Unusual Phosphinoacetylene–Iron Carbonyl Complex: Synthesis and *X*-Ray Structure of $[Fe_3(CO)_7\{Ph_2PC(CO_2Me)C(CF_3)C_2(CF_3)\}(PPh_2)]2C_6H_6$

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Summary Dodecacarbonyltri-iron reacts with 3,3,3-trifluoropropynyldiphenylphosphine to give a trinuclear iron(0) complex having the $Fe_3(CO)_{12}$ skeleton, a new type of delocalized 4-carbon chain, a bridging diphenylphosphido-ligand, and a methoxycarbonyl group derived from both the methanol used as a stabilizer for $[Fe_3(CO)_{12}]$ and a CO molecule.

The reactions of alkynes with metal carbonyls yield many interesting exotic complexes.[1] However, the mode of formation of organoiron derivatives from $[Fe_3(CO)_{12}]$ is not understood, since intermediates are especially reactive and difficult to isolate.[2] The reactions with phosphinoacetylenes could modify the oligomerization, permitting intermediates to be isolated. We find that the reaction of

$[Fe_3(CO)_{12}]$ with $Ph_2PC{\equiv}CCF_3$ yields a new type of organometallic compound, $[Fe_3(CO)_7\{Ph_2PC(CO_2Me)C(CF_3)C_2CF_3)\}(PPh_2)]2C_6H_6$, (I) containing a delocalized acyclic 4-carbon chain and a CO_2Me group presumably formed from a CO group and the methanol commonly used as a stabilizer for $[Fe_3(CO)_{12}]$.†

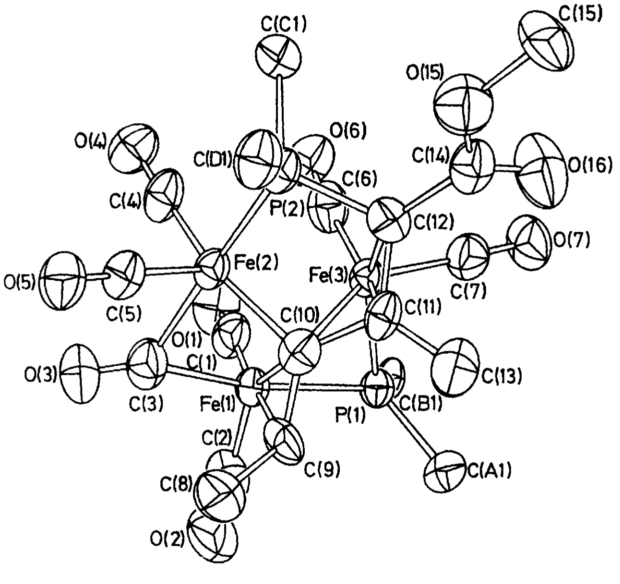

FIGURE. The $[Fe_3(CO)_7\{Ph_2PC_4(CF_3)_2\}(CO_2Me)(PPh_2)]$ molecule. The phenyl rings are shown only by the first atom of the ring [C(A1), C(B1), C(C1) and C(D1)] for clarity. The CF_3 groups are C(8) and C(13) but the fluorine atoms are not shown.

The reaction of $[Fe_3(CO)_{12}]$ with $Ph_2PC{\equiv}CCF_3$ provides several unusual trinuclear complexes.[3] Dark green crystals of the compound later shown to be (I) were obtained from the reaction mixture by chromatography on alumina (eluant ether–acetone) followed by recrystallization from benzene–cyclohexane. Microanalysis indicated a trinuclear formulation with two phosphorus atoms. The i.r. spectrum (mull) showed three groups of ν(CO) bands at 2059s, 2030s, 2019s, 2002s, 1989m; 1929m, 1909m; and 1739sh, 1729m cm^{-1}. An X-ray study was undertaken. *Crystal data:* $[Fe_3(CO)_7\{Ph_2PC(CO_2Me)C(CF_3)C_2(CF_3)\}(PPh_2)]2C_6H_6$, (I) triclinic, space group $P\bar{1}$, a = 10·319(8), b = 14·516(12), c = 17·944(9) Å; α = 90·13(5)°, β = 110·34(5)°, γ = 95·44(6)°, Z = 2; D_c = 1·504 g cm^{-3}, D_m (flotation) = 1·56 g cm^{-3}. The crystals appear to pick up solvent and the observed density increases with time. The intensity data were measured using a Syntex P$\bar{1}$ diffractometer with graphite-monochromatized MoK_α-radiation. The positions of the iron atoms were deduced from the Patterson function and the majority of the other atoms from subsequent Fourier syntheses. The presence of the CO_2Me group was unexpected. However, after three least-squares cycles using the full matrix and individual isotropic thermal parameters, the CO_2Me formulation was the only possibility consistent with the distances and thermal parameters. The two molecules of benzene of crystallization were found in the difference Fourier syntheses. The structure was refined using the block approximation and anisotropic thermal parameters to an R value of 0·067 for the 4396 reflections used in the analysis.

The structure and the atomic numbering are illustrated in the Figure. The two acetylenes have dimerized into the open chain C(9)–C(10)–C(11)–C(12), C(8) and C(13) being CF_3 groups. The distances C(9)–C(10), C(10)–C(11), and C(11)–C(12) are all *ca.* 1·433(11) Å, which suggests delocalization over that portion of the molecule. The C(9)–Fe(1) and C(10)–Fe(2) distances of 2·061(9) and 1·978(9) Å respectively, together with an electron count indicate that C(9) and C(10) are bonded to Fe(1) and Fe(2) *via* predominantly σ-type bonds. For comparison, the six Fe–C (of CO terminal) distances average 1·768 Å. The Fe(3)–C(11) and Fe(3)–C(12) bond lengths of 2·039(9) and 2·077(9) Å are much shorter than the Fe(3)–C(10) bond length of 2·205(8) Å which suggests that either the chain is bonded to Fe(3) *via* two weak σ-bonds or an asymmetrical π-alkyl type linkage.

There is a remarkable resemblance between the $Fe_3(CO)_7$ skeleton to that of $[Fe_3(CO)_{12}]$[4] and related complexes.[5,6] The Fe(1)–Fe(3) and Fe(2)–Fe(3) distances of 2·683(2) and 2·679(2) Å are comparable to the iron–iron distances in $[Fe_3(CO)_{12}]$,[4] both isomers A and B of $[Fe_3(CO)_{11}PPh_3]$,[5] and $[Fe_3(CO)_9(PhPMe_2)_3]$.[6] Also the CO-bridged Fe(1)–Fe(2) bond of 2·543(2) Å is asymmetrical, Fe(1)–C(3) is 1·874(9) Å, and Fe(2)–C(3) is 2·166(10) Å, similar to the corresponding asymmetrical CO-bridged bonds in $[Fe_3(CO)_{12}]$[4] and $[Fe_3(CO)_{11}PPh_3]$.[5]

Another unusual feature is the CO_2Me group attached to C(12). The only reasonable source is the methanol stabilizer present in $Fe_3(CO)_{12}$ since no solvents containing a methoxy-group were used in either the synthesis or purification of the complex. A CO_2Me group could arise either by attack of a methoxide ion on a co-ordinated carbonyl or by insertion of a CO group into the C(12)–OMe bond. Although we know of no other examples of methoxide incorporation into organoiron compounds, the presence of CO_2Me groups may not have been recognized since ν(CO) for this group is very close to that characteristic of bridging carbonyls.

The presence of the bridging phosphido-group between Fe(1) and Fe(3) implies a cleavage of the P(1)–C(10) bond. The isolation of a disubstituted phosphine derivative $[Fe_3(CO)_{10}(Ph_2PC{\equiv}CCF_3)_2]$ and the close relationship to $[Fe_3(CO)_{12}]$ and related derivatives suggest that the dimerization of the alkyne groups occurs after the co-ordination of the phosphorus atoms. The P–C bond cleavage then occurs simultaneously with the co-ordination of the newly formed carbon chain.

The simple phosphine substitution products $[Fe_3(CO)_{11}(Ph_2PC{\equiv}CR)]$ and $[Fe_3(CO)_{10}(Ph_2PC{\equiv}CR)]_2$, as well as the

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† The $[Fe_3(CO)_{12}]$ used in these reactions contains 10% methanol.

π-bonded species[$Fe_2(CO)_6(Ph_2PC{\equiv}CR_2$],[7] have now been characterized from the reaction of phosphinoacetylenes with iron carbonyls.

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