

Unexpected P–O Bond Formation in the Reaction of PPh₂Cl with the Triiron Cluster [PPh₄][Fe₃(CO)₉(μ-H)(μ-CMe≡CPh)]

Josep Ros,^{* a} Ramón Yáñez,^a María Rosario Torres,^b Aurea Perales^b and René Mathieu^c

^a Departament de Química, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona, Spain

^b Instituto Rocasolano, CSIC, Serrano, 119, 28006 Madrid, Spain

^c Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par convention à l'Université P. Sabatier et a l'Institut Polytechnique, 205, route de Narbonne, 31077 Toulouse Cedex, France

PPh₂Cl reacts with [PPh₄][Fe₃(CO)₉(μ-H)(μ-CMe≡CPh)] at room temperature to give a new compound [Fe₂(CO)₆{μ-PPh₂OC(H)C(Me)C(Ph)}] containing the PPh₂OC(H)C(Me)C(Ph) bridging ligand, the X-ray structure of which has been determined.

The phosphido bridge (μ-PR₂) has been studied by many authors over recent years.^{1–3} Although many complexes containing μ-PR₂ ligands are known, chemical transformations of the phosphido bridge are scarce.^{4–8} The PR₂ ligand is easily formed by cleavage of P–C bonds in phosphinoalkynes (PR₂C≡CR) induced by metal complexes, but in some cases after metal complexation the P atom remains bonded to the alkynyl fragment leading to interesting rearrangements.⁹

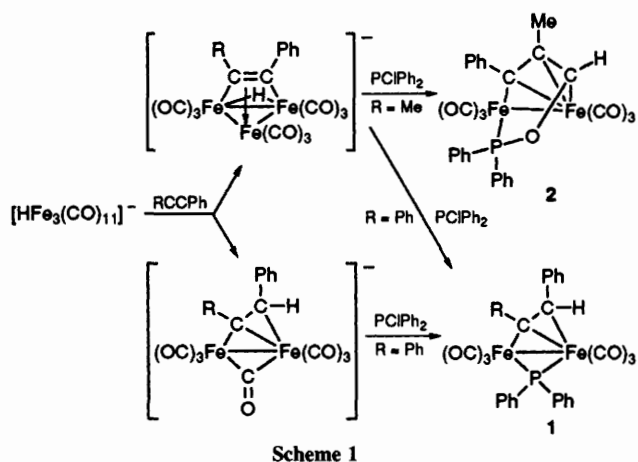
Our group has recently studied the reactivity of the vinyl-bridged diiron complexes [PPh₄][Fe₂(CO)₆(μ-CO)(μ-CR¹=CR²H)] towards different substrates.¹⁰ Its reaction with PPh₂Cl has led to complexes containing both diphenylphosphido and alkenyl bridges [Fe₂(CO)₆(μ-PPh₂)(μ-CR¹=CR²H)] **1**.¹¹ We have also found that compounds of the type **1** can be formed from the reaction of [PPh₄][Fe₂(CO)₆(μ-CO)(μ-PPh₂)] with trifluoroacetic acid and alkynes. No P–C bond formation was observed in these investigations. Furthering our investigations to trinuclear complexes [PPh₄][Fe₃(CO)₉(μ-H)(μ-CR¹≡CR²)]¹² we surprisingly found that these clusters reacted differently towards PPh₂Cl in the presence of TIBF₄ (see Scheme 1). When R¹ = R² = Ph, a degradation of the cluster was observed after three days of reaction and a complex of type **1** was obtained in 34% yield, but when R¹ = Me and R² = Ph (CH₂Cl₂, room temperature, 1 h) the unexpected yellow-brown compound [Fe₂(CO)₆{μ-PPh₂OC(H)C(Me)C(Ph)}] **2** was obtained in 64% yield after

crystallisation.[†] The molecular structure of **2** was determined by X-ray diffraction,[‡] and its structure and some important bond lengths and angles are given in Fig. 1.

The structure of **2** consists of an Fe₂(CO)₆ unit bridged by a PPh₂OC(H)C(Me)C(Ph) group, with each iron linked to three CO ligands. The Fe(1)–Fe(2) distance of 2.679(2) Å is slightly longer than those observed in other phosphido and alkenyl bridged diiron complexes, probably owing to the steric requirements of the bridging ligand.¹¹ The Fe(1)–P(1) dis-

[†] The new complex **2** was characterized by elemental analyses and spectroscopic techniques; ν(CO)/cm⁻¹ (hexane) 2059s, 2015vs, 2000vs and 1965m; ¹H NMR (CDCl₃) δ 7.5 (m, 15H), 6.19 (d, *J*_{PH} 26.7 Hz, 1H) and 1.64 (s, 3H); ³¹P{¹H} NMR δ 141.9 (from H₃PO₄ 85% as external reference).

[‡] *Crystal data* for C₂₈H₁₉O₆PFe₂, *M* = 610, 12, monoclinic, space group *P*2₁/*n*, *a* = 9.343(6), *b* = 14.659(8), *c* = 20.146(7) Å, β = 102.56(3)°, *U* = 2693.14(3) Å³, *Z* = 4, *D*_c = 1.5047 g cm⁻³, Mo-Kα radiation (λ = 0.71070 Å), *R* = 0.059 for 2202 observed reflexions with *I* > 2σ(*I*) and 2 < θ < 28°. Intensities were collected in the ω–2θ scan mode using graphite monochromatized Mo-Kα radiation (Enraf-Nonius CAD4 diffractometer). The structure was solved by direct methods and anisotropically refined except H atoms. The H atoms were placed to calculated positions. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



tance [2.201(3) Å] is in the normal range of other iron-phosphine bonds. The rest of the organic group behaves as an η^3 -allyl ligand which is almost symmetrically bonded to Fe(2) with C(7)–C(8) and C(8)–C(9) distances of 1.44(1) and 1.41(1) Å respectively, whilst C(9) acts as a unsymmetrical bridge between Fe(1) [2.004(9) Å] and Fe(2) [2.082(8) Å].

The most interesting feature of the structure **2** is the unprecedented formation of an allenediyl diphenylphosphinite [P(Ph)₂OC(H)C(Me)C(Ph)] ligand from the coupling of a PPh₂ fragment with a CO ligand and an η^3 -C(Me)C(Ph) group with a subsequent migration of the hydride ligand and the loss of an Fe(CO)₃ fragment. The formation of related phosphido-carbon bonds has been reported previously (PPh₂-alkenyl,⁸ PPh₂-alkyne⁴ and PPh₂-CO⁴) but to our knowledge complex **2** is the first case of a PPh₂-carbonyl coupling through the oxygen atom. The formation of the P–O bond can be explained by an electrophilic attack of the PPh₂⁺ cation on a bonded CO followed by a coupling with the C(Me)C(Ph) fragment and a migration of the hydride ligand. This is another example of the versatility and the reactivity of the CO ligands in anionic polynuclear iron complexes. We are now investigating the possible mechanism of this reaction and developing alternative routes to the preparation of **2**.

This work has been supported by the CICYT of Spain (Project No. PB89-0306).

Received, 1st June 1993; Com. 3/03082B

References

- 1 A. J. Carty, *Adv. Chem. Ser.*, 1982, **196**, 163, and references therein.
- 2 S. H. Breckenridge, N. J. Taylor and A. J. Carty, *Organometallics*, 1991, **10**, 837, and references therein.
- 3 B. Walter, H. Hartung, J. Reinhold, P. G. Jones, C. Mealli, H. C. Böttcher, U. Baumeister, A. Krug and A. Möckel, *Organometallics*, 1992, **11**, 1542.
- 4 R. Regragui, P. H. Dixneuf, N. J. Taylor and A. J. Carty, *Organometallics*, 1984, **3**, 814.
- 5 A. A. Cherkas, S. Doherty, M. Cleroux, G. Hogarth, L. H. Randall, S. M. Breckenridge, N. J. Taylor and A. J. Carty, *Organometallics*, 1992, **11**, 1701.
- 6 Y. F. Yu, J. Gallucci and A. Wojcicki, *J. Chem. Soc., Chem. Commun.*, 1984, 653.
- 7 S. Rosenberg, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1985, **4**, 1184.
- 8 G. Conole, K. A. Hill, M. McPartlin, M. J. Mays and M. J. Morris, *J. Chem. Soc., Chem. Commun.*, 1989, 688.
- 9 D. Montlló, J. Suades, M. R. Torres, A. Perales and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 1989, 97.
- 10 R. Yáñez, J. Ros and R. Mathieu, *J. Organomet. Chem.*, 1991, **414**, 209, and references therein.
- 11 R. Yáñez, J. Ros, R. Mathieu, X. Solans and M. Font-Bardía, *J. Organomet. Chem.*, 1990, **389**, 219.
- 12 M. Lourdichi and R. Mathieu, *Nouv. J. Chem.*, 1982, **6**, 231.

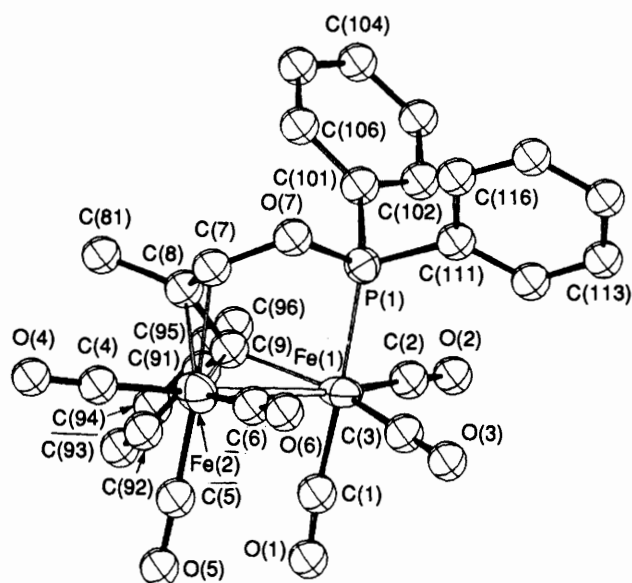


Fig. 1 Structure of compound [Fe₂(CO)₆{μ-PPh₂OC(H)C(Me)C(Ph)}] **2**. Selected bond distances (Å) and angles (°): Fe(1)–Fe(2) 2.679(2), Fe(1)–P(1) 2.201(3), Fe(1)–C(9) 2.004(9), Fe(2)–C(9) 2.082(8), Fe(2)–C(8) 2.073(9), Fe(2)–C(7) 2.058(9), C(8)–C(9) 1.4075(13), C(7)–C(8) 1.437(14), C(7)–O(7) 1.42(1), O(7)–P(1) 1.611(6); P(1)–Fe(1)–C(1) 174.3(4), Fe(2)–Fe(1)–P(1) 89.8(1), Fe(1)–C(9)–Fe(2) 81.9(3), Fe(1)–P(1)–O(7) 110.4(3), O(7)–C(7)–C(8) 122.1(8), C(7)–C(8)–C(9) 117.6(8).