

## Isolation of a Tetranuclear Iron Cluster Promoting CO<sub>2</sub> Reduction and Intermediate to Iron Carbonyl Disproportionation

Giuseppe Fachinetti,<sup>\*a</sup> Giovanni Fochi,<sup>a</sup> Tiziana Funaioli,<sup>a</sup> and Pier Francesco Zanazzi<sup>b</sup>

<sup>a</sup> Dipartimento di Chimica e Chimica Industriale dell'Università di Pisa, via Risorgimento, 35, I-56100 Pisa, Italy

<sup>b</sup> Dipartimento di Scienze della Terra dell'Università di Perugia, piazza dell'Università, I-06100 Perugia, Italy

(py)Fe(CO)<sub>4</sub> (py = pyridine) is formed on carbonylation of [Fe(py)<sub>6</sub>][Fe<sub>4</sub>(CO)<sub>13</sub>], and the 56 electron tetranuclear cluster [(py)<sub>2</sub>FeFe(CO)<sub>4</sub>]<sub>2</sub>, the crystal structure of which has been determined, is produced on dissolving (py)Fe(CO)<sub>4</sub> in organic solvents; it behaves as a bifunctional molecule in reducing CO<sub>2</sub> to CO, FeCO<sub>3</sub> 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<sub>2</sub>(CO)<sub>8</sub> (**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.<sup>1,2</sup> In order to ascertain whether similar pathways can be followed by other metal carbonyls, we investigated the chemistry of (py)Fe(CO)<sub>4</sub> (**2**) (py = pyridine), the product of the photochemical substitution of CO by pyridine in Fe(CO)<sub>5</sub> (**3**).<sup>†</sup>

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)<sub>6</sub>][Fe<sub>4</sub>(CO)<sub>13</sub>] (**4**),<sup>3</sup> 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 stoichiometry 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<sup>-1</sup> region, the four observed bands being attributed to iron-co-ordinated pyridine (1606 cm<sup>-1</sup>) and to CO groups (1968s, 1909s, and 1890s cm<sup>-1</sup> 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

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

