

single small bite bidentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand severely distorts a trigonal bipyramid.

A further comparison of interest is the distorted trigonal bipyramid for the iron(0) coordination in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}$ (Figure 1) in contrast to the square pyramid for the iron(0) coordination in the somewhat related complex $[\text{CH}_3\text{N}(\text{PF}_2)_2\text{Fe}(\text{CO})_3]_2$.⁸ These drastically different coordination polyhedra in otherwise related five-coordinate iron(0) complexes are further indication of the extreme nonrigidity of five-vertex coordination polyhedra as previously demonstrated by the stereochemical nonrigidity of five-coordinate complexes in NMR experiments¹¹ and suggested by a recent graph-theoretical analysis of polyhedra for different coordination numbers.¹²

The mass spectrum of $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}$ exhibits the ions $[\text{CH}_3\text{N}(\text{PF}_2)_2]_n\text{Fe}^+$ ($n = 3, 2, \text{ and } 1$) but not the molecular ion $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}^+$. This suggests that $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Fe}$ decomposes in the mass spectrometer with the loss of one $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligand to give $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Fe}$ containing two bidentate and one monodentate $\text{CH}_3\text{N}(\text{PF}_2)_2$ ligands.

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References and Notes

- (1) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).
- (2) J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, **13**, 363 (1970).
- (3) K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975).
- (4) P. L. Timms and T. W. Turney, *Adv. Organomet. Chem.*, **15**, 53 (1977).
- (5) E. L. Muettterties and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 850 (1974).
- (6) C. A. Tolman, L. W. Yarbrough, II, and J. G. Verkade, *Inorg. Chem.*, **16**, 479 (1977).
- (7) R. B. King, *Top. Curr. Chem.*, **14**, 92 (1970).
- (8) R. B. King and J. Gimeno, *J. Chem. Soc., Chem. Commun.*, 142 (1977).
- (9) M. G. Newton, R. B. King, M. Chang, and J. Gimeno, *J. Am. Chem. Soc.*, **99**, 2802 (1977).
- (10) R. B. King and J. Gimeno, unpublished results.
- (11) E. L. Muettterties, *Acc. Chem. Res.*, **3**, 266 (1970).
- (12) R. B. King, *Inorg. Chem.*, **16**, 1822 (1977).
- (13) University of Georgia Graduate Fellow, 1976–1978.

M. Chang,¹³ R. B. King,* M. G. Newton

Department of Chemistry, University of Georgia
Athens, Georgia 30602

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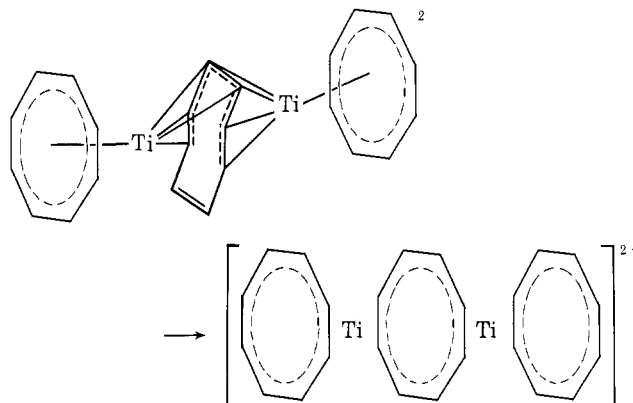
Triple Decker Sandwich Compounds: Paramagnetic Tris(cyclooctatetraene)ditanium and Its Dianion

Sir:

In connection with our interest in the reactions of titanium atoms, we prepared the previously described tris(cyclooctatetraene)ditanium^{1,3} (a triple decker sandwich compound)² by the atom method. The compound thus prepared did not, however, give any proton magnetic resonance signals when dissolved in C_6D_6 ; the only signal which appeared was due to the protium impurities in the solvent. A sample of the same compound prepared by wet chemistry methods gave identical ^1H NMR results. However, air oxidation of the solutions produced a large cyclooctatetraene singlet suggesting the presence of a paramagnetic substance which affects the spectrum of the titanium compound but not that of the benzene solvent.

A magnetic susceptibility measurement (Gouy method) indicated $2.56 \mu_B$ as the magnetic moment, indicating two unpaired electrons.⁴ Hoffmann and co-workers² describe an orbital diagram for this molecule which has a degenerate pair of HOMOs, each occupied by a single electron. Thus, experiment and theory are in agreement.

The paramagnetic yellow tris(cyclooctatetraene)ditanium, which is only slightly soluble in THF, is reduced rapidly with potassium to make a green solution of the diamagnetic anion free of any precipitate. Although the solution showed no signs of decomposition over a 24-h period, the unsolvated solid decomposed to black material as the last of the solvent was removed by pumping. Analysis of the green solution obtained from 50 mg of tris(cyclooctatetraene)ditanium (0.123 mmol) gave on hydrolysis 0.256 mmol of KOH and 0.269 mmol of TiO_2 . The failure to form titanium metal during the reduction, the analytical data, and the presence of a single sharp peak in the ^1H NMR spectrum are all consistent with the formulation of this green anion as shown.⁵ This appears to be the first in-



stance of such a triple decker anion and it is attractive to speculate that it is representative of a broader class of analogous compounds.

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References and Notes

- (1) H. Breil and G. Wilke, *Angew. Chem.*, **78**, 942 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 898 (1966).
- (2) J. W. Lauher, M. Elian, R. H. Summerville, and R. H. Hoffmann, *J. Am. Chem. Soc.*, **98**, 3219 (1976).
- (3) H. Dierks and H. Dietrich, *Acta Crystallogr. Sect. B*, **24**, 59 (1968).
- (4) The EPR spectrum of the solution of $\text{Ti}_2(\text{COT})_3$ in THF shows one strong signal without hyperfine splitting (3298 G; 9.035 GHz; $g = 1.95538$).
- (5) One disturbing feature of this proposal is that we do not see two sharp peaks in 2:1 ratio, but this may be explained by noting that all cyclooctatetraene derivatives show a remarkably similar chemical shift: cyclooctatetraene, 5.69 ppm; cyclooctatetraene dianion, 5.69 ppm; bis(cyclooctatetraene)titanium, 6.14 ppm (fast equilibrium);⁶ bis(cyclooctatetraene)zirconium, 5.90 ppm;⁷ bis(cyclooctatetraene)zirconium complex with THF, 5.50 ppm.⁷
- (6) J. Schwartz and J. E. Sadler, *J. Chem. Soc., Chem. Commun.*, 172 (1973).
- (7) Work done in these locations.
- (8) N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, U.S.S.R., Leninsky Prospect, 47, Moscow B-334, U.S.S.R.

Stanislav P. Kolesnikov,⁸ Jerry E. Dobson
Philip S. Skell*^{*}

Department of Chemistry, 152 Davey Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

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Conformational Equilibrium of the 17(20) Rotamers of (*E*)-20(22)-Dehydrocholesterol

Sir:

We recently reported¹ that hydrogenation of (*E*)-20(22)-dehydrocholesterol (**1**) in the presence of Pt yields a ~1:1 mixture of cholesterol (**5**)² and 20-isocholesterol (**4**).² Since the steroid nucleus should be held to the Pt on the former's back