approach to the Construction of Chiral β-Dicarbonyl Synthons[1]

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In conjuction with our general interest in the development of chiral enolate systems derived from oxazolidone imides,[3] we recently made the striking observation that these enolates undergo highly diastereoselective acylation reactions (eq 1). Although

(1)
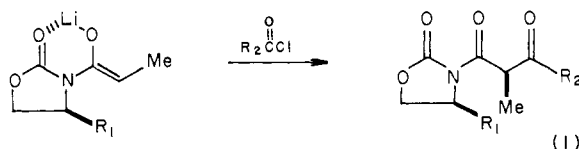
conventional wisdom suggests that the integrity of the newly created asymmetric center in these β-dicarbonyl adducts might be readily lost via enolization, we have found that this has not

(3) (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Evans, D. A.; Ennis, M. D.; Mathre, D. J. *Ibid.* **1982**, *104*, 1737. (c) Evans, D. A. *Aldrichimica Acta* **1982**, *15*, 23.