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.

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(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

$$\textcircled{P}{-}CH_2O_2C{-}HC{=}CH{-}CO_2H{-}CO_2H$$

Obviously, it should be

$$\textcircled{P}{-}CH_2O_2C{-}HC{=}CH{-}CO_2H$$

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.

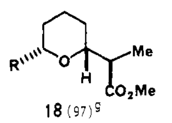
Structures and Conformation of Dihydro Aromatic Compounds. 3. Cis- and Trans-Disubstituted 1,4-Dihydrobenzenes, 1,4-Dihydronaphthalenes, and 9,10-Dihydroanthracenes [*J. Am. Chem. Soc.* **1984**, *106*, 3119]. P. W. Rabideau,* K. B. Lipkowitz,* and R. B. Nachbar, Jr.

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

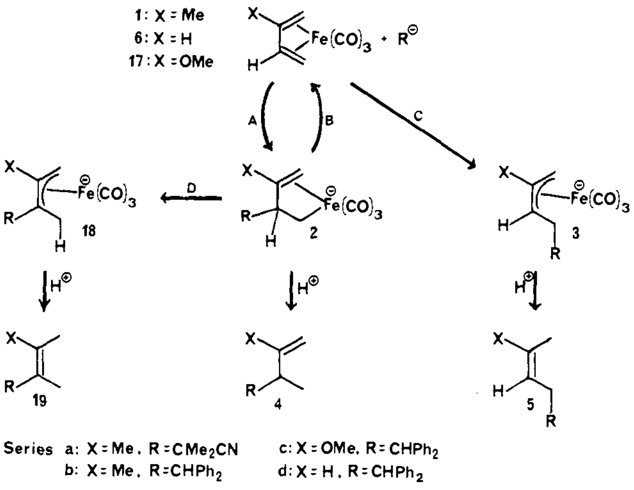


18 (97)^g

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

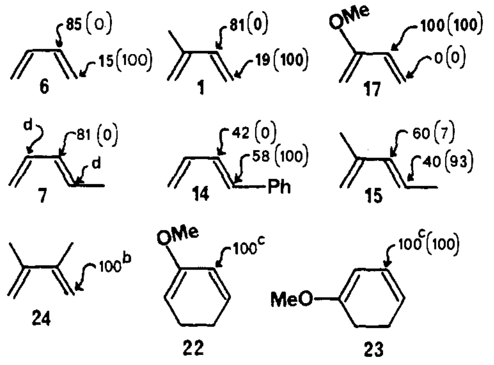
Page 2715: Structures **3** and **18** were redrawn with a misleading representation of the allyl ligands, in Scheme I. That scheme should be replaced by the one below.

Scheme I



Page 2716: Several parts of the drawings of the structures in Table II were left out. The correct version is shown below.

Table II. Selectivity in Addition of $LiCHPh_2$ to Diene-$Fe(CO)_3$ Complexes



Vibration-Induced Electron Detachment in Molecular Anions [*J. Am. Chem. Soc.* **1984**, *106*, 3402–3407]. P. K. ACHARYA, RICK A. KENDALL, and JACK SIMONS*

Page 3405: Table II is in error and should be replaced by the table given below.

Table II. OH^- Detachment Rates (10^5 s^{-1}) and Lifetimes (10^{-6} s)[a]

v', v	O–H bond length	5	6	7	8	9	10	11
0	*M*	0.632	0.758	0.186	0.038	0.009	0.003	0.002
	N	0.001	0.173	0.206	0.095	0.029	0.007	0.001
	P	0.370	1.14	0.396	0.064	0.004	0.000	0.001
1	*M*			2.81	1.23	0.327	0.084	0.026
	N			0.229	0.767	0.566	0.254	0.088
	P			3.36	2.37	0.683	0.109	0.005
2	*M*				1.60	3.35	1.37	0.436
	N				0.018	1.00	1.40	0.938
	P				1.44	5.51	2.88	0.851
3	*M*						2.50	2.89
	N						0.257	1.50
	P						3.27	5.44
lifetimes	*M*		13.2	3.34	3.49	2.71	2.53	2.98
	N		57.8	23.0	11.4	6.27	5.21	3.96
	P		8.77	2.66	2.58	1.61	1.60	1.59

[a] *N* denotes the equilibrium bond length (R_e = 0.9705 Å) for OH, and *M* and *P* denote OH bond lengths of $R_e - 0.0164$ and $R_e + 0.0159$ Å, respectively.

The numerical values given in this corrected Table II are not sufficiently different from those reported earlier to affect the conclusions drawn in the original paper. However, it appears that at the equilibrium bond length of OH, the corrected $OH^- \rightarrow OH + e^-$ detachment rates are lower than those obtained when the OH bond length is slightly increased or decreased. This is attributed to the fact that, at the actual equilibrium bond lengths, the separation between the OH and OH^- potential curves remains virtually constant for all values of *R*; any shift in the relative separation of OH and OH^- curves gives rise to an increase in detachment rate.

Book Reviews

Comprehensive Treatise of Electrochemistry. Volume 7. Kinetics and Mechanisms of Electrode Processes. Edited by Brian E. Conway (University of Ottawa), J. O'M. Bockris (Texas A&M University), Ernest Yeager (Case Western Reserve University), S. U. M. Khan (Texas A&M University), and Ralph E. White (Texas A&M University). Plenum Press, New York. 1983, xviii + 762 pp.

The stated purpose of the series, "Comprehensive Treatise of Electrochemistry", is to present"... a mature statement about the present position..." in the vast area of electrochemistry; Volume 7, covering Kinetics and Mechanisms of Electrode Processes, lives up to this purpose. Moreover, it tries to present a fair treatment in a subject that is still unsettled and hotly disputed.

The book contains ten contributions. The first two introductory articles deal with complementary (and often contradictory) approaches to a quantum theory of electrode processes. This is followed by a more traditional or phenomenological description of electrochemical kinetics. As expected, electrocatalysis, both organic and inorganic, receives a well-deserved and thorough treatment. Other articles deal with deposition and electrodissolution of metals and alloys, molten salt electrochemistry, and semiconductor electrodes. A well-balanced combination of theoretical approaches and experimental facts provides the reader with an in-depth and valuable understanding of these areas.

Taken together, these articles constitute an encylcopedic source of essential knowledge on electrode kinetics. Most of the contributions show a great deal of diligence and a high level of competence.

The editors have succeeded, in spite of obvious difficulties, in selecting authors and subjects that cover a wide spectrum of the field.

This volume is recommended to all those deeply interested in electrochemical kinetics and electrochemistry generally.

Norman Hackerman, *Rice University*

Quantitative Analysis of Steroids. Studies in Analytical Chemistry. Volume 5. By S. Görög (Chemical Works G. Richter Ltd., and Semmelweis University Medical School [Budapest]). Elsevier Scientific Publishing Co., Amsterdam, Oxford and New York. 1983. 440 pp. $95.75.

The present volume is the latest in the series of "Studies in Analytical Chemistry". Like its predecessors, the high standards of production and content are maintained in the present work.

The emphasis of this book is to give a survey of the quantitative analysis of steroids, with special emphasis on the developments in this area during the last 10 years. The author restricts his coverage to the quantitative aspects of analysis, omitting the problems associated with identification and structure elucidation. Spectroscopic methods such as infrared and NMR spectroscopy, together with mass spectrometry, are considered only from the point of view of their quantitative analytical applications. In addition, chromatography is also treated as a quantitative analytical tool, with special emphasis on gas chromatography, high-performance liquid chromatography, and thin-layer densitometry. The techniques of column and thin-layer chromatography are treated as sample preparation steps for quantitative analysis. Theoretical and practical aspects of chromatography including structure–chromato-