

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<sup>10</sup> 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<sub>2</sub> vs. R = CH<sub>2</sub>-*t*-Bu or CH<sub>2</sub>Ph 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<sup>1</sup> and is contrainuitive. The formation of a triple bond in the present d<sup>3</sup>-d<sup>3</sup> dimers may be viewed in the context of combining two ML<sub>5</sub> fragments.<sup>11</sup> 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.<sup>12</sup>

Although qualitative MO theory predicts a  $\pi^4\delta^2$  configuration,<sup>13</sup> we cannot rule out a  $\pi^4\sigma^2$  configuration in which  $\sigma$  has dropped

(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<sup>3</sup>-d<sup>3</sup> dimers such as Re<sub>2</sub>Cl<sub>10</sub><sup>2-</sup> formed by the coupling of two ML<sub>5</sub> fragments: Hoffmann, R.; Shaik, S.; Fisel, C. R.; Summerville, R. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

below  $\delta$  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  $\sigma$  W-W bonding MO of  $W_2(O_2CH)_4Me_2$  to be more W-W bonding than the  $\sigma$  bond in  $W_2(O_2CH)_4$  ( $\sigma^2\pi^4\delta^2$ ). The  $\sigma$  MO in  $W_2(O_2CH)_4Me_2$  is more bonding because S and p<sub>z</sub> mix with d<sub>z<sup>2</sup></sub> 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<sub>z<sup>2</sup></sub> and p<sub>z</sub> orbitals has been noted before in many dimers of the later transition elements, particularly the d<sup>8</sup>-d<sup>8</sup> dimers of Rh(I) and Pt(II) where, if only d<sub>z<sup>2</sup></sub>-d<sub>z<sup>2</sup></sub> interactions are considered, a nonbonding or repulsive interaction is expected:  $\sigma^2\sigma^*2$ .<sup>14,15</sup>

Finally we note that the linear C-W≡W-C unit results in  $\sigma$  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.<sup>16</sup>

**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.

(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*-tolylmercapto)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.\*

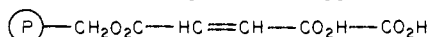
Page 6527, Table I: Entry 11 in which now reads *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl should read *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl.

**Total Synthesis of Vineomycin B<sub>2</sub> Aglycon** [*J. Am. Chem. Soc.* **1984**, *106*, 2453]. SAMUEL J. DANISHEFSKY,\* BINNJIUN UANG, and GEORGE QUALLICH

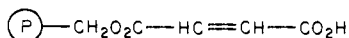
Page 2454, second line: A yield is reported as 8%. In fact, this should be shown as 84%.

**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



Obviously, it should be



**300-MHz <sup>1</sup>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.

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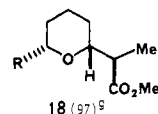
**Structures and Conformation of Dihydro Aromatic Compounds. 3. Cis- and Trans-Disubstituted 1,4-Dihydrobenzenes, 1,4-Dihydronaphthalenes, and 9,10-Dihydroanthracenes** [*J. Am. Chem. Soc.* **1984**, *106*, 3119]. P. W. RABIDEAU,\* K. B. LIPKOWITZ,\* and R. B. NACHBAR, JR.

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 single imaginary frequency.

**Intramolecular Alkoxy-palladation/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



**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