Figure 2. ^1H NMR spectra of the $PhCH_2$ protons as a function of temperature of a crystalline sample of $(i-PrO)_3Mo\equiv Mo(CH_2Ph)_2(O-i-Pr)(PMe_3)$ dissolved in toluene-d_8. At -20 °C the $PhCH_2$ protons appear as an ABX spectrum (X = ^{31}P) with the downfield portion of the spectrum partially obscured by the septet of the $(i-PrO)_3Mo\equiv$ methyne protons (*). Upon raising the temperature the growth of the singlet (C) at ca. 4.1 ppm corresponds to the increase in concentration of $(i-PrO)_2(PhCH_2)Mo\equiv Mo(CH_2Ph)(O-i-Pr)_2$. The signals arising from the $PhCH_2$ protons of the $(i-PrO)_3Mo\equiv Mo(CH_2Ph)_2(O-i-Pr)(PMe_3)$ molecule decrease in intensity as the former grows (C) and coupling of A/B to ^{31}P is lost indicating rapid reversible loss of PMe_3 at +60 °C. Spectra were recorded at 360 MHz.

(1) Å. Also the Mo–O distances at the 3- and 4-coordinate ends of the molecule are comparable to those seen in $Mo_2(OCH_2-t-Bu)_6$ and $Mo_2(O-i-Pr)_6(py)_2$, respectively. The long Mo–P distance is consistent with its lability toward PMe_3 dissociation (vide infra). The Mo–C distances are longer than those in $1,2-Mo_2-(CH_2Ph)_2(NMe_2)_4$,[9] but the increase in Mo–C distance is comparable to that seen previously in going from 3- to 4-coordinate molybdenum, c.f., , Mo–C = 2.16 (1) Å in $1,2-Mo_2Et_2(NMe_2)_4$[15] and Mo–C = 2.21 (1) Å in $Mo_2Et_2(NMe_2)_2(PhN_3Ph)_2$.[16]

The ^1H NMR spectrum[11] of a crystalline sample of $(i-PrO)_3Mo\equiv Mo(CH_2Ph)_2(O-i-Pr)(PMe_3)$ dissolved in toluene-d_8 at -20 °C is entirely consistent with expectations based on the observed molecular structure allowing for rapid rotation about the Mo–Mo bond. Ther are two types of O-i-Pr ligands in the ratio 1:3, and the methylene protons of the benzyl ligand are diastereotopic and appear as part of an ABX spin system (X = ^{31}P). When the temperature is raised, the spectrum changes and is interpretable in terms of PMe_3 dissociation and the equilibrium shown in eq 1.

$$(i-PrO)_3Mo\equiv Mo(CH_2Ph)_2(O-i-Pr)(PMe_3) \rightleftharpoons$$
$$(i-PrO)_2(PhCH_2)Mo\equiv Mo(CH_2Ph)(O-i-Pr)_2 + PMe_3 \quad (1)$$
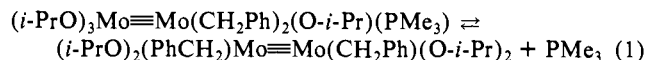
The temperature dependence of the equilibrium is easily followed in the $PhCH_2$ region of the NMR spectrum as shown in Figure 2. It is tempting to attribute the stability of the PMe_3 adduct to the favorable binding of the soft P donor ligand to the soft (i.e., bis-alkylated) molybdenum center.

The present findings provide the first observation of facile, reversible alkyl/alkoxy exchange at a $(Mo\equiv Mo)^{6+}$ center. These are of obvious relevance to previous findings of Rothwell and co-workers[17,18] and are of potential importance when one considers viable mechanisms for dinuclear reductive eliminations[19] which convert M–M triple to M–M quadruple bonds.[20,21]

Further studies are in progress.[22]

Supplementary Material Available: Listing of atomic coordinates and isotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

(15) Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046.
(16) Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2138.

(17) Compounds of the $X_2RMo\equiv MoR_3$ and $XR_2Mo\equiv MoR_2X$ where X = O-t-Bu or NMe_2 do not isomerize in toluent-d_8 solution: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 251.
(18) The conversion of $L_3Mo\equiv MoL_3$ compounds to $L_3Mo(\mu-L)_3MoL_3$ compounds has been noted: Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 3178.
(19) Trinquier, G.; Huffman, R. *Organometallics* **1984**, *3*, 370.
(20) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 1153.
(21) Chisholm, M. H.; Chiu, H. T.; Huffman, J. C. *Polyhedron* **1984**, *3*, 759.
(22) We thank the Department of Energy, Office of Basic Research, Chemical Sciences Division and the Wrubel Computing Center for financial support.

Dibenzyl- and Dineopentyltetrakis(propionato)ditungsten($M\equiv M$). Axial Ligation and Unprecedentedly Short W–W Distances for the $RW\equiv WR$ Unit

Malcolm H. Chisholm,* David M. Hoffman, John C. Huffman, William G. Van Der Sluys, and Steven Russo

Department of Chemistry and Molecular Structure Center, Indiana University Bloomington, Indiana 47405

Of all the compounds containing multiple bonds between metal atoms,[1] the d^3–d^3 dimers of molybdenum and tungsten show the most varied and fascinating coordination chemistry. There are compounds with M–M triple bonds of configuration $\sigma^2\pi^4$ in which the metal atoms are each coordinated to three, four, five, and even six ligand atoms.[2,3] Though *ligands* may span the two metal atoms, there are no bridging *atoms* in this group of d^3–d^3 dimers. However, compounds with bridging atoms are known as in

(1) Cotton, F. A.; Walton, R. A. In "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
(2) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.
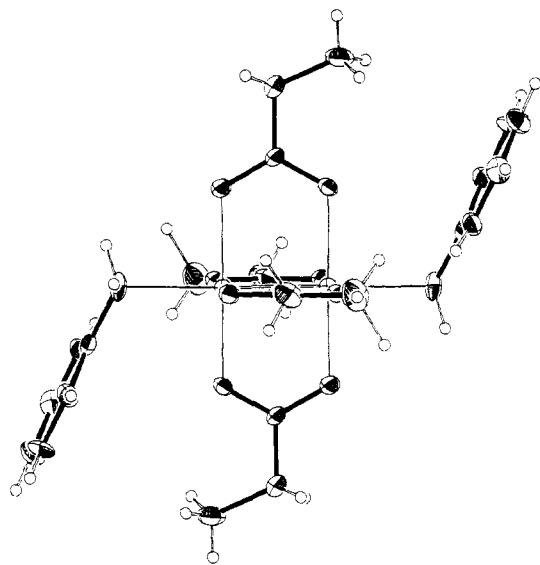(3) Chisholm, M. H. *Faraday Soc. Symp.* **1980**, *No. 14*, 194.

Figure 1. ORTEP view of the centrosymmetric $W_2(CH_2Ph)_2(O_2CEt)_4$ molecule. Pertinent bond distances (Å) and angles (deg), averaged where appropriate, are W–W = 2.186 (1), W–C = 2.18 (1), W–O = 2.084 (9), O–C = 1.28 (1), W–W–C = 178.7 (4), W–C–C = 113.2 (7), W–W–O = 90.5 (2), W–OC = 119.4 (9), O–CO = 120.4 (8).

$W_2Cl_6(py)_4$[4] and $M_2X_9{}^{3-}$ salts (X = Cl, Br)[5] which adopt structures based on edge- and face-shared octahedra, respectively. Within the former group of compounds, the M–M triple bond, $\sigma^2\pi^4$, is cylindrical and does not exhibit a preference for staggered or eclipsed geometries with respect to each end of the molecule.[6] The observed conformations are determined by ligand interactions across the M–M bond. The compounds $W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ provide the only structurally characterized examples of compounds where the metal atoms are coordinated to five and six ligand atoms and adopt the structures depicted by I and II. Near-eclipsed geometries result from the presence of

I   II
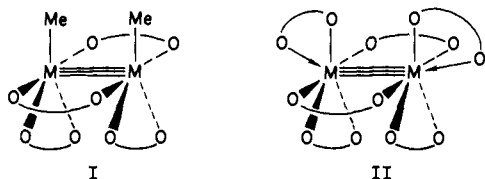
a pair of O_2CNR_2 ligands that span the W≡W bond.

Within the series of structurally characterized compounds of formula $X_nM\equiv MX_n$, where M = Mo or W, X = a ligand atom, and n = 3–6, we see an apparent reluctance to form bonds colinear with the M–M axis. Only in $W_2(O_2CNMe_2)_6$ (II) is weak axial ligation observed: W---O = 2.67 Å. We describe here a new type of geometry for d^3–d^3 dimers of tungsten where strong axial ligation is observed and results in extremely short W–W distances.

Following our discovery of a general synthesis of ditungsten carboxylates by reductive–elimination (alkyl group disproportionation), eq 1,[8] we extended our studies to alkyl groups lacking

$$W_2R'_2(NMe_2)_4 + 4RCOOCOR \xrightarrow[W_2(O_2CR)_4]{}$$
R' = Et, Pr, Bu

$$+ 4RCONMe_2 + alkene + alkane \quad (1)$$

(4) Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

(5) See: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 864–866 and references cited therein.

(6) The $X_3M\equiv MX_3$ molecules have been the subject of numerous theoretical studies: Dobbs, K. W.; Francl, M. H.; Hehre, W. J. *Inorg. Chem.* **1984**, *23*, 24. Ziegler, T. *J. Am. Chem. Soc.* **1983**, *105*, 7543. Kok, R. A.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 728. Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. *J. Am. Chem. Soc.* **1980**, *102*, 4579. Hall, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 2104. Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141. Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *100*, 7736.

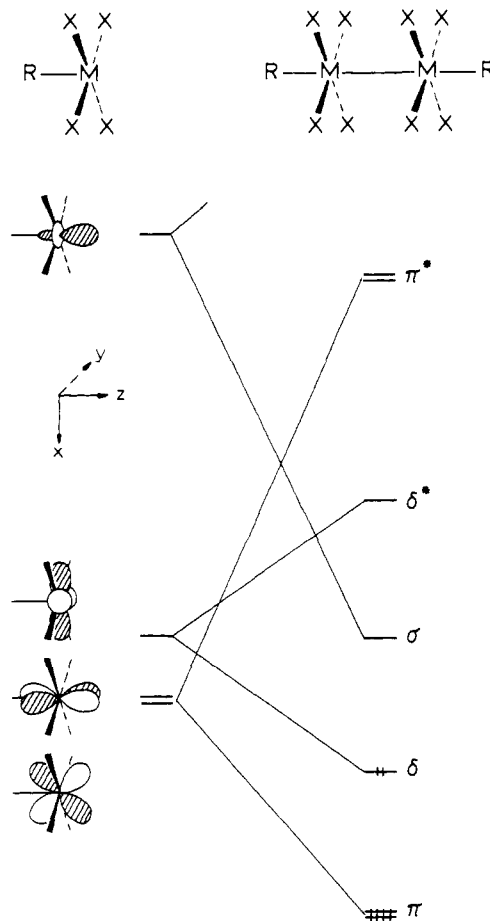(7) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603.

Figure 2. Schematic drawing showing the derivation of the molecular orbitals of the d^3–d^3 dimer RX_4MMX_4R (right), from the molecular orbitals of a RX_4M fragment (left).

β-hydrogen atoms. This has allowed isolation of crystalline, air-sensitive compounds of formula $W_2R'_2(O_2CEt)_4$, where R' = CH_2Ph and CH_2-t-Bu.[9]

A variety of carboxylic anhydrides and R' groups can be envisaged for reactions of this type. Our initial choice of propionic anhydride and R' = benzyl was motivated by a desire to seek an alternate synthesis of the structurally characterized $W_2(O_2CEt)_4$ compound, and indeed $W_2(CH_2Ph)_2(O_2CEt)_4$ upon photolysis in hydrocarbon solvents yields $W_2(O_2CEt)_4$ and dibenzyl by W–C bond homolysis. The ^1H NMR spectrum of $W_2(CH_2Ph)_2$-$(O_2CEt)_4$ was, however, not reconcilable with a structure analogous to that of $W_2Me_2(O_2CNEt_2)_4$.[9] Consequently, we resorted to a single-crystal X-ray diffraction study which revealed[10] the molecular structure shown in Figure 1. The structure is consistent with the NMR data but is quite unexpected in view of the previously established geometries for d^3–d^3 dimers of tungsten. The W–W distance and the parameters of the central $W_2(O_2C)_4$ core are essentially identical with those seen in $W_2(O_2CEt)_4$,[8] which, being a d^4–d^4 dimer, has a quadruple bond. The W–W distance is ca. 0.1 Å shorter than that in $W_2Me_2(O_2CNEt_2)_4$ and shorter than any seen before for a tungsten d^3–d^3 dimer. The W–C distance is the same as the Mo–C distance in $Mo_2(CH_2Ph)_2$-$(NMe_2)_4$.

(8) Chisholm, M. H.; Chiu, H. T.; Huffman, J. C. *Polyhedron.* **1984**, *3*, 759.

(9) Satisfactory elemental analyses have been obtained. ^1H NMR data obtained from benzene-d_6 solutions at +21 °C for $W_2(CH_2Ph)_2(O_2CEt)_4$: benzyl CH_2 δ 3.64, J_{WH} = 13.7 Hz; proprionate CH_2 δ 2.77, quartet; CH_3 δ 0.88, triplet, J_{HH} = 7.6 Hz.

(10) Crystal data for $W_2(CH_2Ph)_2(OCEt)_4$ at -157 °C: a = 10.877 (5) Å, b = 8.414 (3) Å, c = 15.153 (7) Å, β = 94.65 (3)°, Z = 2, d_{calcd} = 2.024 g cm^{-3}, and space group $P2_1/c$; R_F = 0.035 and R_{wF} = 0.036. For W_2-$(CH_2$-t-Bu)$_2(O_2CEt)_4$ at -158 °C: a = 12.141 (8) Å, b = 9.133 (5) Å, c = 7.37 (4) Å, α = 63.06 (3)°, β = 101.85 (4)°, γ = 80.47 (4)°, z = 1, d_{calcd} = 1.957 g cm^{-3}, and space group $P\bar{1}$; F_F = 0.059 and $R^w{}_F$ = 0.062.

Lest the present structure be anomalous because of some unique property of the benzyl ligand, we prepared the related neopentyl compound. A single crystal X-ray diffraction study[10] revealed a similar centrosymmetric structure with W–W = 2.187 (2) Å, W–C = 2.21 (2) Å, W–O = 2.08 (1)° (averaged), and W–W–C = 169.7(4)°.

Several questions are raised by these findings, in particular: (1) For a molecule of formula $W_2R_2(O_2CX)_4$, what factors favor the adoption of a structure akin to that seen for R = Me and X = NEt_2 vs. R = CH_2-*t*-Bu or CH_2Ph and X = Et? (2) Why should strong axial ligation of neopentyl or benzyl groups result in a shortening of the W≡W bond?

The latter effect is just the opposite of what has been observed in the chemistry of M–M quadruple bonds[1] and is contraintuitive. The formation of a triple bond in the present d^3–d^3 dimers may be viewed in the context of combining two ML_5 fragments.[11] This leads one to anticipate a triple bond of configuration $\pi^4\delta^2$, rather than $\sigma^2\pi^4$, as shown in Figure 2. The $\pi^4\delta^2$ configuration is further supported by extended Hückel (EH) calculations for the model system $W_2(O_2CH)_4R_2$, where R = H or Me.[12]

Although qualitative MO theory predicts a $\pi^4\delta^2$ configuration,[13] we cannot rule out a $\pi^4\sigma^2$ configuration in which σ has dropped

below δ in Figure 2. A $\pi^4\sigma^2$ configuration would readily explain the shortness of the W–W bond. As measured by the W–W overlap population (a measure of bonding), EHMO calculations show the σ W–W bonding MO of $W_2(O_2CH)_4Me_2$ to be more W–W bonding than the σ bond in $W_2(O_2CH)_4$ ($\sigma^2\pi^4\delta^2$). The σ MO in $W_2(O_2CH)_4Me_2$ is more bonding because S and p_z mix with d_{z^2} in such a way as to enhance the W–W bonding and decrease the W–C antibonding. Thus, according to the calculations, the W–W overlap population in $W_2(O_2CH)_4Me_2$ with a $\pi^4\sigma^2$ configuration is roughly the same as in $W_2(O_2CH)_4$ with a $\sigma^2\pi^4\delta^2$ configuration. The mixing of metal d_{z^2} and p_z orbitals has been noted before in many dimers of the later transition elements, particularly the d^8–d^8 dimers of Rh(I) and Pt(II) where, if only d_{z^2}–d_{z^2} interactions are considered, a nonbonding or repulsive interaction is expected: $\sigma^2\sigma^{*2}$.[14,15]

Finally we note that the linear C—W≡W—C unit results in σ molecular orbitals that mix W–C and W–W bonding. Consequently, to represent the W–W configuration as either $\pi^4\delta^2$ or $\pi^4\sigma^2$ is only an approximation. Further studies are in progress.[16]

Supplementary Material Available: Fractional coordinates, thermal parameters, and atom number schemes for $W_2(CH_2Ph)_2(O_2CEt)_4$ and $W_2(CH_2$-*t*-Bu$)_2(O_2CEt)_4$ (4 pages). Ordering information is given on any current masthead page.

(11) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(12) Extended Hückel calculations with weighted Hij's were used: Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179; **1962**, *37*, 2872. Ammeter, J. H.; Burgi, H. B.; Thiebault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. The tungsten parameters are from Kubacek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

(13) The M–M triple bond of configuration $\pi^4\delta^2$ was predicted previously for d^3–d^3 dimers such as $Re_2Cl_{10}^{2-}$ formed by the coupling of two ML_5 fragments: Hoffmann, R.; Shaik, S.; Fisel, C. R.; Summerville, R. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

(14) Balch, A. L. *A.S.C. Symp. Ser.* **1981**, *155*, 167 and references therein.

(15) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II *Inorg. Chem.* **1978**, *17*, 828. Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461. Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553.

(16) We thank the National Science Foundation and the Wrubel Computing Center for support.

Additions and Corrections

Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-Type Halides. VII [*J. Am. Chem. Soc.* **1958**, *80*, 1916]. WILLIAM E. TRUCE* and RUDOLPH KASSINGER

The oxidation product from tris(*p*-tolymercapto)ethene is bis(*p*-tolylsulfonyl)methane and *not* the trisulfone.

Hydrogen Atom Transfer Reactions: The Nature of the Transition State As Delineated from the Temperature Dependence of the Primary KIE [*J. Am. Chem. Soc.* **1983**, *105*, 6526–6528]. HENRY L. STRONG, MARILYN L. BROWNAWELL, and JOSEPH SAN FILIPPO, JR.*

Page 6527, Table I: Entry 11 in which now reads p-$CH_3C_6H_4CH_2Cl$ should read p-$CH_3OC_6H_4CH_2Cl$.

Total Synthesis of Vineomycin B_2 Aglycon [*J. Am. Chem. Soc.* **1984**, *106*, 2453]. SAMUEL J. DANISHEFSKY,* BIING JIUN UANG, and GEORGE QUALLICH
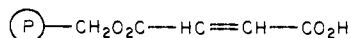
Page 2454, second line: A yield is reported as 8%. In fact, this should be shown as 84%.

Reactivity of Free Cyclopentadienone in Cycloaddition Reactions [*J. Am. Chem. Soc.* **1984**, *106*, 2077]. F. GAVIÑA,* A. M. COSTERO, P. GIL, and S. V. LUIS

Page 2078, Table I: Compound VIII appears as

$$\text{(P)}\!-\!CH_2O_2C\!-\!HC\!\equiv\!CH\!-\!CO_2H\!-\!CO_2H$$
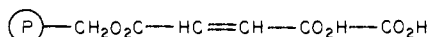
Obviously, it should be

$$\text{(P)}\!-\!CH_2O_2C\!-\!HC\!\equiv\!CH\!-\!CO_2H$$

300-MHz ^1H NMR Study of Parabactin and Its Gallium(III) Chelate [*J. Am. Chem. Soc.* **1984**, *106*, 3089]. RAYMOND J. BERGERON* and STEVEN J. KLINE

Page 3098: The following should be added.

Acknowledgment. We would like to acknowledge the National Institutes of Health Grant AM-29936 and the Veterans Administration for their support.

Structures and Conformation of Dihydro Aromatic Compounds. 3. Cis- and Trans-Disubstituted 1,4-Dihydrobenzenes, 1,4-Dihydronaphthalenes, and 9,10-Dihydroanthracenes [*J. Am. Chem. Soc.* **1984**, *106*, 3119]. P. W. RABIDEAU,* K. B. LIPKOWITZ,* and R. B. NACHBAR, JR.

Page 3122: Figures 5 and 6 should have their captions exchanged.

It should be added that the transition-state state structures for *trans*-9,10-di-*tert*-BuBHA were calculated without constraints with the program BIGSTRN-3 (R. B. Nachbar, Jr., and K. Mislow, to be submitted to QCPE) using Allinger's MM2 force field (N. L. Allinger and Y. H. Yuh, *QCPE*, **1981**, *13*, 395), and were characterized by a singel imaginary frequency.

Intramolecular Alkoxypalladation/Carbonylation of Alkenes [*J. Am. Chem. Soc.* **1984**, *106*, 1496–1498]. M. F. SEMMELHACK* and CHRISTINA BODUROW

Page 1497, Table I, entry 4: the product is drawn incorrectly; it should be

18 (97)[9]
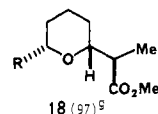
Regioselectivity and Rearrangement upon Addition of Nucleophiles to (Diene)iron Complexes [*J. Am. Chem. Soc.* **1984**, *106*, 2715–2717]. M. F. SEMMELHACK* and HANH T. M. LE

Page 2715: Structures 3 and 18 were redrawn with a misleading representation of the allyl ligands, in Scheme I. That scheme