Isolation of a Tetranuclear Iron Cluster Promoting CO₂ Reduction and Intermediate to Iron Carbonyl Disproportionation

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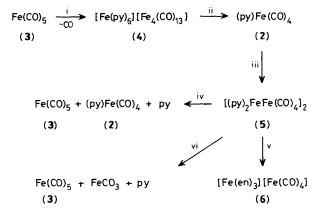
 $(py)Fe(CO)_4$ (py = pyridine) is formed on carbonylation of $[Fe(py)_6][Fe_4(CO)_{13}]$, and the 56 electron tetranuclear cluster $[(py)_2FeFe(CO)_4]_2$, the crystal structure of which has been determined, is produced on dissolving $(py)Fe(CO)_4$ in organic solvents; it behaves as a bifunctional molecule in reducing CO₂ to CO, FeCO₃ being formed during this reaction.

In their catalytic applications, metal carbonyls act as precursors to electronically and co-ordinatively unsaturated intermediates, able to activate simple molecules and organic substrates. In the case of $Co_2(CO)_8$ (1), the substitution of CO groups by Lewis bases brings about the formation of such active intermediates when not too large an excess of base is employed.^{1,2} In order to ascertain whether similar pathways can be followed by other metal carbonyls, we investigated the chemistry of (py)Fe(CO)₄ (2) (py = pyridine), the product of the photochemical substitution of CO by pyridine in Fe(CO)₅ (3).[†]

We have now found that amounts of (2) (30% yield) sufficient for our study can be obtained by recarbonylating [in tetrahydrofuran (THF) at room temperature and atmospheric

pressure] $[Fe(py)_6][Fe_4(CO)_{13}]$ (4),³ formed on refluxing (3) in pyridine (Scheme 1). Complex (2) is indefinitely stable in the solid state; in organic solvents, however, it slowly decomposes at room temperature. In n-hexane, toluene, and diethyl ether the decomposition is apparent from solid formation, while in THF the original orange colour gradually darkens. In toluene the decomposition is complete in two days at 38 °C, pyridine, (3), and a maroon crystalline solid being the products. Analysis of the precipitate and quantitative determination of pyridine and (3) in the mother liquor indicate the stoicheiometry shown in equation (1). I.r. spectra of the solid product in Nujol mull or in THF solutions are quite similar in the 1600-2200 cm⁻¹ region, the four observed bands being attributed to iron-co-ordinated pyridine (1606 cm^{-1}) and to CO groups (1968s, 1909s, and 1890s cm^{-1} in THF solution). In order to elucidate the nature of the solid substance we attempted to grow a single crystal suitable for an X-ray analysis. The best results were obtained by slow diffusion of diethyl ether into a THF solution of the product. In spite of

[†] This method of preparation was reported to give poor yields of the product, isolated in 100 mg quantities. E. H. Shubert and R. K. Sheline, *Inorg. Chem.*, 1966, **5**, 1071.



Scheme 1. Reagents: i, py, reflux; ii, THF, 4 days, CO (1 atm), 28 °C; iii, toluene, 40 °C; iv, THF, CO; v, en; vi, THF, CO₂.

several attempts, the crystals were small and of poor quality; nevertheless, the results of the structure determination‡ are sufficient to show the main structural features of the compound as shown in Figure 1. The molecule has an approximate D_2 symmetry and consists of a tetranuclear iron cluster $[(py)_2FeFe(CO)_4]_2$ (5) with four Fe atoms at the vertices of a rhomb with an edge of 2.55 Å (average of the eight values from the two independent molecules in the asymmetric unit; Fe-Fe separation in the range 2.53—2.59 Å). The two opposite Fe atoms on the shortest diagonal (2.76 Å) are each linked to two pyridine groups in a distorted tetrahedral co-ordination, whereas the other two Fe atoms are linked to four carbonyl groups in a distorted octahedron.

$$3(py)Fe(CO)_4 \rightarrow 2 Fe(CO)_5 + 2 py + '(py)Fe(CO)_2'$$
 (1)
(2) (3)

Cluster (5) behaves chemically as if it were a tetracarbonylferrate of Fe^{2+} in a homonuclear ion pair (HNIP)¹ arrangement (Scheme 1). Thus the addition of stoicheiometric amounts of ethylenediamine (en) to THF solutions of (5) at room temperature brings about the instantaneous formation of a colourless precipitate of $[Fe(en)_3][Fe(CO)_4]^4$ (6). On the other hand, (5) in THF solution reacts promptly with CO at atmospheric pressure to give (2) and (3) in a 1:1 ratio. On these grounds, (5) behaves as an intermediate in the base-

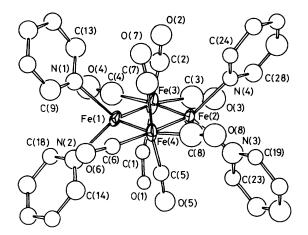


Figure 1. The molecular structure of (5). Bond angles: Fe(3)-Fe(1)-Fe(4) and Fe(3)-Fe(2)-Fe(4) 114.2, Fe(1)-Fe(3)-Fe(2) and Fe(1)-Fe(4)-Fe(2) 65.8 (± 0.5)° (averaged values from two independent molecules). Shortest diagonal $Fe(1) \cdots Fe(2)$ 2.76 (± 0.02) Å. Average Fe–N bond length 2.16 (± 0.03) Å.

promoted disproportionation of (3). This chemical behaviour is similar to that of the $\text{Co}^{2+}\text{Co}(\text{CO})_{4}^{-}$ HNIP² which is converted by excess pyridine into separate ions, and by CO into neutral carbonyls of formula $\text{Co}_2(\text{CO})_{8-n}(\text{py})_n$.

Complex (5) reacts with CO₂ in THF solution at room temperature yielding pyridine, (3), and FeCO₃ (Scheme 1). ¹³COFe(CO)₄ (m/z 197) is formed upon reaction with ¹³CO₂, thus confirming that CO₂ is reduced by (5) to Fe-co-ordinated CO. The reaction is similar to that of Na₂Fe(CO)₄⁵ which is converted by CO₂ into Na₂CO₃ and (3), and this analogy further supports our view of (5) as a tetracarbonylferrate of Fe²⁺. We note, however, that in our case CO₂ reduction has been achieved without the intervention of external reducing agents such as alkali metals. Correspondingly FeCO₃ rather than Na₂CO₃ constitutes the oxygen atom sink: the problem of a cyclic CO₂ reduction to CO should be solved by reducing FeCO₃ to (3) under CO.

These findings confirm that the substitution of CO groups by bases in a metal carbonyl can result in the formation of electronically and co-ordinatively unsaturated species. These can be described as HNIPs between the ions formed during their base-promoted disproportionation reaction. A better understanding of known catalytic processes and designing of new ones requires this aspect of metal carbonyl chemistry to be taken into account.

We thank Professor F. Calderazzo for helpful discussions and the Ministero della Pubblica Istruzione, Roma, for financial support.

Received, 12th June 1986; Com. 806

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 $[\]ddagger$ Crystal data: C₂₈H₂₀Fe₄N₄O₄, $M_r = 744$, monoclinic, space group $P2_1/a, a = 21.511(3), b = 16.766(3), c = 19.253(3)$ Å, $\beta = 117.94(2)^\circ$, $U = 6134.3 \text{ Å}^3$, $D_c = 1.611 \text{ g cm}^{-3}$, Z = 8. Data were collected on a Philips PW 1100 diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71069$ Å). A total of 1018 reflections [$I > 2\sigma(I)$] out of 6204 were used. The structure was solved by Patterson and direct methods, and refined by full matrix least squares with SHELX-76.6 Owing to the unfavourable observation-to-parameter ratio some problems of instability during the refinement arose both for atomic co-ordinates and thermal parameters. To avoid unreasonable shifts in atomic co-ordinates leading to unrealistic bond distances, the pyridine groups were constrained to perfect hexagons (edge length = 1.395 Å), the Fe-C bond lengths were fixed at 1.85 Å, and the C-O distance in the carbonyl groups was assumed to be 1.15 Å. Anisotropic thermal parameters were refined only for the Fe atoms; with these assumptions, the refinement converged to an R value of 0.070 for 297 parameters. The asymmetric unit consists of two molecules which after refinement exhibit equal (in the limit of the standard deviation) distances and angles between corresponding atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.