

Preliminary communication

σ, π -Acetylide complexes via P-C bond cleavage of phosphinoacetylenes: X-ray structure of $\text{Fe}_2(\text{CO})_6(\text{C}\equiv\text{CPh})(\text{PPh}_2)$

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There are very few examples in which the triple-bond of a σ -bonded acetylide group is π -bonded to a second metal atom** although many acetylene complexes of transition metal carbonyls have been characterized¹. We have characterized the novel complex $\text{Fe}_2(\text{CO})_6(\text{C}\equiv\text{CPh})(\text{PPh}_2)$, I, which is formed in the room temperature reaction of $\text{Ph}_2\text{PC}\equiv\text{CPh}$ with $\text{Fe}_2(\text{CO})_9$ and found that I contains an acetylide group σ -bonded to one iron atom and intramolecularly π -bonded to a second iron atom. The interest in and importance of I stems from the unusually facile cleavage of the P-C(acetylene) bond by metal carbonyls and the fact that I may be an intermediate in the formation of the trinuclear species $\text{Fe}_3(\text{CO})_8[\text{Ph}_2\text{PC}_4(\text{CF}_3)_2](\text{PPh}_2)$ ⁵. In addition, σ -bonded acetylides similar to I have been postulated as intermediates in the metal carbonyl catalyzed trimerization of acetylenes⁶.

The reaction of $\text{Ph}_2\text{PC}\equiv\text{CPh}$ ⁷ with $\text{Fe}_2(\text{CO})_9$ in benzene at room temperature, followed by chromatography on alumina and recrystallization from benzene/heptane, afforded red crystals of a complex analyzing as $\text{Fe}_2(\text{CO})_6[\text{Ph}_2\text{PC}_2\text{Ph}]$. An NMR spectrum indicated only phenyl ring protons. The mass spectrum gave a parent ion at m/e of 566 and successive loss of the six CO groups to give an ion $[\text{Fe}_2\text{C}_{20}\text{H}_{15}\text{P}]^+$ in high abundance. The IR spectrum [C_6H_{14} ; $\nu(\text{CO})$ region at 2074 s, 2036 vs, 2010 s, 1992 s, 1991 s, 1975 w] in conjunction with the mass spectrum suggested two non-equivalent $\text{Fe}(\text{CO})_3$ groups and a

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**The simple acetylides $[\text{M}(\text{C}\equiv\text{CR})_n]$, phosphine derivatives $[(\text{PR}_3)_m\text{M}(\text{C}\equiv\text{CR})_n]$ ($\text{M} = \text{Cu}, \text{Ag}$)² and the recently characterized polynuclear species $[(\pi\text{-C}_2\text{H}_2)_2\text{Fe}(\text{CO})_2(\text{C}_2\text{Ph})\text{CuCl}]_2$ ³ and $\text{Cu}_4\text{Ir}_2(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_8$ ⁴ are notable examples.

coordinated triple-bond since $\nu(\text{C}\equiv\text{C})$ of the ligand at 2198 cm^{-1} was missing. An X-ray crystal structure study was undertaken to establish unequivocally the molecular geometry of this interesting complex.

Crystal data: $\text{Fe}_2(\text{CO})_6(\text{Ph}_2\text{P})(\text{C}_2\text{Ph})$, Mol. wt. 566.07, monoclinic crystals, space group $P2_1/c$; a 9.507(1), b 30.565(8), c 9.763(3) Å, β 117.21(2); U 2523(1) Å³, D_m 1.48 g/cm³, Z = 4, D_c 1.490 g/cm³. The structure was solved by the heavy atom method and refined by least-squares methods. The current R value is 0.052 for 2349 independent, non-zero reflections measured with graphite monochromatized Mo- K_α radiation, using a variable scan rate on a Syntex $P\bar{1}$ diffractometer.

The molecular geometry, atomic numbering and the thermal ellipsoids are illustrated in Fig. 1. The two $\text{Fe}(\text{CO})_3$ moieties are joined by a metal-metal bond, a bridging diphenylphosphido group, and the unique acetylide ligand which is σ -bonded to Fe(1) and π -bonded to Fe(2). The Fe-Fe distance of 2.597(2) Å is intermediate in the range of values (2.42–2.88 Å) found in other organometallic compounds^{8,9}. The Fe-P distances (Fe(1)-P of 2.213(2) Å and Fe(2)-P of 2.224(2) Å) are shorter than the values in the related compound $\text{Fe}_3(\text{CO})_8[\text{Ph}_2\text{PC}_4(\text{CF}_3)_2(\text{Ph}_2\text{P})]$ ⁵, but the Fe-P-Fe angle of 71.64(7)^o is much smaller than was found in the other phosphido bridge (98.17(8)^o)⁵. The acute angle in the present structure is certainly a consequence of the Fe-Fe bond.

The coordinated acetylide must function as a 1-electron donor to Fe(1) via a σ -bond and also as a 2-electron donor to Fe(2) via a π -bond if adherence to the 18-electron rule is to be maintained. This dual interaction is reflected in the deviation of the Fe(1)-C(7)-C(8) (160.3(6)^o) and the C(7)-C(8)-C(31) (162.3(8)^o) angles from linearity. The Fe(1)-C(7) bond length of 1.891(6) Å is in agreement with the formulation of an

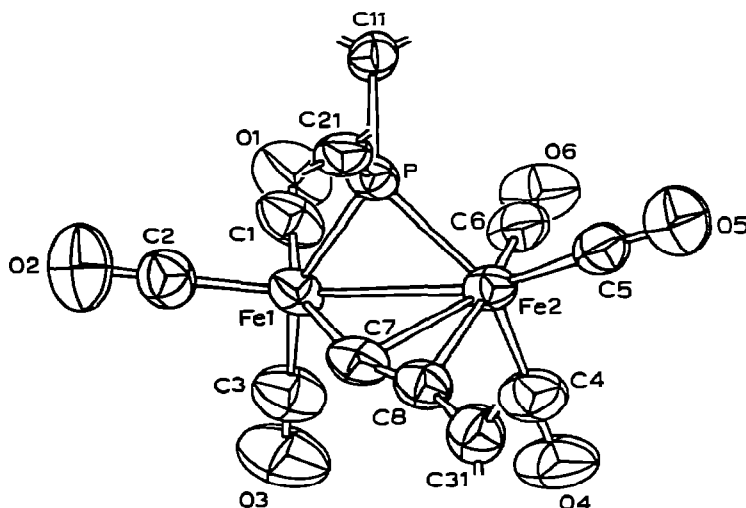


Fig. 1. A view of the $\text{Fe}_2(\text{CO})_6(\text{C}\equiv\text{CPh})(\text{PPh}_2)$ molecule showing the molecular geometry, atomic numbering and thermal ellipsoids. Only the first carbon atom of each of the three phenyl groups is shown together with the two bonds to ring carbons.

Fe-C(sp) single bond¹⁰, especially if one compares the Fe(1)-C(7) distance to the Fe-C(CO group) distances, av. 1.78 Å, which are considered to have multiple-bond character. The Fe(2) to C(7) and C(8) distances of 2.125(8) Å and 2.304(7) Å are reasonable relative to the usual Fe-C(olefinic-bond) distances¹¹. The C(7)-C(8) bond distance of 1.232(10) Å is longer than the average triple bond length of 1.202(5) Å¹², reflecting the interaction of the triple bond with Fe(2). A similar distance, 1.235(18) Å, was reported for a coordinate acetylene bond in PtCl₂(t-BuC≡CBu-t)(CH₃C₆H₄NH₂)¹³. It is interesting that reaction of I with P(OEt)₃ proceeds via initial displacement of the σ-bonded acetylide from Fe(2) yielding yellow crystals of Fe₂(CO)₆(C≡CPh)(PPh₂)P(OEt)₃ rather than the CO substitution product Fe₂(CO)₅(C≡CPh)(PPh₂)P(OEt)₃.

The facile fragmentation of the P-C bond in Ph₂PC≡CPh by Fe₂(CO)₉ at room temperature is remarkable. A few other examples of M-C (M = P, As) bond cleavage in reactions of Group V ligands with transition metal carbonyls have been reported but usually require elevated temperatures¹⁴. The cleavage in Ph₂PC≡CPh may be related to the rigid linear P-C≡C-R skeleton which cannot remain intact if both the phosphorus atom and the triple-bond are to coordinate in a binuclear metal-metal bonded complex. An analogous P-C fragmentation occurs in the formation of Fe₃(CO)₈[Ph₂PC₄(CF₃)₂][PPh₂] from Ph₂PC≡CCF₃ and Fe₃(CO)₁₂⁵. A comparison of the structure of I with that of Fe₃(CO)₈[Ph₂PC₄(CF₃)₂][PPh₂] clearly suggests that the latter could be formed from the CF₃ analogue of I by the addition of the uncoordinated triple bond of the phosphine complex Fe(CO)₄(Ph₂PC≡CCF₃)^{*} to the coordinated acetylide in I, followed by a rearrangement. We are currently exploring this possibility and the wider implications of P-C bond cleavage in the reactions of phosphinoacetylenes with metal carbonyls.

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REFERENCES

- 1 For recent reviews see F.L. Bowden and A.B.P. Lever, *Organometal. Chem. Rev.*, 3 (1967) 227. W. Hübel, in I. Wender and P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls, Vol. 1*, Interscience, New York, 1968, p. 273-342.
- 2 P.W.R. Corfield and H.M.M. Shearer, *Acta Crystallogr.*, 20 (1966) 502; P.W.R. Corfield and H.M.M. Shearer, *Acta Crystallogr.*, 21 (1966) 957.
- 3 M.I. Bruce, R. Clark, J. Howard and P.W. Woodward, *J. Organometal. Chem.*, 42 (1972) C107.
- 4 O.M. Abu Salah, M.I. Bruce, M.R. Churchill and S.A. Bezman, *Chem. Commun.*, (1972) 858;
- 5 T. O'Connor, A.J. Carty, M. Mathew and G.J. Palenik, *J. Organometal. Chem.*, 38 (1972) C15.

*Fe(CO)₄(Ph₂PC≡CCF₃) and Fe(CO)₃(Ph₂PC≡CCF₃)₂ are the major products from the reaction of (π-C, H₈)Fe(CO)₃ with Ph₂PC≡CCF₃. Both have been fully characterized.

- 6 C. Hoogzand and W. Hübel in I. Wender and P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls, Vol. 1*, Interscience, New York, 1968, p. 343-371 and references therein.
- 7 A.J. Carty, N.K. Hota, T.W. Ng, T.J. O'Connor and H.A. Patel, *Can. J. Chem.*, 49 (1971) 2706.
- 8 M.R. Churchill, *Inorg. Chem.*, 6 (1967) 190.
- 9 M.I. Bruce, *Organometal. Chem. Rev., B*, 6 (1970) 937.
- 10 M.R. Churchill, *Perspectives in Structural Chemistry*, 3 (1970) 91.
- 11 See for example J.A.D. Jeffreys and G.M. Willis, *J. Chem. Soc. Dalton*, (1972) 2169 or A. Gieren and W. Hoppe, *Acta Crystallogr., B*, 28 (1972) 2766.
- 12 *Chem. Soc. Special Publ. No. 18*, 1965.
- 13 G.R. Davies, W. Hewertson, R.H.B. Mais, P.G. Owston and C.G. Patel, *J. Chem. Soc. (A)*, (1970) 1873.
- 14 See for example W.R. Cullen, D.A. Harbourne, B.V. Liengme and J.R. Sams, *Inorg. Chem.*, 9 (1970) 702.