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$$\text{THF–Cu}^{+}\text{–L} \xrightarrow{h\nu} \text{THF–Cu}^{2+}\text{–L}^{-} \rightarrow \text{THF–Cu}^{+}\text{–L}^{-} \qquad +$$

The absence of readily reducible ligands and the formation of reduced metal appear to be in better agreement with ligand-to-metal charge-transfer excitation. The identity of the reactive excited state is under continued investigation.

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Novel Iron Complexes from Cocondensations of Iron Vapor with Aminodifluorophosphines

Sir:

The dialkylaminodifluorophosphines form relatively stable homoleptic zerovalent nickel complexes $(R_2NPF_2)_4Ni$ by displacement of all four CO groups from $Ni(CO)_4$.[1,2] However, no other homoleptic zerovalent dialkylaminodifluorophosphine metal complexes are known. This communication describes the first reported examples of the cocondensation of metal vapors[3,4] with aminodifluorophosphines. Such reactions are interesting since they provide routes to novel zerovalent metal complexes exhibiting relatively high stabilities and unusual structures.

About 0.5 g (8.93 mg-atoms) of iron metal was evaporated over a period of 30 min at 0.0001-mm pressure from an alumina coated tungsten wound crucible heated electrically. The resulting vapors were cocondensed at −196 °C with an excess (~8 mL) of dimethylaminodifluorophosphine. Excess ligand was then removed by pumping at −78 °C. The resulting black slurry was extracted with hexane and the resulting hexane solution chromatographed on a Florisil column. Elution of the yellow band with hexane gave 0.8 g (14% yield) of yellow $[(CH_3)_2NPF_2]_5Fe$. Anal. Calcd for $C_{10}H_{30}F_{10}FeN_5P_5$: C, 19.3; H, 4.9; N, 11.3. Found: C, 19.6; H, 4.7; N, 11.1.

This iron(0) derivative $[(CH_3)_2NPF_2]_5Fe$ is a yellow solid which appears indefinitely stable in air in contrast to many other iron(0) derivatives such as $[(CH_3O)_3P]_5Fe$.[5,6] Its ^1H NMR spectrum exhibits the expected broad peak at τ 7.0. Its mass spectrum exhibits the complete sequence of ions $[(CH_3)_2NPF_2]_nFe^+$ (n = 5, 4, 3, 2, and 1) indicating stepwise loss of $(CH_3)_2NPF_2$ ligands similar to the stepwise loss of carbonyl groups in the mass spectra of most metal carbonyls.[7]

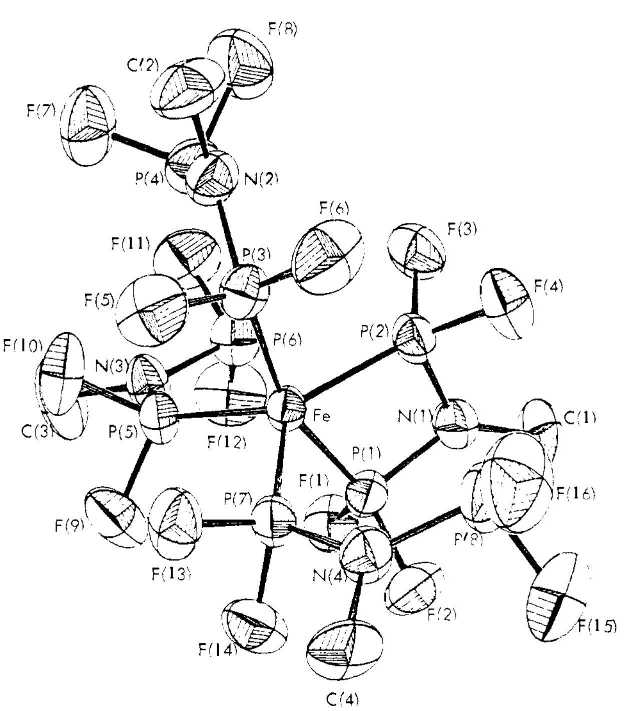

Figure 1. ORTEP drawing of the structure of $[CH_3N(PF_2)_2]_4Fe$.

The potentially bidentate ligand $CH_3N(PF_2)_2$ forms the relatively stable homoleptic complexes $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, and W) by ultraviolet irradiation with the corresponding metal hexacarbonyls.[8] However, all reactions of $CH_3N(PF_2)_2$ with iron carbonyls, even under photochemical conditions, give products still containing carbonyl groups.[9,10] In an attempt to prepare an iron(0) derivative containing only $CH_3N(PF_2)_2$ ligands, iron vapor was cocondensed with excess $CH_3N(PF_2)_2$ using a procedure completely analogous to that described above for the cocondensation of iron vapor with $(CH_3)_2NPF_2$. Chromatography of the resulting reaction mixture on silica gel using hexane as solvent gave a yellow band. Elution of this yellow band followed by crystallization from n-hexane at −20 ° gave yellow crystals. The yield of this product was low (<1%) owing to the concurrent formation of iron particles and unidentified iron compounds which could neither be sublimed or chromatographed without decomposition. In view of the limited quantity of this yellow product for the usual characterization by elemental analyses and spectroscopic methods, the structure of this product was instead determined by single-crystal x-ray diffraction.

The iron complex $[CH_3N(PF_2)_2]_4Fe$ forms monoclinic crystals by slow evaporation of an n-hexane solution at room temperature: space group $P2_1/n$; a = 16.777 Å, b = 10.486 Å, c = 15.538 A, β = 117.048°, Z = 4. Least-squares anisotropic refinement using the 2656 observed reflections (R = 0.0391, R_w = 0.0373) indicates the structure depicted in Figure 1. In this structure the iron(0) atom attains the expected coordination number of five since one of the $CH_3N(PF_2)_2$ ligands is bidentate whereas the remaining three $CH_3N(PF_2)_2$ ligands are only monodentate.

The coordination polyhedron of the five-coordinate iron(0) atom can be interpreted as a trigonal bipyramid which is severely distorted by the small-bite bidentate $CH_3N(PF_2)_2$ ligand. The ten angles around the five-coordinate iron atom are as follows: P(1)-Fe-P(3) = 161.96, P(1)-Fe-P(2) = 69.12, P(1)-Fe-P(7) = 93.07, P(1)-Fe-P(5) = 96.78, P(3)-Fe-P(2) = 93.61, P(3)-Fe-P(7) = 93.57, P(3)-Fe-P(5) = 97.85, P(2)-Fe-P(7) = 127.37, P(5)-Fe-P(7) = 104.03, P(5)-Fe-P(2) = 126.36°. The bidentate $CH_3N(PF_2)_2$ ligand (P(1) and P(2)) thus bridges an equatorial and an axial position of the iron(0) trigonal bipyramid and because of its small bite reduces the P_{ax}-Fe-P_{eq} angle from the idealized value of 90° to 69°. Part of this distortion involves bending the relevant Fe-P_{ax} bond so that the P_{ax}-Fe-P_{ax} angle is no longer the ideal value of 180° but instead 162°. Thus the introduction of a single small bite bidentate $CH_3N(PF_2)_2$ ligand severely distorts a trigonal bipyramid.

A further comparison of interest is the distorted trigonal bipyramid for the iron(0) coordination in $[CH_3N(PF_2)_2]_4Fe$ (Figure 1) in contrast to the square pyramid for the iron(0) coordination in the somewhat related complex $[CH_3N(PF_2)_2Fe(CO)_3]_2$.[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 experiments[11] and suggested by a recent graph-theoretical analysis of polyhedra for different coordination numbers.[12]

The mass spectrum of $[CH_3N(PF_2)_2]_4Fe$ exhibits the ions $[CH_3N(PF_2)_2]_nFe^+$ (n = 3, 2, and 1) but not the molecular ion $[CH_3N(PF_2)_2]_4Fe^+$. This suggests that $[CH_3N(PF_2)_2]_4Fe$ decomposes in the mass spectrometer with the loss of one $CH_3N(PF_2)_2$ ligand to give $[CH_3N(PF_2)_2]_3Fe$ containing two bidentate and one monodentate $CH_3N(PF_2)_2$ ligands.

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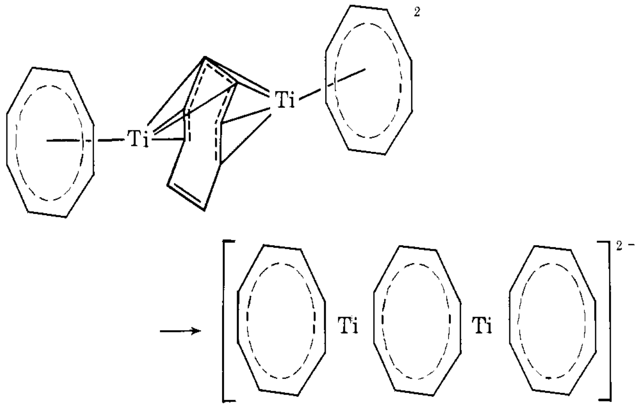
Triple Decker Sandwich Compounds: Paramegnetic Tris(cyclooctatetraene)dititanium and Its Dianion

Sir:

In connection with our interest in the reactions of titanium atoms, we prepared the previously described tris(cyclooctatetraene)dititanium[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 ^{1}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 μ_B as the magnetic moment, indicating two unpaired electrons.[4] Hoffmann and co-workers[2] 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)dititanium, 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)dititanium (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 ^{1}H NMR spectrum are all consistent with the formulation of this green anion as shown.[5] This appears to be the first instance 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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(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]
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Conformational Equilibrium of the 17(20) Rotamers of (*E*)-20(22)-Dehydrocholesterol

Sir:

We recently reported[1] 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