Journal of Organometallic Chemistry, 340 (1988) C37–C39
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

First examples of η^5- and η^5–η^1-coordination in triphosphorus analogues of ferrocene. Crystal structure of the iron sandwich complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2R_2P_3)W(CO)_5]$ (R = Bu^t)

Rainer Bartsch, Peter B. Hitchcock and John F. Nixon*

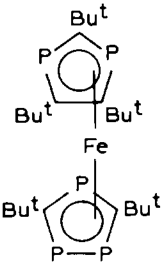
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex (Great Britain)

(Received November 6th, 1987)

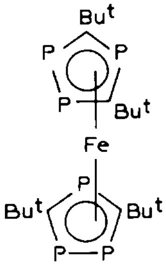
Abstract

Syntheses of the novel sandwich compounds $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2R_2P_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2R_2P_3)W(CO)_5]$, (R = Bu^t), are described. The mode of attachment of the $[W(CO)_5]$ fragment in the latter compound has been determined by NMR and single crystal X-ray diffraction studies.

Recently [1] we described the preparation and structural characterisation of the first examples of penta- and hexa-phosphorus analogues of ferrocene I and II. These complexes have further ligating potential towards other metal centres by use of their phosphorus lone pair electrons. In order to study the steric effects of the R substituents in the $C_2R_2P_3$ and $C_3R_3P_2$ rings (R = Bu^t) on the donor properties of these phosphorus lone pairs we have synthesised the first examples of di- and tri-phosphorus analogues of ferrocene III and IV and studied their interactions with the $[W(CO)_5]$ fragment:

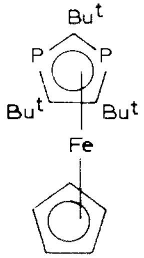


(I)

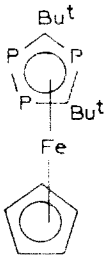


(II)

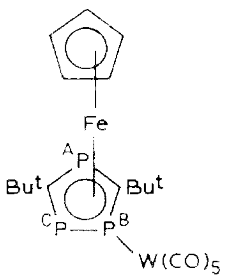
0022-328X/88/$03.50



(III)



(IV)



(V)

Treatment of $FeCl_2$ with a mixture of LiC_5H_5 and $Li(dme)_3$ salts of the $C_2R_2P_3$ and $C_3R_3P_2$ anions [1] (dme = 1,2-dimethoxyethane), affords a mixture of ferrocenes I and II and the new di- and tri-phosphorus ferrocene compounds $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_3R_3P_2)]$ (III, R = Bu^t), and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5C_2R_2P_3)]$ (IV, R = Bu^t).

Compounds III and IV, which can be separated as a mixture from the other products by column chromatography were obtained as orange oils, and fully characterised by their ^1H and ^{31}P NMR spectra *. Because both phosphorus atoms in III are sterically protected by the Bu^t groups, treatment of the mixture of III and IV with $[W(CO)_5THF]$ leads only to the formation of the red-orange, air stable, crystalline complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2R_2P_3)W(CO)_5]$ (V, R = Bu^t) and unchanged III. The structure of V can be elucidated from its ^1H and ^{31}P NMR spectra **. The former shows a singlet at 4.73 ppm (5H) for the C_5H_5 ring and two singlets at 1.41 ppm (9H) and 1.28 ppm (9H) for the two non equivalent Bu^t groups suggesting that the $[W(CO)_5]$ fragment is attached to one of the least sterically hindered phosphorus atoms. This is confirmed by the ^{31}P NMR spectrum of V which exhibits the expected ABC spectrum with only P_B showing further coupling to tungsten.

---

* Preparations of III, IV and V. $FeCl_2$ (127 mg, 1 mmol) was added to 14 ml of a solution containing $Li(C_5H_5)$ (1 mmol) and $Li[C_2Bu^t{}_2P_3]/Li[C_3Bu^t{}_3P_2]$ (1 mmol) in monoglyme and the mixture stirred at room temperature for 16 h. After removal of solvent the residue was extracted with hexane (10 ml) and column chromatography (kieselgel/hexane) afforded ferrocene, the known green complexes I and II, and an orange oily mixture of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_3Bu^t{}_3P_2)]$ (III) and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2Bu^t{}_2P_3)]$ (IV).

A solution containing III and IV (63 mg) in THF was added to a solution of $[W(CO)_5(THF)]$ (100 mg) and the mixture stirred for 3 h at room temperature. Work up as described above gave $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2Bu^t{}_2P_3)W(CO)_5]$ (V) and unchanged III.

** NMR spectra. Δ(H) (ppm) III: 1.34(s), 1.44(s), 4.56(s) (integration ratio 18/9/5); IV: 1.18(s), 4.50(s) ppm (integration ratio 18/5); δ (^{31}P) (relative to phosphoric acid): III +17.2(s); IV AB_2 P_A +38.9 ppm; P_B +37.9 ppm; $J(P_AP_B)$ 45 Hz.

NMR spectrum: V: (^{31}P) ABC $\delta(P_A)$ +30.0 ppm; $\delta(P_B)$ +23.4 ppm; $\delta(P_C)$ +13.3 ppm: $J(P_AP_B)$ 47.7 Hz; $J(P_AP_C)$ 38.8 Hz; $J(P_BP_C)$ 411.6 Hz; $J(P_BW)$ 224 Hz. IR: ν(CO) for V 2060(w), 1920(s) cm^{-1}.

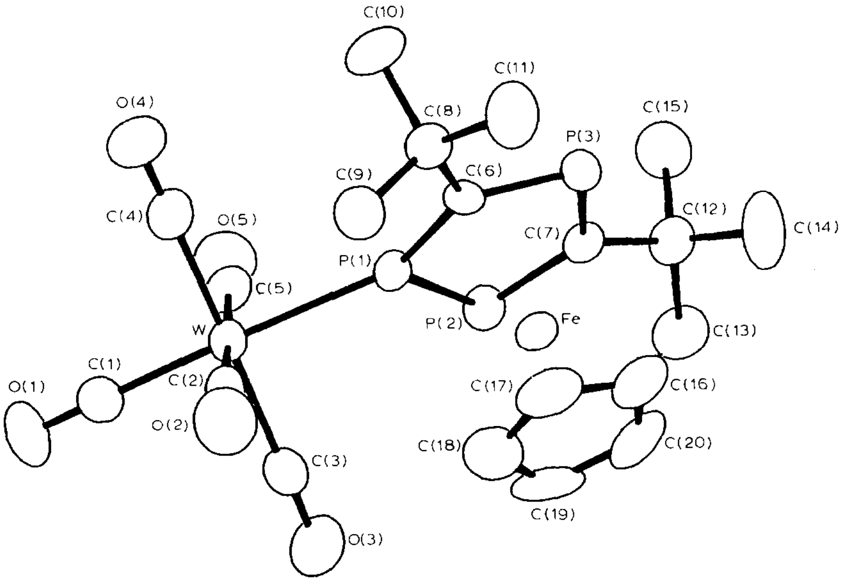


Fig. 1. Molecular Structure of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2R_2P_3)\ W(CO)_5]$ (V). Selected bond lengths; W–P 2.510(2), P(1)–P(2) 2.098(2), P(1)–C(6) 1.753(7), P(2)–C(7) 1.764(8), P(3)–C(6) 1.777(7), P(3)–C(7) 1,.763(6), Fe–P(1) 2.299(2), Fe–P(2) 2.344(3), Fe–P(3) 2.294(2), Fe–C(6) 2.141(4), Fe–C(7) 2.133(8) Å.

The molecular structure of V was confirmed by a single crystal X-ray diffraction study *, indicating that the $C_2R_2P_3$ ring is bonded in an η^5–η^1 fashion to the iron and tungsten atoms, with the iron atom sandwiched between the two five-membered rings (Fig. 1). The geometry of the 2,5-di-t-butyl-1,3,4-triphosphacyclopentadienyl ring in V is hardly changed on complexation from that in I or II. The η^1-P bonded metal lies approximately in the plane of the 2,5-di-t-butyl-1,3,4-triphosphacyclopentadienyl ring.

These results together with our earlier reports [2,3] on the coordinating ability of ligated (P_2C_2) ring systems in syntheses of metal aggregate compounds further underlines the synthetic potential of unsaturated phosphorus ring systems derived from phosphaalkynes RC≡P.

We thank the S.E.R.C for their continuing support for this work, and Dr. A.G. Avent for NMR spectral analysis.

References

1 R. Bartsch, P.B. Hitchcock and J.F. Nixon, J. Chem. Soc. Chem. Commun. (1987) 1146.
2 P.B. Hitchcock, M.J. Maah and J.F. Nixon, J. Chem. Soc. Chem. Commun., (1986) 737.
3 P.B. Hitchcock, M.J. Maah, J.F. Nixon and C. Woodward, J. Chem. Soc. Chem. Commun., (1987) 844.

---

* Crystal data: V, $C_{20}H_{23}FeO_5P_3W$, $M = 676.0$, monoclinic, space group $C2/c$, a 27.878(8), b 11.142(2), c 20.068(5) Å, β 129.86°, U 4784.6 Å^3, $Z = 8$, D_c 1.88 g cm^{-3}, monochromated Mo-K_α radiation, λ 0.71069 Å, μ 57.4 cm^{-1}. The structure was solved by routine heavy atom methods and refined by full matrix least squares with non hydrogen atoms anisotropic, using 3011 unique reflections with $|F^2| > \sigma(F^2)$, measured on an Enraf–Nonius CAD4 diffractometer. Hydrogen atoms were held fixed at calculated positions with B_{iso} of 6.0 Å^2. The final residuals were $R = 0.033$, $R' = 0.038$. Lists of atomic coordinates and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.