Inorganica Chimica Acta
LETTER

Synthesis and Structure of a Phosphido-ethylidyne Bridged Triiron Cluster

RAMÓN YÁÑEZ, JOSEP ROS*, JAVIER DE GEA

Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra (Spain)

RENÉ MATHIEU

Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077 Toulouse Cédex (France)

M. ROSARIO TORRES and AUREA PERALES

UEI de Cristalografía, Instituto Rocasolano CSIC, Serrano 119, 28006 Madrid (Spain)

(Received July 11, 1989)

The phosphido bridge has received special interest over the last few years [1]. The capability of this ligand to hold different metals has converted the PR_2 group into one of the most used three-electron-bridging ligands in metal clusters. Several groups have studied the chemistry of polynuclear phosphido-bridged complexes [2] and have shown that the PR_2 groups are not inert, leading to phosphino organic ligands by coupling reactions of the phosphido bridge with organic fragments [3, 4].

The reactivity of the first period clusters is complicated by the easy fragmentation of the molecules. To avoid this fragmentation, strong bridging ligands are frequently needed. This is the case with the anion cluster $[HFe_3(CO)_{11}]^-$ that reacts with acetylene giving rise to $[Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CCH_3)]^-$ (1), a trinuclear complex, the structure of which is maintained by a carbyne ligand [5]. The anionic nature of 1 allows electrophilic attack by carbocations such as Et^+ leading to a bis-carbyne trinuclear complex which is very stable to fragmentation [6].

The anionic nature of 1 and its reactivity with electrophiles prompted us to check its reactivity with PPh_2Cl, in an attempt to introduce the PPh_2 fragment into the cluster and to show some coupling with the $\mu_3\text{-}CCH_3$ ligand.

The reaction of $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CCH_3)]$ (1) with stoichiometric amounts of PPh_2Cl and $TlBF_4$ in dichloromethane solution at room temperature (1 h) and evaporation of the solution, followed by extraction with hexane, gave a solution containing a solid which was crystallized in a CH_2Cl_2/MeOH solution at −20 °C. A black crystalline product (2) was isolated in 46% yield. The IR spectrum of 2 in hexane solution shows three terminal CO bands at 2078m, 2016s and 1984m cm^{-1} and one broad band at 1914w cm^{-1} corresponding to a bridging CO. The ^1H NMR spectrum of the complex 2 in $CDCl_3$ solution presents signals at 2.9d (J = 1.14 Hz; CH_3) and 7.15m (Ph) ppm. The small coupling of CH_3 with phosphorus and a signal at 357.0 ppm (C–CH_3) in the ^{13}C spectrum suggest that ethylidyne and phosphido groups remain separated in the molecule. *Anal.* Found: C, 43.37; H, 2.59. Calc. for $Fe_3C_{23}H_{13}O_9P$: C, 43.72; H, 2.07%. This and the spectral data confirm the neutral nature of 2, containing phosphido and ethylidyne groups $[Fe_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}CCH_3)]$.

The molecular structure of 2 was resolved by X-ray diffraction methods. Crystal data: $Fe_6C_{46}H_{26}O_{18}P_2$, space group $P1$; a = 13.244(4), b = 10.973(3),

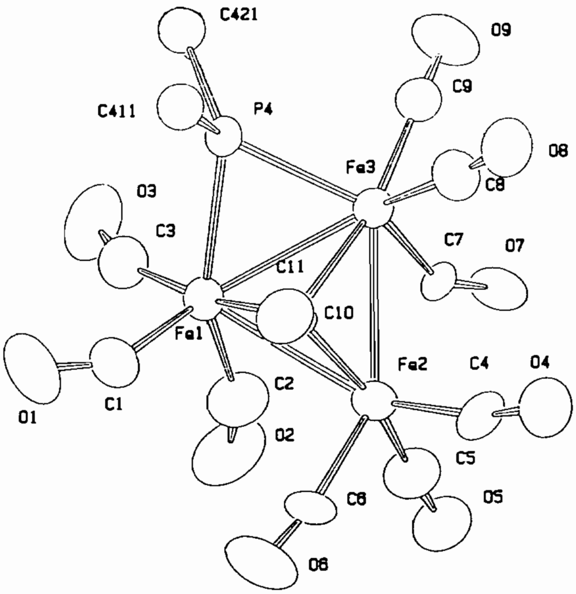

Fig. 1. Molecular structure of **2A** $[Fe_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}CCH_3)]$ showing the atomic numbering scheme (phenyl groups are omitted). Selected molecular parameters for **2A**: Fe(1)–Fe(2), 2.576(3); Fe(1)–Fe(3), 2.572(3); Fe(2)–Fe(3), 2.582(3); Fe(1)–P(4), 2.170(4); Fe(3)–P(4), 2.190(4); Fe(1)–C(10), 2.000(12); Fe(2)–C(10), 1.898(12); Fe(3)– C(10), 1.886(14) Å. For **2B**: Fe(1)–Fe(2), 2.545(3); Fe(1)– Fe(3), 2.548(2); Fe(2)–Fe(3), 2.657(2); Fe(1)–P(4), 2.208(4); Fe(2)–P(4), 2.261(3); Fe(1)–C(10), 2.076(16); Fe(2)–C(10), 1.918(13); Fe(3)–C(10), 1.957(14) Å.

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

$c = 8.889(2)$ Å; $\alpha = 103.649(2)$, $\beta = 76.41(2)$, $\gamma = 90.76(3)^\circ$; $D_{calc} = 1.72$, $M = 1263.73$, $Z = 1$. A crystal was mounted on a Nonius CAD-IV four-circle diffractometer and intensity data were recorded by the $\omega - 2\theta$ scan technique. A total of 6991 reflections with $2 < \theta < 28^\circ$ were measured; 2885 were considered observed ($I > 2\sigma(I)$). Absorption corrections were made. The solution of the structure was made [7] by direct methods and the refinement was anisotropic, except for the phenyl groups (isotropic) [8–10]. The H atoms were fixed. The function minimized by least-squares refinements was $\Sigma\omega[F]^2$. The refinement converged at $R = 0.042$ ($R_w = 0.045$) for observed reflections only. Atomic scattering dispersion corrections factors were applied for Fe, O and P [11].

Each unit cell of **2** contains two independent $Fe_3C_{23}H_{13}O_9P$ molecules, **2A** and **2B**, related by a pseudo-centre of symmetry. The molecular structures of **2A** and **2B** are similar as a whole, and only **2A** is presented in Fig. 1. The molecules consist of a triangle of iron atoms with Fe(1) and Fe(2) symmetrically bridged by a diphenylphosphido ligand, while the other two sides are bridged by semibridging carbonyl groups. An ethylidyne group is symmetrically bonded to the three irons. Selected bond distances are presented in Fig. 1. The complex **2** is a 48-electron cluster containing two three-electron bridges located at different sites of the molecule: PPh_2 in the plane of the irons and CCH_3 centred over this plane. This special situation causes a redistribution of charge in the molecule through the formation of two semibridging carbonyl ligands in the same way as in other iron clusters [12].

Acknowledgement

We thank the CICYT of Spain for financial support (Project PB86-0274).

References

1 (a) A. J. Carty, *Adv. Chem. Ser., 196* (1982) 163; (b) A. J. Carty, *Pure Appl. Chem., 54* (1982) 113.

2 D. Nucciarone, S. A. MacLaughlin, N. J. Taylor and A. J. Carty, *Organometallics, 7* (1988) 106.

3 W. F. Smith, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, (1976) 896.

4 R. Regragui, P. H. Dixneuf, N. J. Taylor and A. J. Carty, *Organometallics, 5* (1986) 2067.

5 M. Lourdichi and R. Mathieu, *Organometallics, 5* (1986) 2067.

6 D. Nuel, F. Dahan and R. Mathieu, *Organometallics, 4* (1985) 1436.

7 N. Walker and P. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

8 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, *MULTAN*, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. Universities of York, U.K. and Louvain, Belgium, 1980.

9 P. T. Beurkens, W. P. Bosman, H. M. Doesburs, R. O. Gould, Th. E. M. van der Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens and V. Parthasarathi, *DIRDIF Manual 81,* Crystallography Laboratory, Toernooinveld, The Netherlands, 1981.

10 M. Martinez-Ripoll and F. H. Cano, *PESOS*, a computer program for the automatic treatment of weighting schemes. Instituto Rocasolano CSIC, Madrid, Spain.

11 *International Tables for X-Ray Crystallography,* Vol. 4, Kynoch Press, Birmingham, 1974.

12 R. H. Crabtree and M. Lavin, *Inorg. Chem., 25* (1986) 805.