Two-carbon Three-electron Ligands. Phosphonium–Betaine Complexes *via* Nucleophilic Attack by Phosphites on a σ-π-Acetylide Di-iron Hexacarbonyl Derivative

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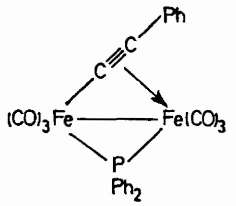
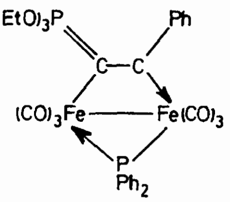
Summary Phosphonium–betaine (ylide–carbene) complexes have been synthesised *via* nucleophilic attack by $P(OR)_3$ on a σ-π-acetylide complex $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$, and a single crystal *X*-ray study of the triethylphosphite derivative $Fe_2(CO)_6\{C[P(OEt)_3]CPh\}(PPh_2)$ has confirmed the presence of a new type of 2-carbon, 3-electron ligand.

Work on the conversion of *cis*-$MCl_2(Ph_2PC{\equiv}CCF_3)_2$ (M = Pd,Pt) to several unusual inorganic complexes[1] led us to investigate the reactivity of the σ-π-acetylide in $Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$ (I).[2] Preliminary work has revealed that (I) is susceptible to attack at the α-carbon of the acetylide by a variety of nucleophiles. Of particular interest are the reactions with trialkyl or aryl phosphites which provide a synthetic route to complexes containing a new type of 2-carbon, 3-electron donor hydrocarbyl[3] ligand. These complexes can be described as ylide–carbene or phosphonium–betaine derivatives. A triethyl phosphite complex $Fe_2(CO)_6C[P(OEt)_3]CPh(PPh_2)$ (II) has been fully characterised by a single crystal *X*-ray structure determination. The intermediacy of phosphonium betaines analogous to the trapped ligand in (II) has previously been postulated.[4]

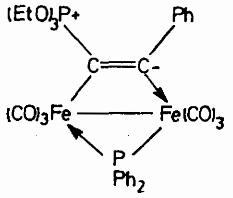
(I)



(IIa)



(IIb)



The complex (I) is quantitatively converted to (II) (m.p. 128—129°; ν(CO) C_6H_{12}, 2045s, 1996s, 1976s, 1955m, 1947s, 1933m) *via* the reaction with an equimolar quantity of $P(OEt)_3$ at room temperature in benzene. The Mossbauer spectrum of (II) is an incompletely resolved doublet (δ = 0·12, Δ = 0·26; Γ = 0·39 mm s^{-1}) indicating slight non-equivalence of iron sites with near octahedral sysmmetry.

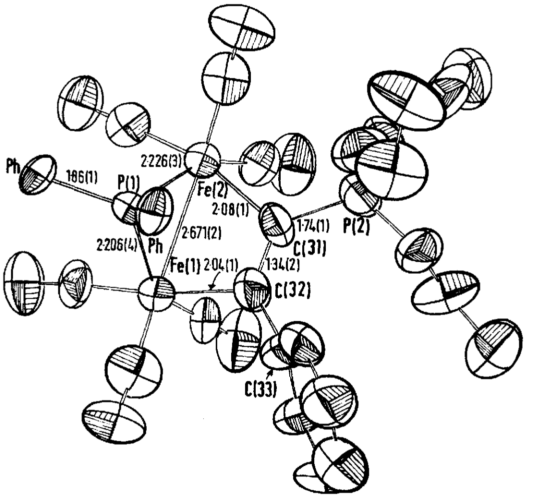


Figure. The molecular structure (ORTEP) of $Fe_2(CO)_6$ {C[P(OEt)$_3$]CPh}(PPh_2). The C(31)–Fe(1) and C(32)–Fe(2) distances of 2·762 Å and 2·812 Å respectively are considered non-bonding. For clarity only two carbon atoms (labelled Ph) of the phenyl rings attached to P(1) are shown.

Crystal data. $Fe_2(CO)_6C[P(OEt)_3]CPh(PPh_2)$, diamagnetic yellow crystals, monoclinic, space group $P2_1/n$, $Z = 4$, a = 10·368(11), b = 17·173 (16), c = 20·110(15) Å, β = 95·24(6)°. The structure was solved by conventional heavy-atom methods using 2421 intensity data collected on a G. E. XRD6 diffractometer with Mo-K_α radiation. Refinement by full-matrix least-square methods has proceeded to an R value of 0·077. The two iron atoms in the binuclear molecule (Figure) are bridged by a diphenylphosphido group and two carbon atoms derived from the original acetylide. It is apparent from the P(2)–C(31) [1·74(1) Å] and Fe(1)–P(2), Fe(2)–P(2) (both >3·35 Å) distances that the phosphorus atom of the phosphite has attacked the α-carbon atom of the acetylide in (I) rather than the iron tricarbonyl fragments. The P(2)–C(31) bond length is considerably shorter than the P–C(sp^2) distances [1·798—1·800(7) Å] in $[MePh_3P]^+ Ni[S_2C_2(CN)_2]_2^-$ (ref. 5) and related phosphonium salts[6] but very similar to the P=C bond lengths found in stabilised phosphorus ylides.[6] The C(31)–C(32) distance of 1·34(2) Å indicates appreciable multiple bond character. Thus the structure of the ligand in (II) is best described in terms of contributions from both (IIa) (an ylide–carbene) and (IIb) (a betaine). The differences in Fe–C bond character predictable from the carbenoid nature of C(32) compared to the alkenyl character of C(31) in (IIa) and (IIb) are manifested in the significantly shorter (Δ/σ = 4·0) Fe(1)–C(32) [2·04(1) Å] bond length as compared to Fe(2)–C(31) [2·08(1) Å]. The carbon atom C(32) protrudes only 0·01 Å from the best plane defined by the atoms Fe(1), C(32), C(31), C(33) hence the stereochemistry at C(32) is planar. The formulation of the ligand in (II) as a 3-electron donor allows both iron atoms to achieve the krypton configuration. The structure of (II) bears a formal resemblance to the complexes $Fe_2(CO)_6[C(C_6H_3(OMe)_2]OEt$ (ref. 7) and $Fe_2(CO)_6[CPh(O)]_2$ (ref. 8) although in the former, the carbene system functions as a 4 electron donor. The generality of the reaction of (I) with phosphites has been demonstrated by the isolation of yellow, crystalline complexes analogous to (II) with $P(OMe)_3$, $P(OBu^n)_3$ and $P(OMe)Ph_2$.

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