

$\pi_2 \rightarrow \pi_5^*$  at 273 nm ( $f = 0.29$ ), and  $\pi_1 \rightarrow \pi_5^*$  at 232 nm ( $f = 0$ ). These  $\lambda_{\max}$  values are in good agreement with the observed spectrum of hexaphenylpentalene<sup>6</sup> ( $\lambda_1$  720 nm ( $\log \epsilon$  1.95),  $\lambda_2$  380 nm ( $\log \epsilon$  3.99), and  $\lambda_3$  310 nm ( $\log \epsilon$  4.52)) if one assumes that the presence of the phenyl groups shifts each peak to lower energy by  $\sim 50$  nm. The calculated positions and intensities for the first two transitions agree well with those observed<sup>7</sup> for methylpentalene, which has a broad, weak absorption at  $\sim 620$  nm and strong bands at 335 and 210 nm.<sup>14</sup> The strong band observed at  $\sim 210$  nm<sup>7</sup> cannot be due to the forbidden  $\pi_1 \rightarrow \pi_5^*$  transition, and may well correspond to the allowed ( $f \sim 1$ )  $\pi_4 \rightarrow \pi_6^*$  excitation predicted at 149 nm.

One of the interesting features predicted for pentalene is the relatively small energy difference of  $\sim 24$  kcal mol<sup>-1</sup> between the ground state and the lowest  $\pi$ - $\pi^*$  triplet (both in their optimum geometries). Further, the equilibrium geometry of this triplet is predicted to be of  $D_{2h}$  symmetry, with calculated bond lengths of 1.412, 1.407, and 1.467 Å for the C<sub>1</sub>-C<sub>2</sub>, C<sub>2</sub>-C<sub>3</sub>, and C<sub>1</sub>-C<sub>5</sub> linkages. Thus the lowest triplet is well represented by the symmetrical cyclooctatetraene structure **1c**.

(14) There is some uncertainty as to whether the 285-nm band is due to methylpentalene or to its dimer.<sup>7</sup>

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### Synthesis and Crystallographic Characterization of [Me<sub>4</sub>N<sup>+</sup>]<sub>2</sub>[Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>], a Hexanuclear Carbido-carbonyl Derivative of Iron

Sir:

Hexanuclear metal carbonyl species are known for elements of the cobalt triad (Co,<sup>1</sup> Rh,<sup>2</sup> Ir<sup>3</sup>) and for ruthenium,<sup>4,5</sup> but not for other transition metals. We now report the synthesis and characterization, by X-ray diffraction techniques, of a hexanuclear carbido-carbonyl derivative of iron, [Me<sub>4</sub>N<sup>+</sup>]<sub>2</sub>[Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>].

The reaction of Fe(CO)<sub>5</sub> with [Mn(CO)<sub>5</sub><sup>-</sup>] in diglyme has previously<sup>6</sup> been shown to yield the trinuclear "mixed-metal" anion, [MnFe<sub>2</sub>(CO)<sub>12</sub><sup>-</sup>]. However, a reinvestigation of this system reveals that [Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>] is also formed in the reaction mixture and that the relative yields of the two anions are critically dependent on reaction conditions.

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A solution of NaMn(CO)<sub>5</sub>, obtained by the sodium amalgam reduction of Mn<sub>2</sub>(CO)<sub>10</sub> (2 g) in dry diglyme (50 ml), was added to Fe(CO)<sub>5</sub> (4 ml) and the mixture was refluxed for 1 hr. A deep blue solution (characteristic of [MnFe<sub>2</sub>(CO)<sub>12</sub><sup>-</sup>]) was obtained after 5 min, but after 40 min the color of the solution had changed to red-brown. After cooling, the reaction mixture was added to water and the filtered aqueous solution was treated with an excess of Me<sub>4</sub>NCl, yielding a red precipitate. This was dissolved in methanol; red-black crystals (2.5 g) of [Me<sub>4</sub>N<sup>+</sup>]<sub>2</sub>[Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>] were obtained after partial evaporation of the solution by a stream of N<sub>2</sub>. The [Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>] ion was also obtained by heating [Et<sub>4</sub>N<sup>+</sup>][MnFe<sub>2</sub>(CO)<sub>12</sub><sup>-</sup>] in diglyme at 160°, thus indicating it to be a direct decomposition product of the mixed-metal anion.

The [Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>] ion exhibits only four bands in the carbonyl stretching region: 1964 (s), 1957 (sh), 1930 (sh), 1775 (w, br) cm<sup>-1</sup> (THF solution) or 1956 (sh), 1944 (s), 1925 (sh), 1750 (w, br) cm<sup>-1</sup> (Nujol mull).

An X-ray crystallographic study of [Me<sub>4</sub>N<sup>+</sup>]<sub>2</sub>[Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>] was undertaken in order to establish unequivocally the stereochemistry of the anion.

The compound crystallizes in the centrosymmetric orthorhombic space group  $Pnma$  ( $D_{2h}^{16}$ ; no. 62) with  $a = 10.10$ ,  $b = 18.79$ ,  $c = 36.71$  Å,  $V = 6961$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.891$  g cm<sup>-3</sup> for mol wt 987.69 and  $Z = 8$ ,  $\rho_{\text{obsd}} = 1.82$  (2) g cm<sup>-3</sup> (floatation in bromoform-hexane). No symmetry is necessarily imposed on the anion (however, *vide infra*).

Intensity data ( $\sin \theta_{\max} = 0.34$ , Mo K $\alpha$  radiation) for the levels  $h(0-18)l$  and  $(0-6)kl$  were collected with a Supper-Pace automated diffractometer, corrected for Lorentz, polarization, and absorption ( $\mu = 24.38$  cm<sup>-1</sup>) effects, and merged to a common scale. The structure was solved by Patterson, Fourier, and least-squares refinement techniques (anisotropic thermal parameters for iron atoms, isotropic for all other atoms). The final discrepancy index is  $R_F = 11.9\%$  for the 1584 independent, nonzero reflections.<sup>8</sup>

The unit cell contains two sets of [Me<sub>4</sub>N<sup>+</sup>] ions (each in a general position) and two sets of [Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>] ions (each in special position 4c, and centered at 0.27,  $1/4$ , 0.13 and 0.23,  $1/4$ , 0.63). The two anions thus each have crystallographically imposed  $C_s(m)$  symmetry and are geometrically equivalent. Dimensions referred to below are the mean of values within the two crystallographically independent dianions.

The essential geometry of the [Fe<sub>6</sub>(CO)<sub>16</sub>C<sup>2-</sup>] dianion is shown in Figure 1. There are 13 terminal carbonyl ligands; two per iron atom except for Fe(4), which is associated with three. (Fe(4) is also the only iron atom not to participate in a bridging carbonyl system.) There are three carbonyl bridges: Fe(5)-[C(1)-O(1)]-Fe(1) and the symmetry-related Fe(5)-[C(1')-O(1')]-Fe(1'), in which Fe(1)-C(1) = 1.79 (5) and Fe(5)-C(1) = 2.19 (5) Å; and the system Fe(2)-[C(5)-O(5)]-Fe(3), lying in the mirror plane of the dianion, in which Fe(2)-C(5) = 1.94 (6) and Fe(3)-C(5) = 2.16 (6) Å. Dimensions within these carbonyl

(7) *Anal.* Calcd for C<sub>25</sub>H<sub>24</sub>Fe<sub>6</sub>N<sub>2</sub>O<sub>16</sub>: C, 31.7; H, 2.5; Fe, 35.5; N, 3.0. Found: C, 31.6; H, 2.7; Fe, 35.5; N, 3.2.

(8) The relatively high discrepancy index and low percentage of non-zero (*i.e.*,  $>3\sigma$ ) reflections result from (i) the poor quality of obtainable crystals, (ii) decomposition of crystals within the X-ray beam.

bridges are essentially in agreement with values found for the three asymmetric basal carbonyl bridges in the  $[\text{Fe}_6(\text{CO})_{13}^{2-}]$  dianion ( $\text{Fe}-\text{C} = 1.82$  and  $2.28 \text{ \AA}$ ).<sup>9</sup>

The central carbon atom is, within the limits of experimental error, equidistant from the six iron atoms, individual distances being  $\text{Fe}(1)-\text{C}(11) = \text{Fe}(1')-\text{C}(11) = 1.89$  (4),  $\text{Fe}(2)-\text{C}(11) = 1.97$  (4),  $\text{Fe}(3)-\text{C}(11) = 1.93$  (4),  $\text{Fe}(4)-\text{C}(11) = 1.84$  (4), and  $\text{Fe}(5)-\text{C}(11) = 1.82$  (4)  $\text{ \AA}$ .

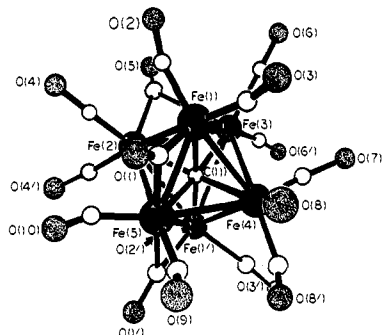


Figure 1. Stereochemistry of the  $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$  ion. Note that the terminal carbonyl group defined by  $\text{C}(2')-\text{O}(2')$ , which is linked to  $\text{Fe}(1')$ , is hidden beneath  $\text{Fe}(5)$ . The anion has a mirror plane passing through  $\text{Fe}(2)$ ,  $\text{Fe}(3)$ ,  $\text{Fe}(4)$ , and  $\text{Fe}(5)$ . Individual iron-iron distances within the two crystallographically independent units are:  $\text{Fe}(1)-\text{Fe}(2)$ , 2.706 (9) and 2.688 (9);  $\text{Fe}(1)-\text{Fe}(3)$ , 2.682 (9) and 2.695 (9);  $\text{Fe}(1)-\text{Fe}(4)$ , 2.699 (9) and 2.654 (9);  $\text{Fe}(1)-\text{Fe}(5)$ , 2.632 (10) and 2.621 (9);  $\text{Fe}(2)-\text{Fe}(3)$ , 2.609 (10) and 2.553 (10);  $\text{Fe}(3)-\text{Fe}(4)$ , 2.743 (10) and 2.729 (10);  $\text{Fe}(4)-\text{Fe}(5)$ , 2.682 (11) and 2.646 (10);  $\text{Fe}(5)-\text{Fe}(2)$ , 2.662 (11) and 2.725 (10)  $\text{ \AA}$ .

The only previously known iron carbonyl carbide species is  $\text{Fe}_5(\text{CO})_{15}\text{C}$ .<sup>10</sup> As with this former compound,  $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$  exhibits considerable thermal stability and also a degree of stability toward aerobic oxidation (the solid is only partially decomposed after exposure to air for 3 days) not shared by the simple iron carbonyl anions.

The  $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$  anion is evidently closely related to the only other known molecular carbides,  $\text{Ru}_6(\text{CO})_{17}\text{C}^{4a,c}$  and  $\text{Ru}_6(\text{CO})_{14}\text{C}(\text{arene})$ ,<sup>4a,b</sup> but it is the first known *anionic* carbidocarbonyl complex of any metal. Its high stability suggests that it may be possible to prepare an extended range of carbidocarbonyl complexes, and we may predict the series  $\text{Fe}_6(\text{CO})_{17}\text{C}$ ,  $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$ ,  $[\text{Fe}_6(\text{CO})_{15}\text{C}^{4-}]$  by analogy with the known series<sup>1</sup> based on  $\text{Co}_6(\text{CO})_{16}$ . Acidification of  $[\text{Fe}_6(\text{CO})_{16}^{2-}]$  does, in fact, yield a black crystalline complex which is soluble in petroleum ether ( $30-60^\circ$ ) and is almost certainly a neutral carbidocarbonyl [ir  $\nu_{\text{CO}}$  2050 (s), 2032 (s), 2011 (m), 1989 (m)  $\text{cm}^{-1}$  (*n*-hexane solution) or 2096 (sh), 2065 (sh), 2030 (s), 2001 (m), 1988 (m), 1960 (sh), 1834 (m)  $\text{cm}^{-1}$  (KBr disk)].

The crystal structure of this neutral species, as well as further reactions of the  $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$  dianion, is currently under investigation in these laboratories.

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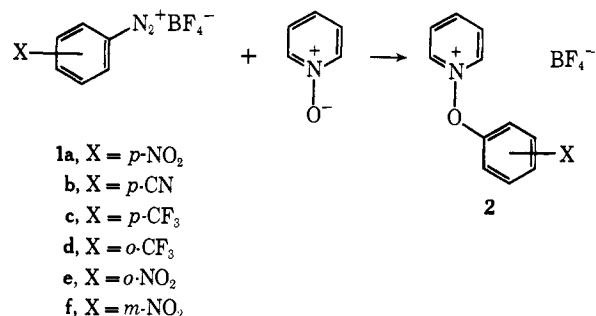
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## *N*-Aryloxy pyridinium Salts and Their Base-Catalyzed Rearrangement

Sir:

The chemistry of *N*-alkoxy pyridinium salts is well documented.<sup>1</sup> In contrast, the *N*-aryloxy compounds are not known. We now report a convenient one-step synthesis of such compounds and a novel molecular rearrangement which they undergo.

The diazonium tetrafluoroborate (1) of an aromatic amine bearing an electron-withdrawing substituent is added to a solution of pyridine 1-oxide in acetonitrile and the solution is either stirred at room temperature for 24 hr or warmed gently. The product, 2, usually precipitates and more is recovered by evaporation of the solvent. Yields are in the range 24-70%.



The structures of the products 2 were established by spectroscopic methods and microanalysis, as illustrated for *N*-*p*-nitrophenoxypyridinium tetrafluoroborate (2a): mp 157.5-159°; ir 1390, 1090  $\text{cm}^{-1}$  ( $\text{BF}_4^-$ );<sup>2</sup>  $\lambda_{\text{max}}$  260 nm;  $\epsilon$  14,000; nmr [acetone-*d*<sub>6</sub>]  $\delta$  9.65 (2 H, d,  $J_{2,3} = J_{5,6} = 6$  Hz, H-2,6), 9.00 (1 H, t,  $J_{3,4} = J_{4,5} = 7$  Hz, H-4), 8.56 (2 H, d of d, H-3,5), 8.39 (2 H, d,  $J_{\text{ortho}} = 9$  Hz, phenyl meta hydrogens), and 7.50 (2 H, d,  $J_{\text{ortho}} = 9$  Hz, phenyl ortho hydrogens); mass spectrum  $m/e$  216 ( $\text{M}^+$ ), 186 ( $\text{M}^+ - \text{NO}$ ), 170 ( $\text{M}^+ - \text{NO}_2$ ), 139 ( $\text{NO}_2\text{C}_6\text{H}_4\text{OH}^+$ ), 79 ( $\text{C}_5\text{H}_5\text{N}^+$ , base peak). *Anal.* Calcd for  $\text{C}_{11}\text{H}_9\text{BF}_4\text{N}_2\text{O}$ : C, 43.46; H, 2.98; F, 24.99; N, 9.22. Found: C, 43.35; H, 3.09; F, 24.66; N, 9.31. 2b (X = *p*-CN), mp 214-215°, 2c (X = *p*-CF<sub>3</sub>), mp 135-136°, 2d (X = *o*-CF<sub>3</sub>), mp 169-170°, 2e (X = *o*-NO<sub>2</sub>), mp 161-162°, and 2f (X = *m*-NO<sub>2</sub>), mp 148-149°, were similarly prepared and characterized. If X is not electron withdrawing then the only products are those formed by the attack of the phenyl cation upon acetonitrile to give a nitrilium salt

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