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 $W\equiv W$ 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 $C—W\equiv W—C$ 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

Ⓟ—CH_2O_2C—HC$=$CH—CO_2H—CO_2H

Obviously, it should be

Ⓟ—CH_2O_2C—HC$=$CH—CO_2H

300-MHz ^{1}H 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.

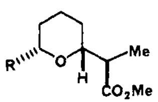
Structures and Conformation of Dihydro Aromatic Compounds. 3. Cis- and Trans-Disubstituted 1,4-Dihydrobenzenes, 1,4-Dihydronaphthalenes, and 9,10-Dihydroanthracenes [*J. Am. Chem. Soc.* **1984**, *106*, 3119]. P. W. RABIDEAU,* K. B. LIPKOWITZ,* and R. B. NACHBAR, JR.

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)^g

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