Journal of Organometallic Chemistry, 304 (1986) C1—C3
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS AND X-RAY ANALYSIS OF A PHOSPHIDOIRON CLUSTER $[\{Fe_3(CO)_{10}\}P\{Fe(CO)_4\}]^-$

ANDRE GOURDON and YVES JEANNIN*

Laboratoire de Chimie des Métaux de Transition, C.N.R.S. U.A. 419, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05 (France)

(Received January 16th, 1986)

Summary

$[X]_2[Fe_4(CO)_{13}]$ ($X = (Ph_3P)_2N$ or $(Ph)_4P$) reacts with PCl_3 in a 2/1 ratio to give $[X][\{Fe_3(CO)_{10}\}P\{Fe(CO)_4\}]$. The phosphorus atom caps a $Fe_3(CO)_{10}$ group and is bonded to a $Fe(CO)_4$ fragment.

Transition metal clusters containing interstitial main group heteroatoms are currently receiving a great deal of attention [1] because of their similarities to metallic interstitial compounds and surface species [2, 3]. While many hydrido, carbido and nitrido clusters are known, as yet no clusters containing an encapsulated phosphorus have been observed in the iron triad. We report herein the synthesis and X-ray structure of an iron cluster containing a tetrahedrally coordinated phosphorus atom.

The complex $[X]_2[Fe_4(CO)_{13}]$ (X = PPN or $(Ph)_4P$) reacts readily in CH_2Cl_2 with PCl_3 in 2/1 ratio to give $[X][\{Fe_3(CO)_{10}\}P\{Fe(CO)_4\}]$*. After removal of the solvent the product is extracted with ether and recrystallized from ether/hexane. Although spectroscopic evidence shows that yield is good (>50%), we have never obtained high yields of recrystallized product, mainly because of the very high solubility of the complex in polar solvents.

The IR spectra** suggest the presence of both bridging and terminal carbonyl ligands. An X-ray study*** of the $[PPh_4]^+$ salt (Fig. 1) shows that the

---

*Satisfactory elementary analysis was obtained for $[(Ph)_4P][Fe_4(CO)_{14}P]$.

**Selected IR data in CH_2Cl_2: (CO) 2040 w, 2020 vs, 1875 vw sh, 1790 w br, 1605 vw br cm^{-1}.

***Crystal data for $[C_{24}H_{20}P][C_{14}Fe_4O_{14}P]$, M = 985.90, monoclinic, space group $P2_1/c$, a 11.467(5), b 28.590(7), c 12.600(6) Å, 100.80(4)°, U 4058 $Å^3$, D_c 1.61 g cm^{-3}, θ range 2—23°, 3405 reflections collected at room temperature with $|F| > 3\sigma(F)$, corrected for absorption, $\mu(Mo\text{-}K_\alpha)$ 15.84 cm^{-1}. The structure was solved from a Patterson map and refined by large-block least-squares to final R 0.047 and R_w 0.051.

0022-328X/86/$03.50

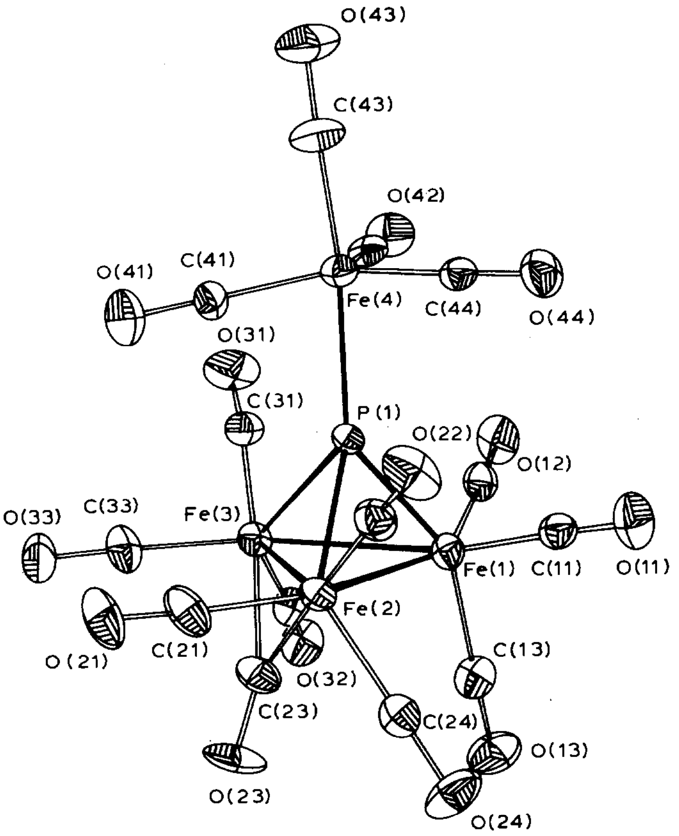

Fig. 1. The structure of the [$\{Fe_3(CO)_{10}\}P\{Fe(CO)_4\}$]$^-$ anion. Important bond lengths (Å) are: Fe—Fe: (1)—(2) 2.620, (1)—(3) 2.641, (2)—(3) 2.593; Fe(1)—P(1) 2.156, Fe(2)—P(1) 2.245, Fe(3)—P(1) 2.237, Fe(4)—P(1) 2.234 max e.s.d. 0.002 Å.

phosphorus atom is bound to four iron atoms. The overall geometry is that of a trinuclear phosphinidene such as [$Fe_3(CO)_{10}PC(CH_3)_3$] [4], with a $Fe(CO)_4P$ group capping a $Fe_3(CO)_{10}$ triangle. A similar geometry is observed in clusters containing Group IV heteroatoms [$Co_3(CO)_9SiCo(CO)_4$] [5], [$Co_3(CO)_9GeCo(CO_4$] [6] and [$CpFe(CO)_2SnFe_3(CO)_9SnFe(CO)_2Cp$] [7].

The structure of the $Fe_3(CO)_{10}P$ group is that of [$Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CO)$]$^{2-}$ [8] but with the phosphorus atom in place of the triply bridging carbon atom. The phosphorus atom is asymmetrically coordinated to the four iron atoms with a P(1)—Fe(1) distance of 2.156(2) Å, shorter than the other three P—Fe bonds (mean 2.239 Å). This suggests an important Fe(1)—P(1) back donation, promoted by the 5 electron donor character of the phosphorus atom, which compensates for the residual charge on Fe(1)*.

The capping $Fe(CO)_4P$ group has a trigonal bipyramid geometry.

---

*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

References

1 J.N. Nicholls, Polyhedron, 3 (1984) 1307.
2 M. Tachikawa and E.L. Muetterties, Prog. Inorg. Chem., 28 (1981) 203.
3 E.L. Muetterties, T.N. Rhodin, E. Bard, C.F.Brucker and W.R. Pretzer, Chem. Rev., 79 (1979) 91.
4 K. Knoll, G. Huttner, L. Zsolnai, I. Jibril and M. Wasiucionek, J. Organomet. Chem., 294 (1985) 91.
5 G. Schmid, V. Bärzel and G. Etzrodt, J. Organomet. Chem., 112 (1976) 345.
6 D.N. Duffy, K.M. Mackay, B.K. Nicholson and W.T. Robinson, J. Chem. Soc., Dalton Trans., (1981) 381.
7 T.J. McNeese, S.S. Wreford, D.L. Tipton and R. Bau, J. Chem. Soc., Chem. Commun., (1977) 390.
8 F.Y.K. Lo, G. Longoni, P. Chini, L.D. Lower and L.F. Dahl, J. Am. Chem. Soc., 102 (1980) 7691.