First Structural Characterisation of a Transition Metal Complex containing a Bridging PCR(CO) Ligand (R = Bu^t). Synthesis, Crystal, and Molecular Structure of $[Fe_2(CO)_5(\mu\text{-dppm})\{\mu\text{-}\eta^2\text{-PCBu}^t(CO)\}]$ (dppm = $Ph_2PCH_2PPh_2$)

Peter B. Hitchcock, Timothy J. Madden, and John F. Nixon*

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, U.K.

The synthesis and molecular structure of $[Fe_2(CO)_5(\mu\text{-dppm})\{\mu\text{-}\eta^2\text{-PCBu}^t(CO)\}]$ (dppm = $Ph_2PCH_2PPh_2$) are described.

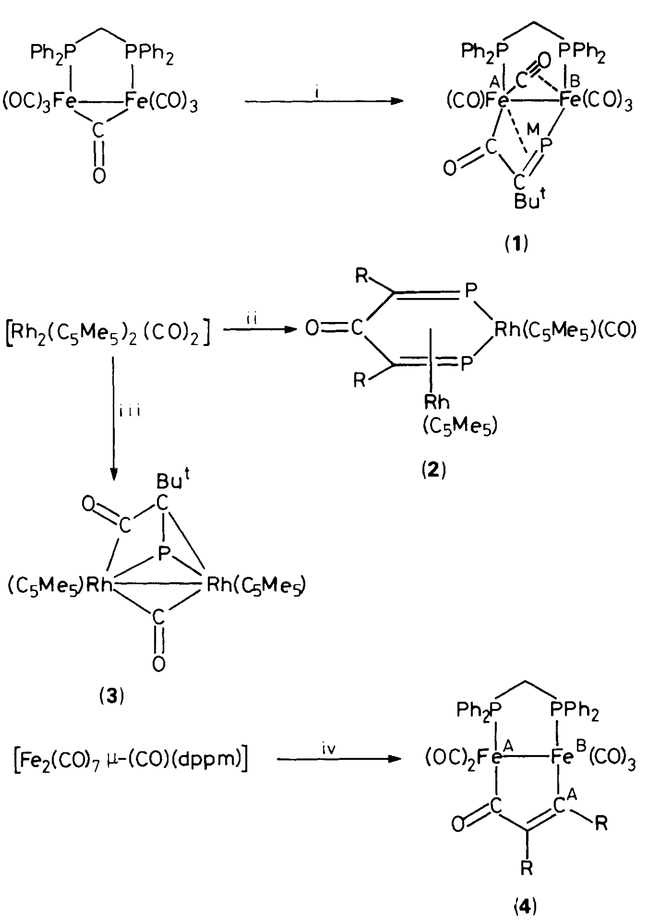
The ligating behaviour of unsaturated organophosphorus compounds is currently an active area of research.[1] Phospha-alkynes, $RC\equiv P$, exhibit a variety of bonding modes towards transition metals[1] and have also proved to be important building blocks in the generation of cyclic ligands such as $(\eta^4\text{-}P_2C_2R_2)$, $(\eta^5\text{-}P_3C_2R_2)^-$, and $(\eta^5\text{-}P_2C_3R_3)^-$, and related ring systems.[2—11] We now report that u.v. irradiation of a mixture of $[Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-dppm})]$[12] (dppm = $Ph_2PCH_2PPh_2$) and Bu^{t}CP affords the red crystalline compound $[Fe_2(CO)_5(\mu\text{-dppm})\{\mu\text{-}\eta^2\text{-PCBu}^t(CO)\}]$ (**1**) (*ca.* 20% yield) (see Scheme 1).

The molecular structure of (**1**), which was established by a single crystal *X*-ray diffraction study† (see Figure 1) can be viewed as resulting from an insertion of the phospha-alkyne into one of the Fe–C bonds of the Fe–C(O)–Fe bridging unit. Previously we reported[13] that two RCP units, (R = Bu^t, adamantyl), could be linked *via* CO in the reaction of $[Rh_2(C_5Me_5)_2(CO)_2]$ with an excess of the phospha-alkyne to form (**2**), the first step presumably involving a carbonyl migration on to the ligated phospha-alkyne. Likewise Becker, Herrmann *et al.*[14] isolated (**3**) from $[Rh_2(C_5Me_5)(CO)_2]$ and Bu^{t}CP, (see Scheme 1), the structure shown being proposed solely on the basis of n.m.r. and i.r. spectroscopies.

Our characterisation of (**1**) containing a bridging Bu^{t}CP(CO) unit lends support to the proposal that (**3**) is an intermediate in the formation of (**2**). The structure of (**1**) exhibits other interesting features which contrast with those of the alkyne complex $[Fe_2(CO)_5(C_2R_2CO)(\mu\text{-dppm})]$ (**4**) (R = H), reported recently by Knox *et al.*[15,16] (see Scheme 1). In (**4**) the bond length between Fe^A and C^A of the bridging RCCR(CO) unit is 2.084(3) Å, which is longer than the corresponding Fe^B–C^A distance [1.980(3) Å]; whereas in (**1**) the Fe^A–P^M distance of the PCR(CO) bridging unit [2.295(3) Å] is shorter than the Fe^B–P^M bond length [2.343(2) Å]. This difference presumably reflects the stronger interaction of the metal–π(P=C) bond than that of the metal–π(C=C) bond. In related work on phospha-allenes, $R^1P{=}C{=}CR^2_2$ (R^1 = 2,4,6-

---

† *Crystal data* for (**1**): $C_{36}H_{31}Fe_2O_6P_3\cdot CH_2Cl_2$, M = 849.2, monoclinic, space group $P2_1/c$, a = 18.176(4), b = 11.696(2), c = 18.312(5) Å, β = 100.29(2)°, U = 3830 Å^3, Z = 4, D_c = 1.47 g cm^{-3}, $F(000)$ = 1736. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation, λ = 0.71069 Å, μ = 10.6 cm^{-1}, T = 295 K. 6716 Unique reflections were measured and 4532 having $I > 1\sigma(I)$ were used in the refinement with the SDP program system. The final residuals were R = 0.078, R_W = 0.109. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1. *Reagents and conditions*: i, Bu^{t}CP, u.v., 9 h, toluene; ii, excess RCP (R = Bu^t, adamantyl); iii, Bu^{t}CP; iv, R_2C_2 (R = H).

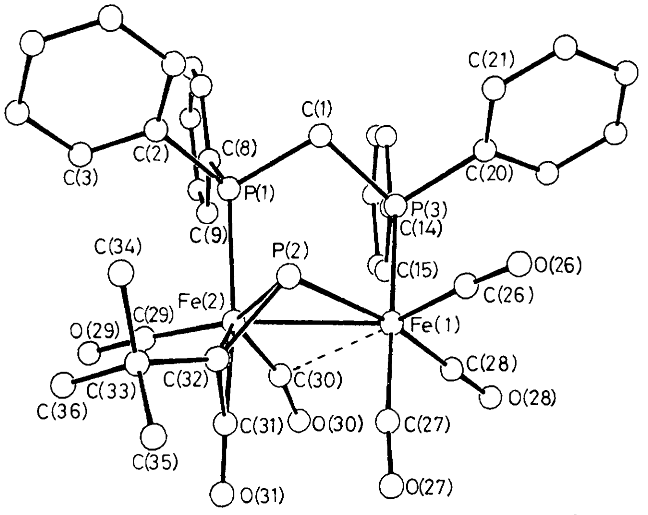


Figure 1. Molecular structure of (**1**). Selected bond lengths (Å) are: Fe(1)–Fe(2) 2.780(2), Fe(1)–P(2) 2.343(2), Fe(1)–P(3) 2.284(2), Fe(2)–P(2) 2.295(3), Fe(2)–P(1) 2.274(2), P(2)–C(32) 1.741(9), C(32)–C(31) 1.450(12), Fe(2)–C(31) 1.965(8).

$Bu^t{}_3C_6H_2$, R^2 = Ph), we have found preferential ligation of the metal–ligand fragments ML_2 (M = Pd, Pt; L = R_3P), to the P=C rather than the C=C unit.[17,18] A further structural difference between (**1**) and (**4**) is the presence of a semi-bridging CO in (**1**) which presumably also results from the enhanced π(P=C)–Fe interaction described above.

The $^{31}P\{^1H\}$ n.m.r. spectrum of (**1**) exhibits an [ABM] pattern {A and B represent dppm resonances, M the RCP(CO) resonance}, indicating that the non-equivalence of the two dppm phosphorus nuclei in the solid state is also maintained in solution at room temperature.‡ The further reactivity of (**1**) towards unsaturated ligands is under investigation.

We thank the S.E.R.C. for financial support (T. J. M.).

Received, 15th May 1989; Com. 9/02015B

References

1 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327, and references therein.
2 P. B. Hitchcock, M. J. Maah, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1986, 737.
3 P. Binger, R. Milczarek, R. Mynott, M. Regitz, and W. Rösch, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 644.
4 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 1146.
5 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1988, **340**, C37.
6 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1988, **356**, C1.
7 R. Bartsch, P. B. Hitchcock, T. J. Madden, M. F. Meidine, J. F. Nixon, and H. Wang, *J. Chem. Soc., Chem. Commun.*, 1988, 1475.
8 R. Bartsch, D. Carmichael, P. B. Hitchcock, M. F. Meidine, J. F. Nixon, and G. J. D. Sillett, *J. Chem. Soc., Chem. Commun.*, 1987, 1615.
9 P. Binger, R. Milczarek, R. Mynott, and M. Regitz, *J. Organomet. Chem.*, 1987, **323**, 1455.
10 P. Binger, B. Biedenbach, R. Mynott, C. Krüger, P. Betz, and M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1988, 1157.
11 P. Binger, B. Biedenbach, R. Mynott, and M. Regitz, *Chem. Ber.*, 1988, **121**, 1455.
12 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 4422.
13 P. B. Hitchcock, M. J. Maah, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 928.
14 G. Becker, W. Herrmann, W. Kalcher, G. W. Kriechbaum, C. Pahl, C. J. Wagner, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 413, *Suppl.* 501.
15 G. Hogarth, F. Kayser, S. A. R. Knox, D. A. V. Morton, A. G. Orpen, and M. L. Turner, *J. Chem. Soc., Chem. Commun.*, 1989, 358.
16 G. Hogarth, S. A. R. Knox, B. R. Lloyd, K. A. Macpherson, D. A. V. Morton, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1988, 360.
17 C. Akpan, D. Phil. Thesis, 1986, University of Sussex.
18 C. Akpan, P. B. Hitchcock, and J. F. Nixon, in preparation.

---

‡ δ (P^A) 52.2; δ (P^B) 50.3; δ (P^M) 316.5 p.p.m. (rel. H_3PO_4); $^2J(P^AP^B)$ 91 Hz; $^2J(P^MP^A)$ ~5 Hz; ^3J (P^MP^B) ~10 Hz.