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The peculiar behavior of a diphosphirenium salt towards sodium η^5-cyclopentadienyl(dicarbonyl)ferrate

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Abstract

The reaction of diphosphirenium salt **1** with η^5-cyclopentadienyl(dicarbonyl)ferrate (NaFp) gives the unexpected complex **2** (90%), which features a phosphaalkene η^2-ligated to the metal. In contrast, treatment of **1** with sterically hindered nucleophiles [Ph_2PLi, $(Me_3Si)_2PLi$, $Mes(Me_3Si)_2SiLi$, Me_3SnLi] affords the corresponding *P*-substituted-*C*-phosphanyl phosphaalkenes **3a**–**d**. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus; Iron; Three-membered ring; Cyclopropenium; Phosphaalkenes

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1. Introduction

The interaction of transition metal complexes with strained cyclopropenylium cations **A** has been widely studied and several different types of ligation modes have been observed [1–3]. Particularly, due to their aromatic character [4] numerous η^3-complexes of cyclopropenylium cations **A1** have been prepared [3]. In the corresponding phosphorus series, the phosphirenylium cation **B**, the simplest 2π-aromatic species containing phosphorus, has been complexed in a η^3-fashion to an electron-rich Ni^0 center giving **B1** [5,6], whereas the diphosphirenylium cation **C** has been ligated in a η^2-manner to tungstenpentacarbonyl as **C1** [7]. Obviously, diphosphirenium salts **D** are not Hückel aromatic systems because of the absence of a p orbital at the σ^4-phosphorus center; however heterocycles **D** are cationic σ^* aromatic derivatives [8] and therefore several ligation modes are potentially accessible. So far, only the insertion of a palladium(0) fragment into the P–P bond of the ring giving **D1** has been observed [9].

Here we report, the surprising fate of the reaction of the diphosphirenium salt **1** with sodium η^5-cyclopentadienyl (dicarbonyl)ferrate (NaFp), (see Scheme 1).

2. Results and discussion

The diphosphirenium salts **1** [10a] react with NaFp in THF solution at −78°C giving **2** in 90% yield (Scheme 2). The ^{31}P-NMR spectrum indicates the complete transformation of **1**, and displays a new AX system [δ: −27.6 and 90.7, $J_{PP} = 217.8$ Hz]. The relatively low field chemical shift of one of the signal indicated the absence of three-membered ring [11], while the large phosphorus-phosphorus coupling constant suggested the presence of a P–P bond. Single crystals of **2**, suitable for an X-ray diffraction study, were obtained from a chloroform solution at −20°C. The molecular structure of **2** (Fig. 1) confirms the cleavage of a carbon-phosphorus bond of the ring and the presence of the P–P bond [2.2557(16) Å]. Derivative **2** features a phosphaalkene moiety η^2-ligated to the metal center (P1Fe1: 2.3004 and Fe1C1: 2.279 Å). As a consequence of this mode of ligation the P=C bond length (1.804 Å) is increased in comparison with the typical value in uncoordinated phosphaalkenes [12]. However, the sum of bond angles at C1 is 356.6°, indicating that the geometry around this atom remains almost planar.

The formation of complex **2** with conservation of the phosphorus–phosphorus bond was totally unexpected. Indeed, we have already shown that the diphosphire-

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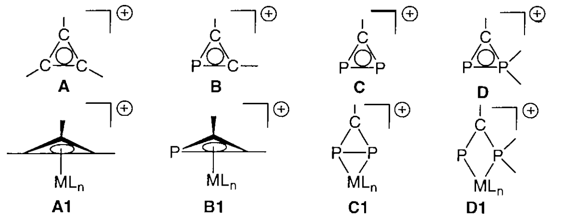
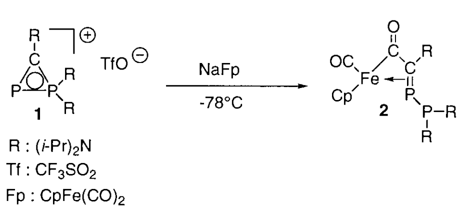
nium salt **1** reacted with nucleophiles such as amides or hydrides affording the corresponding *P*-substituted phosphaalkenes, by cleavage of the phosphorus–phosphorus bond [10b][13]. In the same way, we have checked that the addition of various lithium salts including sterically hindered ones such as of diphenylphosphide, bis(trimethylsilyl)phosphide, bis(trimethylsilyl)mesitylsilyl and trimethylstannyl cleanly led to the corresponding *P*-substituted-*C*-phosphanyl phosphaalkenes **3a–d** (see Scheme 3).



Scheme 1.



Scheme 2.

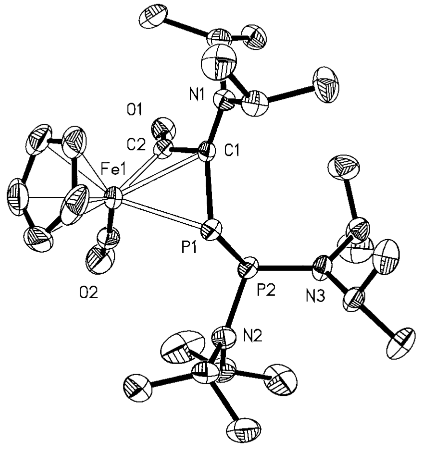
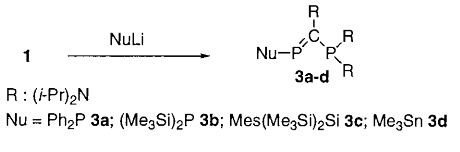


Fig. 1. Selected bond lengths (Å) and angles (°) for compound **2**. P(1)–P(2) 2.2557(16); P(1)–C(1) 1.804(4); C(1)–N(1) 1.371(5); C(1)–C(2) 1.465(5); C(2)–O(1) 1.199(5); Fe(1)– P(1) 2.3004(14); Fe(1)–C(1) 2.279(3); Fe(1)–C(2) 1.918(5); Fe(1)–C(3) 1.723(5); C(3)–O(2) 1.151(5); P(2)–P(1)–C(1) 98.71(13); P(2)–P(1)–Fe(1) 106.48(6); C(1)–P(1)–Fe(1) 66.19(10); P(1)–C(1)–C(2) 109.0(3); P(1)–C(1)–N(1) 125.3(3); C(2)–C(1)–N(1) 122.3(4).



Scheme 3.

The different behaviour of **1** towards NaFp, with respect to the other nucleophiles used, suggests a different pathway. A SET mechanism, in the case of $CpFe(CO)_2^-$ might be envisaged, since **1** undergoes facile one-electron reduction [14], and the involvement of NaFp in this type of pathway has been established [15].

3. Experimental

3.1. General

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on Brucker AC80, AC200, WM250 or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P-NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

*3.2. Synthesis of complex **2***

To a THF solution (5 ml) of diphosphirenium salt **1** (0.46 g, 1 mmol) was added at −78°C a THF solution (5 ml) of $NaFeCp(CO)_2$ (0.2 g, 1 mmol). The solution mixture was stirred for 1 h at −78°C, and after warming to 0°C the salts ($NaBF_4$) were precipitated by adding pentane, and separated by filtration. After evaporation of the solvents compound **2** was obtained as a red solid (0.50 g, 90%). All the operations must be performed at 0°C because **2** slowly decomposes at r.t. Single crystals of **2**, suitable for an X-ray diffraction analysis were obtained from a $CHCl_3$ solution at −20°C. MS (NH_3, CI): *m/z*: 552 [M + 1]. IR (THF): ν(C=O) = 1712, 1957 cm^{-1}. ^{31}P{^{1}H}-NMR (32 MHz, C_7D_8, 213 K): $\delta = -27.6$ (d, ^{1}J(P,P) = 217.8 Hz, =P–), 90.7 (d, ^{1}J(P,P) = 217.8 Hz, $(R_2N)_2P$); ^{1}H-NMR (400 MHz, C_7D_8): $\delta = 4.78$ (m, 1 H, CNCH), 4.56 (s, 5 H, Cp), 4.23 (m d, ^{3}J(P,H) = 6.0 Hz, 2 H, PNCH), 3.82 (m, 2 H, PNCH), 3.20 (m, 1 H, CNCH), 1.68 (m, 3 H, $NCHCH_3$), 1.62 (d, ^{3}J(H,H) = 6.6 Hz, 6 H, $PNCHCH_3$), 1.52 (d, ^{3}J(H,H) = 6.6 Hz, 6 H, $PNCHCH_3$), 1.48 (d, ^{3}J(H,H) = 6.8 Hz, 6 H, $PNCHCH_3$), 1.45 (d, ^{3}J(H,H) = 6.8 Hz, 6 H, $PNCHCH_3$), 1.31 (d, ^{3}J(H,H) = 6.4 Hz, 3 H, $NCHCH_3$), 1.22 (d, ^{3}J(H,H) = 6.2 Hz, 3 H, $NCHCH_3$), 0.93 (d, ^{3}J(H,H) = 5.9 Hz, 3 H, $NCHCH_3$); ^{13}C{^{1}H}-NMR (100 MHz, C_7D_8): δ = 250.0 (s, C=O), 218.2 (d, ^{2}J(P,C) = 17.7 Hz, C=O), 93.1 (dd, ^{1}J(P,C) = 61.6 and 45.9 Hz, P=C), 85.2 (s, Cp), 51.1 (dd, J(P,C) = 15.4 and 8.1 Hz, NCH), 50.7 (d, J(P,C) = 26.3 Hz, NCH), 47.8 (dd, J(P,C) = 11.1 and 1.8 Hz, NCH), 47.7 (s, NCH), 25.7 (d, ^3J(P,C) = 10.1 Hz, CH_3CHN), 25.3 (d, ^3J(P,C) = 1.7 Hz, CH_3CHN), 25.2 (s, CH_3CHN), 24.2 (d, ^3J(P,C) = 5.8 Hz, CH_3CHN), 24.2 (d, ^3J(P,C) = 5.8 Hz, CH_3CHN).

3.3. Synthesis of phosphaalkene ***3a***

To a THF solution (5 ml) of diphosphirenium salt **1** (0.46 g, 1 mmol) was added at − 78°C a THF solution (5 ml) of Ph_2PLi (0.19 g, 1 mmol). The solution mixture was stirred for 1 h at − 78°C, and after warming to r.t. the solvent was evaporated under vacuum. The residue was dissolved in pentane and filtered. After evaporation of pentane compound **3a** was obtained as a yellow oil (0.44 g, 80%). $^{31}P\{^1H\}$-NMR (32 MHz, C_6D_6): $\delta = - 9.7$ (d, ^1J(P,P) = 305.5 Hz, Ph_2P), 57.8 (d, ^2J(P,P) = 26.2 Hz, $(R_2N)_2P$), 85.3 (dd, ^1J(P,P) = 305.5 Hz, ^2J(P,P) = 26.2 Hz, $Ph_2P–P = C$); ^1H-NMR (200 MHz, C_6D_6): $\delta = 7.76–7.70$ (m, 4 H, H_{aro}), 7.16–7.00 (m, 6 H, H_{aro}), 5.09 (sept d, ^3J(H,H) = 7.1 Hz, ^4J(P,H) = 7.2 Hz, 2 H, CNCH), 3.94 (sept d, ^3J(H,H) = 6.6 Hz, ^3J(P,H) = 1.4 Hz, 4 H, PNCH), 1.25 (d, ^3J(H,H) = 6.6 Hz, 12 H, $PNCHCH_3$), 1.24 (d, ^3J(H,H) = 7.1 Hz, 12 H, $NCHCH_3$), 1.21 (d, ^3J(H,H) = 6.6 Hz, 12 H, $PNCHCH_3$); $^{13}C\{^1H\}$-NMR (50 MHz, C_6D_6): $\delta = 205.3$ (ddd, J(P,C) = 135.7, 51.3 and 3.4 Hz, P=C–P), 141.8 (dd, J(P,C) = 24.0 and 10.6 Hz, C_i), 134.0 (dd, J(P,C) = 17.4 and 3.8 Hz, C_o), 128.0 (d, ^3J(P,C) = 5.8 Hz, C_m), 127.4 (s, C_m), 54.4 (ddd, J(P,C) = 17.0, 14.8 and 2.4 Hz, CNCH), 47.6 (dd, J(P,C) = 12.9 and 5.1 Hz, PNCH), 23.9 (d, ^3J(P,C) = 6.6 Hz, CH_3), 23.8 (d, ^3J(P,C) = 5.8 Hz, CH_3), 22.7 (s, $NCHCH_3$). $C_{31}H_{52}N_3P_3$: Anal. Calc. C, 66.53; H, 9.36; N, 7.51. Found C, 66.75; H, 9.50; N, 7.32%.

3.4. Synthesis of phosphaalkene ***3b***

To a THF solution (5 ml) of diphosphirenium salt **1** (0.46 g, 1 mmol) was added at − 78°C a THF solution (5 ml) of $(Me_3Si)_2PLi$ (0.18 g, 1 mmol). The solution mixture was stirred for 1 h at − 78°C, and after warming to r.t. the solvent was evaporated under vacuum. The residue was dissolved in pentane and filtered. After evaporation of pentane compound **3b** was obtained as a yellow oil (0.44 g, 80%). $^{31}P\{^1H\}$-NMR (32 MHz, C_6D_6): $\delta = - 175.2$ (d, ^1J(P,P) = 234.7 Hz, $(Me_3Si)_2P$), 58.2 (d, ^2J(P,P) = 28.4 Hz, $(R_2N)_2P$), 64.8 (dd, ^1J(P,P) = 234.7 Hz, ^2J(P,P) = 28.4 Hz, $(Me_3Si)_2P–P=C$); ^1H-NMR (200 MHz, C_6D_6): $\delta = 5.43$ (sept, ^3J(H,H) = 7.1 Hz, 2 H, CNCH), 3.96 (sept d, ^3J(H,H) = 6.7 Hz, ^3J(P,H) = 1.7 Hz, 4 H, PNCH), 1.33 (d, ^3J(H,H) = 7.1 Hz, 12 H, $NCHCH_3$), 1.30 (d, ^3J(H,H) = 6.7 Hz, 12 H, $PNCHCH_3$), 1.27 (d, ^3J(H,H) = 6.7 Hz, 12 H, $PNCHCH_3$), 0.44 (d, ^3J(H,H) = 4.2 Hz, 18 H, Si–CH_3); $^{13}C\{^1H\}$-NMR (50 MHz, C_6D_6): $\delta = 209.0$ (ddd, J(P,C) = 143.1, 50.6 and 5.6 Hz, P=C–P), 53.6 (dd, J(P,C) = 21.6 and 12.9 Hz, NCH), 47.5 (dd, J(P,C) = 13.1 and 5.5 Hz, NCH), 23.8 (d, ^3J(P,C) = 5.8 Hz, CH_3CHN), 23.0 (s, CH_3CHN), 1.9 (d, ^2J(P,C) = 11.8 Hz, Si–CH_3). $C_{25}H_{60}N_3P_3Si_2$: Anal. Calc. C, 54.41; H, 10.96; N, 16.84. Found C, 54.62; H, 11.11; N, 16.88%.

3.5. Synthesis of phosphaalkene ***3c***

To a THF solution (5 ml) of diphosphirenium salt **1** (0.38 g, 0.82 mmol) was added at − 78°C a THF solution (5 ml) of $Mes(Me_3Si)_2SiLi$ (0.27 g, 0.88 mmol). The solution mixture was stirred for 1 h at − 78°C, and after warming to r.t. the solvent was evaporated under vacuum. The residue was dissolved in pentane and filtered. After evaporation of pentane the yellow solid was recrystallized at − 20°C in an ether–acetonitrile solution to afford yellow crystals of **3c** (0.39 g, 66%). M.p. 95–97°C; $^{31}P\{^1H\}$-NMR (32 MHz, C_6D_6): AB system $\delta = 59.4$ (^2J(P,P) = 25.3 Hz); ^1H-NMR (400 MHz, C_6D_6): $\delta = 6.90$ (s, 2 H, H_{aro}), 5.00 (m, 2 H, CNCH), 4.17 (sept d, ^3J(H,H) = 6.0 Hz, ^3J(P,H) = 7.0 Hz, 4 H, PNCH), 2.80 (s, 6 H, Ar–CH_3), 2.24 (s, 3 H, Ar–CH_3), 1.48 (d, ^3J(H,H) = 6.0 Hz, 12 H, $PNCHCH_3$), 1.44 (d, ^3J(H,H) = 6.0 Hz, 12 H, $PNCHCH_3$), 1.30–1.00 (m, 12 H, $CNCHCH_3$), 0.60 (s, 18 H, Si–CH_3); $^{13}C\{^1H\}$-NMR (50 MHz, C_6D_6): $\delta = 145.2$ (s, C_{aro}), 137.8 (s, C_{aro}), 129.3 (s, C_{aro}), 128.7 (s, C_{aro}), 48.0 (dd, ^3J(P,C) = 11.6 Hz and ^5J(P,C) = 5.7 Hz, PNCH), 27.5 (s, *o*-CH_3), 24.9 (d, ^3J(P,C) = 6.7 Hz, $PNCHCH_3$), 24.7 (d, ^3J(P,C) = 6.5 Hz, $PNCHCH_3$), 23.4 (s, $NCHCH_3$), 21.4 (s, *p*-CH_3), 3.4 (d, ^3J(P,C) = 2.6 Hz, Si–CH_3). $C_{34}H_{71}N_3P_2Si_3$: Anal. Calc. C, 61.12; H, 10.71; N, 6.29. Found: C, 61.04; H, 11.00; N, 5.90%.

3.6. Synthesis of phosphaalkene ***3d***

To a THF solution (5 ml) of diphosphirenium salt **1** (0.46 g, 1 mmol) was added at − 78°C a THF solution (5 ml) of Me_3SnLi (0.17 g, 1 mmol). The solution mixture was stirred for 1 h at − 78°C, and after warming to r.t. the solvent was evaporated under vacuum. The residue was dissolved in pentane and filtered. After evaporation of the pentane compound, **3d** was obtained as a yellow oil (0.37 g, 70%). ^{31}P-NMR (32 MHz, C_6D_6): $\delta = 49.3$ (d, ^1J(P,P) = 20.7 Hz, $Me_3Sn–P$), 57.2 (d, ^2J(P,P) = 20.7 Hz, $(R_2N)_2P$); ^1H-NMR (200 MHz, C_6D_6): $\delta = 5.21$ (sept, ^3J(H,H) = 7.0 Hz, 2 H, CNCH), 4.05 (sept d, ^3J(H,H) = 6.6 Hz, ^3J(P,H) = 1.3 Hz, 4 H, PNCH), 1.31 (d, ^3J(H,H) = 6.6 Hz, 12 H, $PNCHCH_3$), 1.25 (d, ^3J(H,H) = 6.6 Hz, 12 H, $PNCHCH_3$), 1.24 (d, ^3J(H,H) = 7.0 Hz, 12 H, $NCHCH_3$), 0.41 (d, ^3J(H,H) = 1.7 Hz, 9 H, Sn–CH_3); $^{13}C\{^1H\}$-NMR (50 MHz, C_6D_6): $\delta = 213.6$ (dd,

$^{1}J(\mathrm{P,C}) = 145.9$, 51.0 Hz, P=C–P), 53.8 (dd, $J(\mathrm{P,C}) = 20.2$ and 3.4 Hz, NCH), 48.0 (dd, $J(\mathrm{P,C}) = 12.9$ and 4.7 Hz, NCH), 24.6 (d, $^{3}J(\mathrm{P,C}) = 6.8$ Hz, CH_3CHN), 24.5 (d, $^{3}J(\mathrm{P,C}) = 7.7$ Hz, CH_3CHN), 22.9 (s, CH_3CHN), -4.5 (d, $^{2}J(\mathrm{P,C}) = 5.2$ Hz, Sn–CH_3); ^{119}Sn NMR (C_6D_6): $\delta = -41.3$ (dd, $^{1}J(\mathrm{P,Sn}) = 1483.6$ Hz, $^{3}J(\mathrm{P,sn}) = 11.5$ Hz, Me_3Sn–P). $C_{22}H_{51}N_3P_2Sn$: Anal. Calc. C, 49.09; H, 9.55; N, 7.81. Found C, 48.85; H, 9.41; N, 7.75%.

3.7. Crystal-structure determination of **2**

$C_{26}H_{47}FeN_3O_2P_2$, M = 551.46, triclinic, $P\bar{1}$, $a = 7.926(2)$, $b = 10.024(3)$, $c = 19.379(5)$ Å, $\alpha = 99.64(3)$, $\beta = 93.43(3)$, $\gamma = 105.07(3)°$, $V = 1457.1(7)$ Å^3, $Z = 2$, D_{calc} 1.257 Mg m^{-3}, $F(000) = 592$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, μ (Mo–K_α) $= 0.654$ mm^{-1}, crystal size $0.3 \times 0.3 \times 0.1$ mm, $2.14 = \theta = 22.98°$, 7626 reflections (3851 independent, $R_{int} = 0.0889$) were collected at low temperatures using an oil-coated shock-cooled crystal on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97) [16] and 340 parameters were refined using the least-squares method on F^2 [17]. Largest electron density residue: 0.321 e Å^{-3}, $R_1 = 0.0493$ (for $F > 2\sigma(F)$) and $wR_2 = 0.1024$ (all data).

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 142845. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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