

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  $[\text{CH}_3\text{N}(\text{PF}_2)_2\text{Fe}(\text{CO})_3]_2$ .<sup>8</sup> 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 experiments<sup>11</sup> and suggested by a recent graph-theoretical analysis of polyhedra for different coordination numbers.<sup>12</sup>

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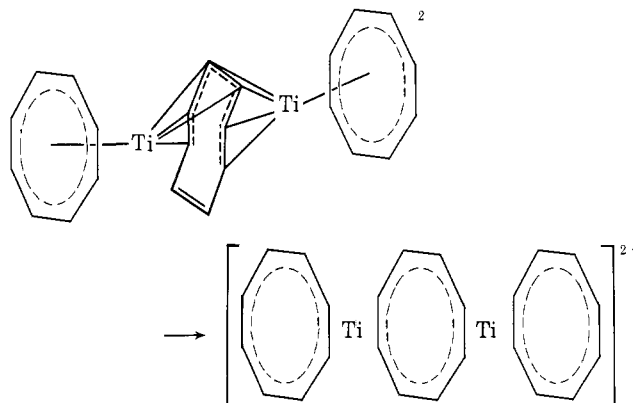
## Triple Decker Sandwich Compounds: Paramagnetic Tris(cyclooctatetraene)dтитanium and Its Dianion

Sir:

In connection with our interest in the reactions of titanium atoms, we prepared the previously described tris(cyclooctatetraene)dтитanium<sup>1,3</sup> (a triple decker sandwich compound)<sup>2</sup> by the atom method. The compound thus prepared did not, however, give any proton magnetic resonance signals when dissolved in  $\text{C}_6\text{D}_6$ ; 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  $^1\text{H}$  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.<sup>4</sup> Hoffmann and co-workers<sup>2</sup> 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)dтитanium, 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)dтитanium (0.123 mmol) gave on hydrolysis 0.256 mmol of KOH and 0.269 mmol of  $\text{TiO}_2$ . The failure to form titanium metal during the reduction, the analytical data, and the presence of a single sharp peak in the  $^1\text{H}$  NMR spectrum are all consistent with the formulation of this green anion as shown.<sup>5</sup> 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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- (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)dтитanium, 6.14 ppm (fast equilibrium);<sup>6</sup> bis(cyclooctatetraene)zirconium, 5.90 ppm;<sup>7</sup> bis(cyclooctatetraene)zirconium complex with THF, 5.50 ppm.<sup>7</sup>
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## Conformational Equilibrium of the 17(20) Rotamers of (*E*)-20(22)-Dehydrocholesterol

Sir:

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

side, H atoms presumably attack C-20 (and C-22) from the rear. If this is so, the formation of cholesterol and its epimer imply the existence of rotamers (**1a** and **1b**) about the 17(20) bond in the  $\Delta^{20(22)}$ -sterol. Since this conclusion has been challenged<sup>3</sup> and space did not permit discussion of the point in the original paper,<sup>1</sup> our theoretical analysis is expanded here.

The addition of H atoms from the rear of a steroid has been well documented. Thus, Hershberg et al.<sup>4</sup> reduced (Pt, H<sub>2</sub>, ETOAc) cholesterol and found the product mixture (alcohol, acetate, and hydrocarbon) to be in the 5 $\alpha$  series except for ~3% of the epimeric material. 5 $\alpha$ -Cholestanol itself was obtained in an 88% yield. That attack from the rear operates at the other end of the molecule is evident from work by Crump and Gut who contributed to a paper<sup>5</sup> which our two laboratories published jointly. Crump and Gut<sup>5</sup> reduced (Pt, H<sub>2</sub>, 45 psi) 100 mg of the 3,5-cyclo-6 $\beta$ -methyl ether of (*Z*)-17(20)-dehydrocholesterol (**6**) and isolated no less than 85 mg of the corresponding cholesterol (**5**)<sup>2</sup> derivative with no apparent epimer present. The stereochemistry would certainly appear to have been dictated by overwhelming adsorption of the sterol on its  $\alpha$  face, as in the  $\Delta^5$  case. Thus, in Pt-catalyzed hydrogenation the tetracyclic system appears to be fixed in space with respect to the incoming H atoms. If the double bond is then moved from the 17(20) to the 20(22) position, the configuration at C-20 should still be determined by attack of an H atom from the rear of the nucleus. It is unreasonable to assume that the catalyst surface has now bent around to the front side of C-20, since the placing of Pt in this position would, as in the  $\Delta^{17(20)}$  case, be prevented by C-18; specifically, a Pt-H complex attacking C-20 from the front would be in a 1,3-diaxial relationship with C-18 which is clearly much less favorable than attack from the rear where C-18 does not interfere. It therefore follows that the configuration at C-20 in the reduction of  $\Delta^{20(22)}$ -sterols should derive primarily from the relationship of C-20 to the steroid nucleus, cholesterol (**5**)<sup>2</sup> being derived from a rotamer with C-22 to the left (**1b**) and 20-isocholesterol (**4**)<sup>2</sup> from the rotamer with C-22 to the right (**1a**) (Scheme I).

We<sup>1</sup> had made a rough estimate of the position of the conformational equilibrium on the basis of the Curtin-Hammett principle.<sup>6-8</sup> The analysis is worth amplifying. We assume that the rate of reduction is slower than the rate of attainment of

conformational equilibrium in which case the product composition (4:5) would be determined by the relative numbers of different molecules in transition which in turn would derive from the relative energies of the transition states (**2** and **3**). Since the ratio of products was ~1:1, the transition states (**2** and **3**) would have about the same energies. On the reasonable assumption that the platinum surface does not differ on the right and left sides of C-20, the steric requirements of the planar or pseudoplanar C-20 in the transition states (**2** and **3**) should be essentially the same as those of the trigonal ground states of the starting material (**1a** and **1b**). The primary difference between transition and initial ground states should only be the partial attachment of an H atom to the rear of C-20 (and C-22) which should not make a differential contribution to the energies of one vs. the other of the molecules. The relative populations of right- and left-handed molecules in transition (**2** and **3**, respectively) should then reflect the relative populations of the rotamers (**1a** and **1b**) in the initial 20(22)-dehydrocholesterol, which we suggest must then approximate a 1:1 ratio, since this is the product ratio which has reflected the ratio of transition states.

In the unlikely event that perpendicular conformers (C-22 in front or in back) of the  $\Delta^{20(22)}$ -sterol undergo reduction in the Pt-catalyzed hydrogenation, our conclusion indicating conformational equilibrium remains unchanged. Reduction would then have to occur from the ring-D end of the molecule (the bulk of the nucleus preventing approach to the catalyst from the ring-A end), and the side of C-20 attacked would still remain dependent on its rotameric condition with respect to the nucleus. Of course, if the double bond being reduced were further removed from the nucleus, say at C-24, the influence of the nucleus would be less than in the case under consideration.

In other work<sup>9</sup> dealing with (*E*)- and (*Z*)- $\Delta^{17(20)}$ -sterols, we have shown that C-22 must be on the right when sterols are metabolized by *Tetrahymena pyriformis* to their 7-dehydro derivatives (**8** and not **6** being dehydrogenated). Since the present theoretical analysis permits 20(22)-dehydrocholesterol to exist in the biologically active form with C-22 to the right (**1a**), the sterol should be and experimentally is metabolized to its  $\Delta^{5,7}$  analogue.<sup>10,11</sup>

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Scheme I

