Journal of Organometallic Chemistry, 479 (1994) C28–C29

Preliminary Communication

A convenient synthesis of pentaphosphorus analogues of ferrocene $[Fe(\eta^5\text{-}P_2C_3R_3)(\eta^5\text{-}P_3C_2R_2)]$

Paul Binger and Gerald Glaser

Max-Planck-Institut für Kohlenforschung, Postfach 10 13 53,
D-45466 Mülheim an der Ruhr (Germany)

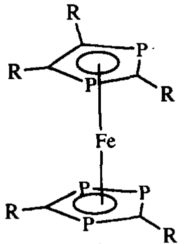
(Received April 22, 1994)

Abstract

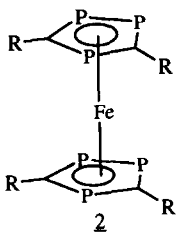
A convenient synthesis is described of the ferrocene analogues $[Fe(\eta^5\text{-}P_2C_3R_3)(\eta^5\text{-}P_3C_2R_2)]$ (**1a**) (R = tert-Bu) and **1b** (R = adamantyl) from bis(cyclooctatetraene)iron(0) (**3**) with the phosphaalkynes **4a** (R = tert-Bu) and **4b** (R = adamantyl).

Key words: Cyclisation; Pentaphospha-ferrocene; Phosphaalkynes; Synthesis; Cyclooligomerisation

Pentaphosphorus and hexaphosphorus analogues of ferrocene $[Fe(\eta^5\text{-}P_2C_3R_3)(\eta^5\text{-}P_3C_2R_2)]$ (**1**) and $[Fe(\eta^5\text{-}P_3C_2R_2)_2]$ (**2**) have recently been prepared by two different routes which are both based on kinetically stabilized phosphaalkynes R–C≡P [**4a** : R = tert-Bu; **4b** : R-adamantyl(ad)] as starting material. The first approach starts with the easily prepared lithium- or sodium salts of $[P_2C_3R_3]^{\ominus}$ and $[P_3C_2R_2]^{\ominus}$ as a mixture, obtained from $Li[P(SiMe_3)_2$ or Na/Hg and the corresponding phosphaalkynes **4a, b** [1,2], which are reacted with $FeCl_2$ to give a mixture of complexes **1** and **2** in 10% yield [3]. The reaction of (η^4-1-methylnaphthaline)(η^6-toluene)iron with the phosphaalkyne **4a** leads inter alia directly to the complexes **1a** and **2a**, but in low yields [4]. The best results for the synthesis of **1** are obtained when the above-mentioned iron(0) complex reacts with five equivalents of **1a**, at −20°C up to room temperature [5]. The disadvantage of both methods is that **1** and **2** can only be obtained contaminated with a series of other complexes which necessitates tedious chromatographic separation.



1

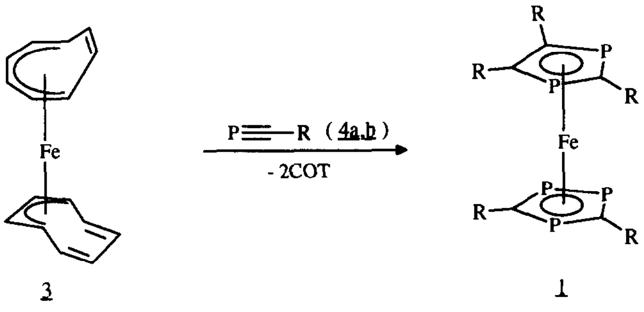


2

We now report a new method for the preparation of the pentaphosphorus analogue of ferrocene **1a, b** by which complexes **1** are directly obtained in pure form as dark-green coloured crystals in reasonable yields; no separations of waste are necessary.

The easily obtainable bis(cyclooctatetraene)iron(0) (**3**) [6,7] reacts smoothly with the kinetically stabilized phosphaalkynes **4a** and **4b** at 80–100°C. After ca. 3 days of heating, the pure iron complex **1** can be obtained by crystallization from pentane as dark-green coloured crystals in yields of 45% (**1a**) and 54% (**1b**). In the reaction mixture **1a** and **1b** are the only products which can be detected by ^{31}P-NMR.

Like ferrocene, the complexes **1a** and **1b** are extremely stable metallorganic compounds which can be handled in air and can be treated with 30% of aqueous H_2O_2 without showing any signs of oxidation. Thermally **1a** remains stable to 216°C, while **1b** can be heated up to 380°C before it decomposes. This thermal stability of **1a, b** is also shown by their mass spectra, which reveals intact molecules as the 100% peak. Their ^{1}H-, ^{13}C- and ^{31}P-NMR spectra are identical with those published earlier [3,4].



a : R = ^{t}Bu
b : R = 1-Ad

Correspondence to: Dr. P. Binger.

0022-328X/94/$7.00
SSDI 0022-328X(94)24740-A

The pathway leading to the formation of **1** by reaction of **3** with five equivalents of **4** is still not well understood, but obviously one of the P≡C triple bonds must be cleaved during the reaction leading to one 1,3-diphospha- and one 1,2,4-triphosphacyclopentadienyl unit. In parallel with these findings, Wilke et al. have published a paper about the formation of pentamethylcyclopentadienyl chromium complexes by oligomerization of five 2-butynes in the coordinationssphere of a chromium(I) species [8]. This dichotomy reaction was explained by the formulation of a C_{10} chain bonded to two chromium atoms which is cleaved giving two five-membered rings as the last step of the reaction sequence. Perhaps the formation of **1** from **3** and **4** could be explained in an analogous manner.

Experimental Part

A solution of the iron complex **3** (0.62 g, 2.35 mmol) and the phosphaalkyne **4b** (40% solution in hexamethyldisiloxane [9]; 6.25 ml, 2.5 g, 14 mmol **4b**) in toluene (50 ml) is heated to 80°C for 3 d; the end of the reaction is determined by ^{31}P-NMR. The toluene is distilled off, the residue redissolved in pentane (40 ml) and cooled to -78°C to give dark-green coloured crystals which are separated by filtration and dried at 10^{-3} mbar; **1b** (1.2 g) is obtained in 54% yield, m.p. 380°C (decomp.). Anal. found: C, 69.59 H, 7.39; calc. for $C_{55}H_{75}P_5Fe$(945.8) C, 69.77 H, 7.93%. MS (70 eV) m/z (%) = 946(100) $[M]^+$, 811(12) $[M - ad.]^+$, 652(57) $[M - C_2ad_2]^+$. ^{31}P-NMR (27°C, $[D_8]$toluene, 81 MHz, H_3PO_4, external) δ (ppm) 41.1 (m (not resolved), P_3-ring), 32.6 (s, P_2-ring).

1a is obtained in an analogous manner from **3** (0.70 g, 2.65 mmol) and **4a** (1.4 g, 14 mmol) after heating to 100°C for 3 days in toluene (5 ml); yield: 0.66 g (45%) as dark-green coloured microcrystals, m.p. 216°C (decomp.). Anal. found: C, 53.86 H, 8.15 P, 27.98, calc. for $C_{25}H_{45}P_5Fe$ C, 53.96 H, 8.09, P 27.87%; ^{31}P-NMR (27°C, $[D_8]$ toluene, 161.5 MHz, H_3PO_4, external). δ (ppm): $AB_2 : 49.0\ (P_A)$; 48.1 $(P_B : J_{P_A,P_B}\text{-}44$ Hz) (P_3-ring); 32.7 (s, P_2-ring). ^{1}H-NMR identical with published data [3].

References

1 G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Weber and M. Westerhausen, *Nova Acta Leopold.*, *59* (1985) 55.

2 R. Bartsch and J.F. Nixon, *Polyhedron*, *8* (1989) 2407.

3 R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1987) 1146.

4 M. Driess, D. Hu, H. Pritzkow, H. Schäufele, U. Zenneck, M. Regitz and W. Rösch, *J. Organomet. Chem.*, *334* (1987) C35.

5 D. Hu, H. Schäufele, H. Pritzkow and U. Zenneck, *Angew. Chem.*, *101* (1989) 929; *Angew. Chem. Int. Ed. Engl.*, *28* (1989) 900.

6 A. Carbonaro, A. Greco and G. Dall'Asta, *J. Organomet. Chem.*, *20* (1969) 177.

7 D.H. Gerlach and R.A. Schunn, *Inorg. Synth.* *15* (1974) 2.

8 G. Wilke, H. Benn, R. Goddard, C. Krüger and B. Pfeil, *Inorg. Chim. Acta*, *200* (1992) 741.

9 Hexamethyldisiloxane is the second reaction product in the synthesis of **4b**. For the preparation of **1b** it is not necessary to separate it completely for **4b**; W. Rösch, U. Vogelbacher, T. Allspach and M. Regitz, *J. Organomet. Chem.*, *306* (1986) 39.