Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Trinuclear ferracyclopentadiene complexes via oligomerization of phosphino- and arsino-acetylenes. X-ray structure of $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2](Ph_2P)$

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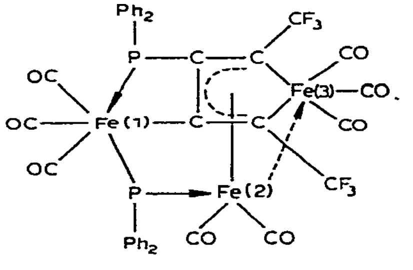
(Received February 29th, 1972)

The reaction of olefins and acetylenes with metal carbonyls has produced a variety of organometallic compounds as well as unusual organic species via oligomerization[1]. However, olefinic[2] and acetylenic[3] derivatives of Group V elements (P and As) have shown little tendency to oligomerise and usually form mononuclear or polynuclear complexes with both the phosphine or arsine and the double or triple bond coordinated to the metal atom although examples are known[2,3] where only one ligand site is coordinated. We now wish to report that a phosphorus substituted ferracyclopentadiene ring is produced from the reaction of $Ph_2MC{\equiv}CCF_3$ ($Ph = C_6H_5$; $M = P$, As) and $Fe_3(CO)_{12}$ which must result from dimerization of the phosphinoacetylene.

The acetylenes $Ph_2MC{\equiv}CCF_3$ reacted with $Fe_3(CO)_{12}$ in benzene at 50° to give, after chromatography, orange crystals of (I) (m.p. 212–213°) and dark red crystals of (II) (m.p. 191–192°). Analytical data for samples from C_6H_6/C_6H_{14} were consistent with the formulae $(C_{15}H_{10}PF_3)_2Fe_3(CO)_x \cdot 0.5C_6H_6$ and $(C_{15}H_{10}AsF_3)_2$ $Fe_3(CO)_x \cdot 0.5C_6H_6$ where x is 7 or 8. IR spectra of (I) and (II) were virtually identical in the



(I)

ν(CO) region; [ν(CO) C_6H_{14}, (I): 1969 w, 1993 w, 2006 s, 2036 m, 2062 s, 2081 m; (II): 1970 w, 1981 m, 2006 s, 2034 m, 2061 s, 2080 m cm^{-1}]. The absence of bands due to ν(C≡C) of the ligands indicated either coordination of the triple bond and/or polymerization of the ligands. Ions corresponding to $(Ph_2PC_2CF_3)_2Fe_3(CO)_{7-n}$ (n=0–7) were observed in the mass spectrum of (I), in addition to a strong peak at m/e 539 due to loss of Ph_2P from $[Ph_2PC_2CF_3)_2Fe_3]^+$. For (II), ions $(Ph_2AsC_2CF_3)_2Fe_3(CO)_{8-n}$ (n=0–8) were identified but loss of Ph_2As from $[(Ph_2AsC_2CF_3)_2Fe_3]^+$ was not apparent. Mössbauer spectra of (I) and (II) appeared as four lines with an intensity ratio of 1/2/1/2. Computer analysis of the spectra gave best fits for six independent Lorentzian lines of approximately equivalent area indicating three non-equivalent iron atoms in each case*. In refluxing benzene (I) reacted with $(MeO)_3P$ and $(EtO)_3P$ to give the monosubstituted complexes $Fe_3(CO)_x(Ph_2PC_2CF_3)_2(RO)_3P$ which had identical infrared spectra [ν(CO) C_6H_{12}: 1967 w, 1976 s, 1998 s, 2032 m, 2046 w, 2061 m], but (II) yielded disubstitution products $Fe_3(CO)_6Ph_2AsC_2CF_3)_2\,[(RO)_3P]_2$. The NMR spectrum of the latter $(MeO)_3P$ complex [100 MHz, $CDCl_3$, τ 6.32 d, ^3J(P–H) 11.9 Hz; 6.8 d, ^3J(P–H) 10.5 Hz] showed the presence of two different ligands presumably on different iron sites. Therefore, an X-ray crystal structure study was undertaken to establish the structure of the phosphine compound (I).

Crystal data: $Fe_3(CO)_8(Ph_2PC_2CF_3)_2\cdot 0.5C_6H_6$, triclinic crystals, space group $P\bar{1}$ (by intensity statistics); a = 11.095, b = 12.082, c = 16.936 Å, α = 94.50; β = 98.15, γ = 114.53°; U = 2020.66 Å^3, D_m = 1.595 g/cm^{-3}, D_c = 1.622 g/cm^{-3}, Z = 2. The structure was solved by the heavy atom method and refined by least-squares methods. The final R was 0.063 for 3851 independent, non-zero reflections measured with graphite monochromatized Mo–K_α radiation, using a variable scan rate on a Syntex $P\bar{1}$

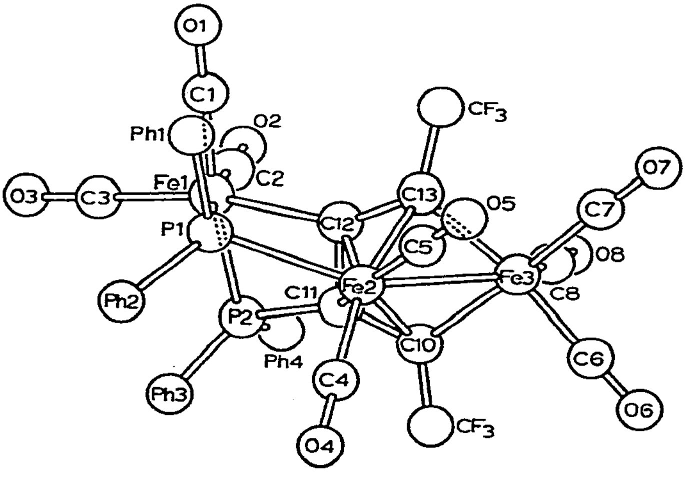


Fig. 1. A view of the $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2]$ (Ph_2P) molecule in an arbitrary direction showing the molecular shape and atomic numbering.

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*The reasoning for the assignment of quadrupole split lines to the three non-equivalent iron atoms will be presented elsewhere.

diffractometer. The principal feature of the structure shown in Fig. 1 is the planar ferracyclopentadiene ring formed by the dimerization of two molecules of $Ph_2PC{\equiv}CCF_3$ across the acetylenic carbon atoms adjacent to the phosphorus atom. The Fe(3)–C (average 1.964 Å) and C–C (average 1.425 Å) distances within the ferradiene ring are similar to those found in $Fe_2(CO)_6(CH_3)_2C_4(OH)_2$, average 1.946 and 1.422 Å[4], $Fe_3(CO)_6PhC_2Ph$, average 1.975 and 1.422 Å[5] and the black isomer of $Fe_3(CO)_8(PhC_2Ph)_2$, average 2.047 and 1.450 Å[6] which also contain ferracyclopentadiene rings. A second novel feature of (I) is the bridging diphenylphosphido group linking Fe(1) and Fe(2), presumably formed during the reaction by a cleavage of the P–C (*sp*) bond of one of the $Ph_2PC{\equiv}CCF_3$ units. Thus, Fe(1) is joined to C(12) by a rather long bond, 2.079 Å, giving an unsymmetrically substituted ferracyclopentadiene ring. The ferracycle is bonded in π fashion to Fe(2) which is bonded to the diphenyl phosphido group, two carbonyls and to Fe(3). The Fe(2)–Fe(3) distance of 2.554 Å is comparable with the distances of 2.531 and 2.534 Å found in *cis*- and *trans*- $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ respectively[7]. The iron atom Fe(2) is displaced slightly toward C(11) and C(12), presumably as a result of the rigid stereochemistry imposed by the phosphido group and the Fe(2)–Fe(3) bond. The distance Fe(1)–Fe(2) of 3.501 Å and Fe(1)–Fe(3) of 4.975 Å precludes any bonding interaction between these atoms.

An electron count indicates that the molecule is two electrons short of attaining the krypton configuration. Consideration of the P(1)–Fe(1) (2.366 Å) and P(1)–Fe(2) (2.283 Å) distances together with the other structural features leads us to suggest the valence bond representation 1 for (I). On this basis the carbonyl groups of the electron deficient atom Fe(3) would be most susceptible to displacement by $(RO)_3P$. Hence, we favor Fe(3) as the substituted site in $Fe_3(CO)_7(Ph_2PC_2CF_3)_2(RO)_3P$.

Although the mechanism of formation of (I) is unclear, comparison with analogous reactions between $R_2PC{\equiv}CR'$ and $Co_2(CO)_8$[3] and between acetylenes and $Fe_3(CO)_{12}$[1] may imply initial attack by the alkyne function followed by dimerization, phosphorus coordination and P–C bond cleavage. Some support for phosphorus coordination preceding P–C bond cleavage derives from the conversion of $(FFars)Fe_3(CO)_{10}$ (FFars is 1,2-bis(dimethylarsino)tetrafluorocyclobutene) to the dimethylarsenido bridged species $(FFars)Fe_3(CO)_9$ under mild conditions[8]. Whether intermediates similar to violet $Fe_3(CO)_8(PhC_2Ph)_2$[6] can be isolated under different conditions remains to be demonstrated.

The arsine analogue (II) appears from infrared data to have a closely related structure yet gives disubstitution products and shows no evidence for bridging Ph_2As groups in the mass spectrum.

ACKNOWLEDGEMENTS

We wish to thank Arapahoe Chemicals, Division of Syntex Corporation for financial support, the Department of Chemistry, University of Florida for a Postdoctoral Fellowship (to M.M.) and the Computing Center, University of Florida for a grant of computer time (G.J.P.).

REFERENCES

1 W. Hübel, in I. Wender and P. Pino (Eds.), *Organic syntheses via metal carbonyls, Vol. 1*, Interscience, New York, 1968, p. 273–342 and references therein.
2 M.A. Bennett, G.B. Robertson, I.B. Tomkins and P.O. Whimp, *Chem. Commun.*, (1971) 341; M. Aresta and R.S. Nyholm, *Chem. Commun.*, (1971) 1459; M.A. Bennett, R.S. Nyholm and J.D. Saxby, *J. Organometal. Chem.*, 10 (1967) 301.
3 N.K. Hota, H.A. Patel, A.J. Carty, M. Mathew and G.J. Palenik, *J. Organometal. Chem.*, 32 (1971) C55; A.J. Carty and T.W. Ng., *Chem. Commun.*, (1970) 149; P.H. Bird and A.R. Frazer, *Chem. Commun.*, (1970) 681.
4 A.A. Hock and O.S. Mills, *Acta Crystallogr.*, 13 (1961) 139.
5 Y. Degreve, J. Meunier-Piret, M. Van Meersche and P. Piret, *Acta Crystallogr.*, 23 (1967) 119.
6 R.P. Dodge and V. Schomaker, *J. Organometal. Chem.*, 3 (1965), 274.
7 R.F. Bryan and P.T. Greene, *J. Chem. Soc. A*, (1970) 3064; R.F. Bryan, P.T. Greene, M.J. Newlands and D.S. Field, *J. Chem. Soc. A*, (1970) 3068.
8 W.R. Cullen, D.A. Harbourne, B.V. Liengme and J.R. Sams, *Inorg. Chem.*, 9 (1970) 702.