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Preliminary communication

NOVEL INTRAMOLECULAR REARRANGEMENTS IN A TRINUCLEAR IRON COMPLEX DERIVED FROM A PHOSPHINOACETYLENE

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Summary

An X-ray structural study of the trinuclear complex $Fe_3(CO)_7[Ph_2PC_4(CF_3)_2PPh_2$ (I) has shown that the conversion of another trinuclear complex $Fe_3(CO)_8$-$[Ph_2PC_4(CF_3)_2]PPh_2$ (II) to (I) involves intramolecular CO elimination, metal—metal bond formation and novel structural changes in a diphenylphosphide bridge.

Although the formation of metal—metal bonds is a recurring feature in organometallic chemistry, there are relatively few examples where intramolecular expulsion of a coordinated ligand results in the synthesis of a 2-electron metal—metal bond***.

Compound II, one of several products from the reaction of $Fe_3(CO)_{12}$ with $Ph_2PC{\equiv}CCF_3$ [3] was refluxed in petroleum ether (80—100°) for 1 h and the reaction mixture chromatographed on alumina. Apart from unchanged starting material the major product was a red complex analysing as $Fe_3(CO)_x(Ph_2PC_2CF_3)_2$ (x = 7—8). The infrared spectrum [ν(CO) (CS_2) 2078s, 2055w, 2022s, 2005m, 1997s, 1953m, 1938w] contained ν(CO) bands at lower frequency than for II. Hence substitution of one or more CO groups in II seemed likely. A full single crystal X-ray structure determination was carried out to establish the nature of the rearrangement process.

Crystal data: $Fe_3(CO)_7[Ph_2PC_4(CF_3)_2]PPh_2$, monoclinic crystals, space group $P2_1/c$, a 12.325(4), b 21.075(4), c 19.701(9) Å, β 133.54(1)°, Z = 4; ρ_c 1.647 g cm^{-3}, ρ_m (flotation) 1.64(1) g cm^{-3}. The structure was solved by the

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***Some interesting instances of this type of behaviour in binuclear complexes have recently come to light [1—3], but no structural data is available. The compound η-$C_5H_5Fe(CO)_2COCH{=}CHPhFe(CO)_4$ can be thermally converted into the complex η-$C_5H_5Fe(CO)(\mu$-$CO)CO{=}CHPhFe(CO)_3$ which contains a direct Fe—Fe bond [1]. Similarly η-$C_5H_5Fe(CO)_2(PPh_2)Fe(CO)_4$ yields the Fe—Fe bonded derivative η-$C_5H_5Fe(CO)(\mu$-$CO)(PPh_2)Fe(CO)_3$ on irradiation [2]. Irradiation of silicon-, germanium-, and tin-bridged metal carbonyls also yields binuclear species with transition metal—metal bonds via CO elimination [3].

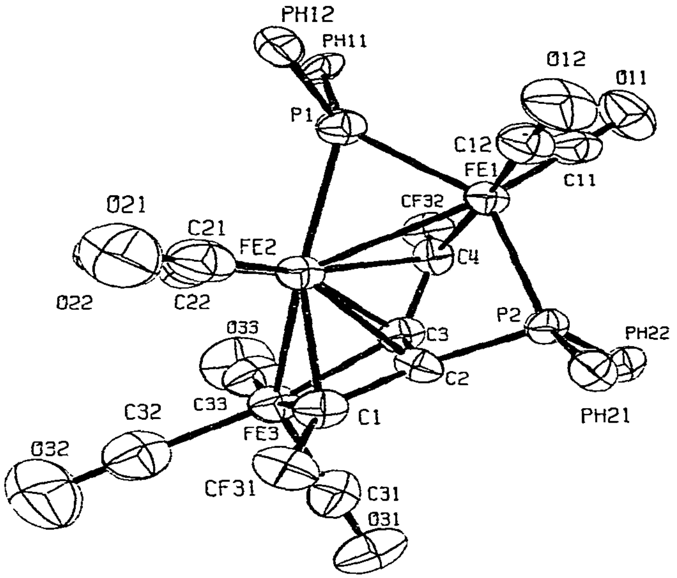

Fig. 1. A view of the molecular structure of $Fe_3(CO)_7[Ph_2PC_2(CF_3)_2](PPh_2)$ drawn by ORTEP.

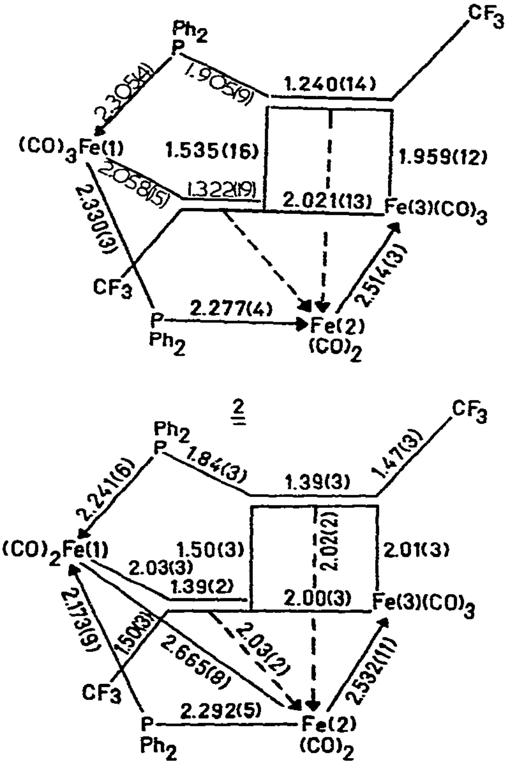

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Fig. 2. Structural changes accompanying the conversion of II to I and valence bond representations.

heavy atom method using 2925 observed reflections measured on a Hilger—Watts automatic diffractometer with graphite-monochromatised Mo-K_α radiation. Refinement by least-squares techniques using anisotropic thermal parameters has proceeded to an R value of 0.063. The molecular structure and atomic numbering are illustrated in Fig. 1. The principal structural features are the presence of a dimerised phosphinoacetylene in the form of a butadiene unit coordinated simultaneously to three iron atoms, a bridging diphenylphosphide group formed by cleavage of a P—C(*sp*) bond of one phosphinoacetylene and two iron—iron bonds of lengths Fe(1)—Fe(2) 2.665(8) Å and Fe(2)—Fe(3) 2.532(11) Å. Structural changes accompanying the conversion of II to I are shown in the valence bond representations 2 and 1 respectively (Fig. 2). In II the Fe(1)—Fe(2) distance of 4.59 Å precludes metal—metal bonding [4]. However, in I the corresponding distance is 2.665(8) Å indicating a strong interaction. Furthermore, the Fe(2)—P(1) distance of 2.292(5) Å in I is longer than the Fe(1)—P(1) bond length [2.173(9) Å] while the reverse is true for II. These trends reflect remarkably on the prediction of a 2-electron donor capacity for P(1) towards Fe(1) in I and a 1-electron donation to Fe(1) in II in order for all three iron atoms to achieve a krypton configuration. The marked decrease in the Fe(1)—P(1)—Fe(2) angle from 98.0(1)° in II to 73.3(2)° in I is also notable. Although these structural observations have not previously been noted, recent interest in the use of organometallic phosphines and arsines such as η-$C_5H_5Fe(CO)_2PPh_2$ [5] and η-$C_5H_5Fe(CO)_2AsMe_2$ [6] as precursors for phosphido- or arsenido-bridged binuclear complexes [2, 5, 6] suggests that the phenomenon may be of general significance.

The butadiene ligand is coordinated in π-diene fashion to Fe(2) and to Fe(1) and Fe(3), via σ-bonds to the terminal atoms C(2) and C(5). Iron—carbon distances to the organic ligand (see 1) and the carbonyl groups appear unexceptional for organoiron complexes.

It is clear that intramolecular elimination of a CO group requires little change in ligand geometry, but also implies considerable flexibility in the diphosphide bridge. Hence similar intramolecular rearrangements may be expected for other polynuclear complexes having non-bonded metal atoms bridged by Group V ligands of the type MR_2 (M = N, P, As).

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