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Preliminary communication

On the nature of Brune's complex

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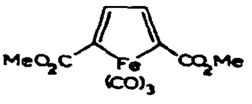
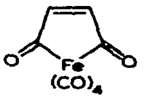
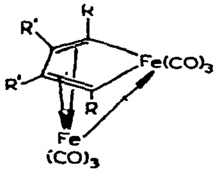
In 1962 Brune and coworkers[1] described an unusual complex which they formulated as (I), containing an uncomplexed ferrole moiety, in which the iron atom is electron-deficient. This complex would be the sole example of this interesting heterocyclic system, although other five-membered rings containing iron, with a lower degree of unsaturation, are known, *e.g.*, the fluorinated compounds $C_4F_6Fe(CO)_4$ [2] and $C_4F_8Fe(CO)_4$ [3], and the diketo complex (II)[4]. On the other hand, many examples of ferroles stabilised by bonding to a second $Fe(CO)_3$ group (III) are known.



(I)

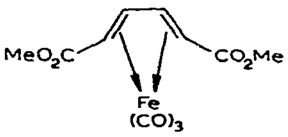


(II)

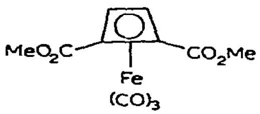


(III)

We have re-examined complex (I), with a view to discovering more about its ring system. In analysing our results we have taken account of two additional possible structures, *viz.* the butadiene–$Fe(CO)_3$ (IV) and the cyclobutadiene–$Fe(CO)_3$ (V).



(IV)



(V)

The Brune complex was readily synthesised from the anion $[Fe(CO)_4]^{2-}$ (obtained by stirring $Fe(CO)_5$ with sodium amalgam for 2 h) and dimethyl dichloromuconate. Chromatography on Florisil gave fractions similar to those described in the original communication[1], and the complex was finally purified by sublimation (90–100°/0.1 mm), to give a bright orange-yellow solid, m.p. 56–58° (lit.[1] 57°). The infrared spectrum showed bands at 2084m, 2052vs, 2022vs, 2009vs, and 1972w cm^{-1} in the terminal carbonyl stretching region, and ν(acyl CO) appeared at 1722 cm^{-1}. The proton NMR spectrum (C_6F_6) showed resonances at τ 3.36s (β-CH; lit.[1] τ 3.46) and 6.18s (CH_3).

Clearly, the ν(CO) region of the spectrum contains more bands than expected for a simple $Fe(CO)_3$ group, and the spectrum resembles that found for complexes of type (III). The presence of an $Fe_2(CO)_6$ group was also suggested by the mass spectrum, the highest ion being at *m/e* 448, with other ions arising by successive loss of carbonyl groups at *m/e* 420, 392, 364, 336, 308, and 280. All these ions were the most intense of clusters with an isotope pattern corresponding to the presence of two iron atoms. Finally, analysis confirmed the formula $C_4H_2(CO_2Me)_2Fe_2(CO)_6$ (Found: C, 37.3; H, 1.69. $C_{14}H_8Fe_2O_{10}$. Calcd.: C, 37.4; H, 1.78; mol. wt. 448. $C_{11}H_8FeO_7$ (I) calcd.: C, 42.84; H, 2.60%; mol. wt., 308).

We therefore conclude that the complex obtained by Brune and his coworkers must be reformulated as (III, R = CO_2Me, R' = H). The remote possibility of rearrangement to the isomeric complex (III; R = OCOMe, R' = H) was eliminated by comparison with an authentic sample[5].

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