Synthesis and X-Ray Structure of Tri-μ-carbonyl-bis-(1,2-diphenyl-3,4-di-t-butylcyclobutadiene)di-iron

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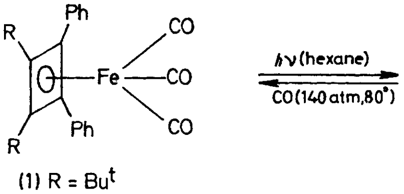
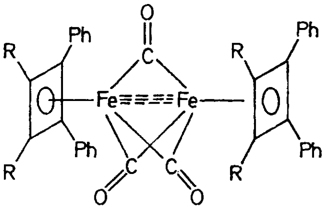
Summary Irradiation of 1,2-diphenyl-3,4-di-t-butylcyclobutadienetricarbonyliron (**1**) gives the new complex, $(C_{24}H_{28})_2Fe_2(CO)_3$ which, from *X*-ray data, appears to contain an iron–iron triple bond [Fe–Fe= 2·177(3) Å].

Only few examples are currently available of the photoreactions of iron complexes of cyclobutadiene.[1] We now describe a new photo-dimeric cyclobutadiene iron complex which appears to contain an iron–iron triple bond.



(1) R = Bu^t
(2) R = Ph



(3) R = Bu^t
(4) R = Ph

Irradiation of a solution of complex (**1**)[2] in hexane followed by quick preparative t.l.c. (silica gel) under argon afforded violet crystals of $(C_{24}H_{28})_2Fe_2(CO)_3$ (**3**),† m.p. 204—205° (decomp.), moderately air stable in the solid state, but unstable in solution. The i.r. spectrum shows bridging CO stretching bands at 1837 and 1830 cm^{-1}. The n.m.r. spectrum showed a similar absorption pattern to that of (**1**), but to slightly lower field [δ 1·35 (t,18H, Bu^t) and 7·13 (m, 10H, Ph). Treatment of complex (**3**) with CO (140 atm) at 80° led to complex (**1**) quantitatively.

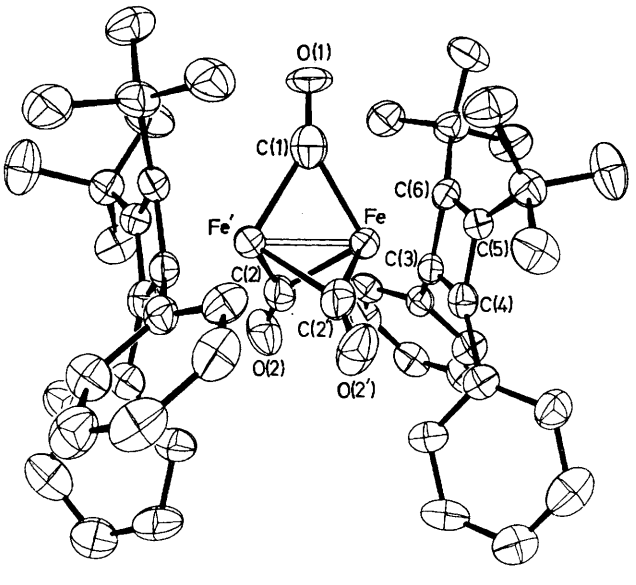


Figure. Molecular structure of tri-μ-carbonyl-bis-(1,2-diphenyl-3,4-di-t-butylcyclobutadiene)di-iron with thermal ellipsoids at 50% probability level.

The analogous photoreaction of complex (**2**)[3] gave dark violet crystals of (**4**), $(C_{28}H_{20})_2Fe_2(CO)_3$ (**4**),† m.p. 132—134° (decomp.), i.r. 1858 and 1849 cm^{-1}, which could be similarly converted into (**2**) on treatment with CO.

The crystal structure of (**3**) was determined by *X*-ray diffraction. *Crystal data:* $C_{51}H_{56}Fe_2O_3$, M = 828·7, tetragonal, $a = b$ = 15·093(5), c = 18·641(4) Å, U = 4246·5(3·1) Å,[3] D_m = 1·305 g cm^{-3} (by flotation), Z = 4, D_c = 1·296 g cm^{-3}, space group $I\bar{4}$; Cu-K_α radiation. 1514 intensity data were collected on a Rigaku automated four-circle

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† Satisfactory elemental analyses were obtained.

diffractometer [(sin θ)/$\lambda \leqslant$ 0·532]. The structure was determined by the heavy atom method and refined by block-diagonal least-squares assuming anisotropic temperature factors for non-hydrogen atoms. Anomalous dispersion of the iron atom was taken into account (for Cu-K_α; $\Delta f' = -1{\cdot}1$, $\Delta f'' = 3{\cdot}4$). The final R value is 0·061 for 1484 non-zero reflections.

The dimeric molecule is located on the crystallographic two-fold axis passing through the centre of the Fe–Fe bond and a carbonyl group [C(1) = O(1)]. The two iron atoms are bridged by three carbonyl groups [average Fe–C(CO) = 1·974 Å]. The cyclobutadiene ring is essentially square-planar; the C–C (av. 1·468 Å) and Fe–C (ring) (av. 2·062 Å) distances agree well with those of $Ph_4C_4Fe(CO)_3$[4] (C–C av. 1·459 Å; Fe–C av. 2·067 Å).

The most remarkable feature is the extremely short Fe–Fe bond, 2·177(3) Å. This distance is much shorter than that in Fe_2CO_9 (2·523 Å[5]) and even shorter than that in $(Bu^tC{\equiv}CBu^t)_2Fe_2(CO)_4$ (2·215 Å), which is the only known example of an Fe–Fe double bond.[6] The effective atomic number rule at its simplest level would suggest that $(C_{24}H_{28})_2Fe_2(CO)_3$ should be formulated as in (**3**) in which each iron atom accepts four electrons from a cyclobutadiene group, one electron from each of three carbonyls, and shares three electron pairs with the other iron. This is consistent with the diamagnetic behaviour and the extremely short Fe–Fe distance of the complex.

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