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Communications

Synthesis and Structure of a 1,1′-Diphospha[2]ferrocenophane

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*Summary: A four-step sequence allows us to transform 1-phenyl-3,4-dimethylphosphole-2-carboxaldehyde (**1**) into the bis(phosphole) **5** with a CH_2CH_2 bridge between the two α-carbons. The cleavage of the two P−phenyl bonds of **5** by lithium, followed by the reaction of the bis(phospholide) thus formed with $FeCl_2$, gives the corresponding 1,1′-diphospha[2]ferrocenophane **7**, which displays a tilt angle of 20°.*

Stabilized sp^2 phosphorus derivatives have recently emerged as a new class of π-acceptor ligands, more similar to carbon monoxide than to classical phosphines.[1] This led to the first attempts to use them in homogeneous catalysis. In practice, these attempts have been essentially restricted to aromatic species such as phosphinines[2] and phosphaferrocenes.[3] In view of these promising developments, it seemed interesting to devise an access to polymers incorporating sp^2 phosphorus centers. It is now well-established that the strained [1]- and [2]ferrocenophanes can be efficiently used in the synthesis of ferrocene-based polymers by ring-opening polymerization.[4] A transposition of this route for the synthesis of 1,1′-diphosphaferrocene-based polymers looked attractive. With these ideas in mind, we decided to synthesize a 1,1′-diphospha[2]ferrocenophane.[5]

Our starting product was the previously described 1-phenyl-3,4-dimethylphosphole-2-carboxaldehyde (**1**).[6] A conventional $NaBH_4$ reduction followed by sulfurization afforded the 2-hydroxymethylphosphole sulfide **2** (Scheme 1).

The reaction of **2** with Ph_3PBr_2 then gave the 2-bromomethylphosphole sulfide **3**. As might be expected, the corresponding tervalent derivative is highly instable and tends to self-quaternize. This is the reason why it is necessary to work in the P−sulfide series. The bromomethyl derivative **3** was then allowed to react with

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[1] For a general review on this class of compounds, see: Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, U.K., 1998.

[2] (a) Breit, B. *J. Chem. Soc., Chem. Commun.* **1996**, 2071. (b) Breit, B.; Winde, R.; Harms, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2681. (c) Knoch, F.; Kramer, F.; Schmidt, U.; Zenneck, U.; Le Floch, P.; Mathey, F. *Organometallics* **1996**, *15*, 831. (d) Le Floch, P.; Knoch, F.; Kramer, F.; Mathey, F.; Scholz, J.; Scholz, W.; Thiele K.-H.; Zenneck, U. *Eur. J. Inorg. Chem.* **1998**, 119.

[3] (a) Ganter, C.; Brassat, L.; Glinsböckel, C.; Ganter, B. *Organometallics* **1997**, *16*, 2682. (b) Ganter, C.; Brassat, L.; Ganter, B. *Chem. Ber./Recl.* **1997**, *130*, 1771. (c) Ganter, C.; Brassat, L.; Ganter, B. *Tetrahedron: Asymmetry* **1997**, *8*, 2607. (d) Ganter, C.; Glinsböckel, C.; Ganter, B. *Eur. J. Inorg. Chem.* **1998**, 1163. (e) Garrett, C. E.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 4534. (f) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1998**, *17*, 773. (g) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168.

[4] Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1603.

[5] A low-yield synthesis of a 1,3,1′,3′-tetraphospha[3]ferrocenophane has been previously described: Sierra, M. L.; Maigrot, N.; Charrier, C.; Ricard, L.; Mathey, F. *Organometallics* **1992**, *11*, 459.

[6] Deschamps, E.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 486.

[7] While C−C coupling of organic halides by magnesium in THF is not a classical reaction, it has some precedent in the literature, for example, with halo sugars: Ariatti, M.; Zemlicka, J. *J. Org. Chem.* **1981**, *46*, 5204.

[8] **2** was chromatographed on silica gel with CH_2Cl_2 as eluent. ^{31}P NMR ($CDCl_3$): δ +49.2. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.09 (d, 3H, $^{4}J_{HP}$ = 2.4 Hz, CH_3), 2.17 (dd, 3H, $^{4}J_{HH} \approx {}^{4}J_{HP}$ = 1.8 Hz, CH_3), 4.45 (m, 2H, CH_2), 6.14 (dd, 1H, $^{2}J_{HP}$ = 30.9 Hz, CH−P), 7.48 (m, 3H, Ph), 7.85 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.52 (d, $^{3}J_{C-P}$ = 14.2 Hz, CH_3), 18.03 (d, $^{3}J_{C-P}$ = 17.5 Hz, CH_3), 57.02 (d, $^{2}J_{C-P}$ = 12.4 Hz, CH_2O), 123.31 (d, $^{1}J_{C-P}$ = 82.5 Hz, CH−P), 127.09 (d, $^{1}J_{C-P}$ = 76.6 Hz, C−P), 128.82 (d, J_{C-P} = 12.4 Hz, CH(Ph)), 130.52 (d, J_{C-P} = 12.0 Hz, CH(Ph)), 132.10 (d, $^{4}J_{C-P}$ = 2.5 Hz, CH para), 136.10 (d, $^{1}J_{C-P}$ = 79.6 Hz, C ipso), 147.74 (d, $^{2}J_{C-P}$ = 24.3 Hz, *C*Me), 155.24 (d, $^{2}J_{C-P}$ = 17.1 Hz, *C*Me). MS (EI, 70 eV): *m*/*z* 250 (M^+, 100). Anal. Calcd. for $C_{13}H_{15}OPS$: C, 62.38; H, 6.04. Found: C, 62.31; H, 5.99. **3** was separated from Ph_3PO by chromatography with CH_2Cl_2 (unstable). ^{31}P NMR (Et_2O): δ +49.4. ^{1}H NMR ($CDCl_3$): δ 2.07 (d, 3H, $^{4}J_{HP}$ = 2.4 Hz, CH_3), 2.15 (dd, 3H, $^{4}J_{HH} \approx {}^{4}J_{HP}$ = 1.8 Hz, CH_3), 4.17 (*A*BX, 1H, $^{2}J_{H-H}$ = 10.8 Hz, $^{3}J_{H-P}$ = 26.4 Hz, CH_2Br), 4.26 (A*B*X, 1H, $^{2}J_{H-H}$ = 10.8 Hz, $^{3}J_{H-P}$ = 17.9 Hz, CH_2Br), 6.16 (dd, 1H, $^{2}J_{H-P}$ = 30.8 Hz, CH−P), 7.40 (m, 3H, Ph), 7.80 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 13.73 (d, $^{3}J_{C-P}$ = 13.7 Hz, CH_3), 17.83 (d, $^{3}J_{C-P}$ = 16.9 Hz, CH_3), 21.75 (d, $^{2}J_{C-P}$ = 16.6 Hz, CH_2Br), 124.9 (d, $^{1}J_{C-P}$ = 82.8 Hz, CH−P), 126.56 (d, $^{1}J_{C-P}$ = 77.7 Hz, C−P), 128.36 (d, J_{C-P} = 12.4 Hz, CH(Ph)), 130.82 (d, J_{C-P} = 12.1 Hz, CH(Ph)), 132.00 (d, $^{4}J_{C-P}$ = 2.6 Hz, CH para), 133.48 (d, $^{1}J_{C-P}$ = 84.1 Hz, C ipso), 150.62 (d, $^{2}J_{C-P}$ = 24.6 Hz, *C*Me), 154.50 (d, $^{2}J_{C-P}$ = 15.3 Hz, *C*Me). MS: *m*/*z* 214 (M^+, ^{81}Br, 27), 212 (M^+, ^{79}Br, 26), 233 ($M^+ -$ Br, 100). **4** was chromatographed on silica gel with CH_2Cl_2. ^{31}P NMR (CH_2Cl_2): δ +49.6; ^{1}H NMR ($CDCl_3$): δ 1.94 (d, 6H, $^{4}J_{HP}$ = 2.5 Hz, CH_3), 2.11 (dd, 6H, $^{4}J_{HH} \approx {}^{4}J_{HP}$ = 1.8 Hz, CH_3), 2.30 (m, 4H, CH_2), 6.02 (dd, 2H, $^{2}J_{H-P}$ = 30.8 Hz, CH−P), 7.37 (m, 6H, Ph), 7.72 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.24 (d, $^{3}J_{C-P}$ = 15.4 Hz, CH_3), 18.82 (d, $^{3}J_{C-P}$ = 17.7 Hz, CH_3), 25.90 (d, $^{2}J_{C-P}$ = 12.9 Hz, CH_2), 122.63 (d, $^{1}J_{C-P}$ = 82.6 Hz, CH−P), 128.47 (d, $^{2}J_{C-P} \approx$ 75 Hz, C−P), 129.34 (d, J_{C-P} = 12.2 Hz, CH(Ph)), 131.14 (d, J_{C-P} = 11.0 Hz, CH(Ph)), 132.46 (d, $^{4}J_{C-P}$ = 2.8 Hz, CH para), 137.57 (d, $^{1}J_{C-P}$ = 77.9 Hz, C ipso), 146.65 (d, $^{2}J_{C-P}$ = 24.6 Hz, *C*Me), 156.32 (d, $^{2}J_{C-P}$ = 18.2 Hz, *C*Me). MS: *m*/*z* 466 (M^+, 100), 433 ($M^+ -$ SH, 77), 233 ($M^+/2$, 52), 201 ($M^+/2 -$ S, 81). Anal. Calcd for $C_{26}H_{28}P_2S_2$: C, 66.93; H, 6.05. Found: C, 66.64; H, 6.01. **5**: $SP(CH_2CH_2CN)_3$ and excess $P(CH_2CH_2CN)_3$ were removed by filtration at room temperature; the evaporation of xylene yielded crude **5** as a white powder very sensitive toward oxidation. ^{31}P NMR (CH_2Cl_2): δ +2.0 and +2.2. ^{1}H NMR (CD_2Cl_2) δ 1.83 (s br, 6H, CH_3), 2.08 (dd, 6H, $^{4}J_{H-H}$ = 1.4 Hz, $^{4}J_{H-P}$ = 3.1 Hz, CH_3), 6.25 (d, 2H, $^{2}J_{H-P}$ = 39.0 Hz, CH−P), 7.21−7.23 (2 s br, 10H, Ph). ^{13}C NMR (CD_2Cl_2): δ 13.72 (s, CH_3), 18.92 (s, CH_3), 30.89 (m, CH_2), 125.40 (quasi s, CH−P), 142.19 (d, $^{2}J_{C-P}$ = 12.3 Hz, *C*Me), 146.70 (d, $^{2}J_{C-P}$ = 8.9 Hz, *C*Me), 151.72 (quasi s, P−*C*−CH_2). MS: *m*/*z* 402 (M^+, 14), 278 (100), 201 ($M^+/2$, 100).

[9] Mathey, F.; de Lauzon, G. *Organometallic Synthesis* **1986**, *3*, 256.

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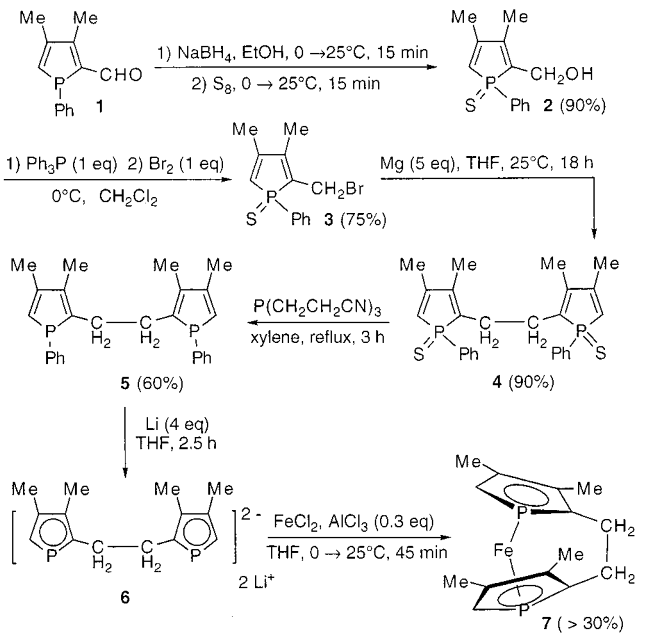
Scheme 1



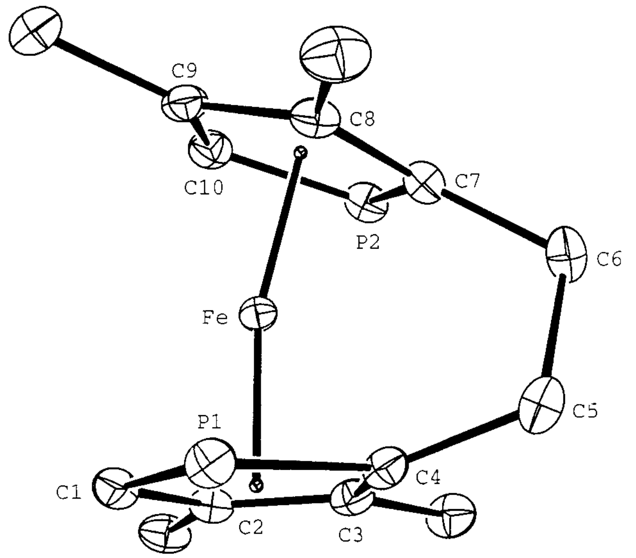


Figure 1. X-ray crystal structure of **7**. Selected bond lengths (Å) and angles (deg): P(1)–C(1) = 1.765(1), P(1)–C(4) = 1.788(1), C(1)–C(2) = 1.423(2), C(2)–C(3) = 1.434(2), C(3)–C(4) = 1.435(2), C(4)–C(5) = 1.520(2), C(5)–C(6) = 1.555(2), C(6)–C(7) = 1.530(2), Fe–phospholyl = 1.6469(1) (P$_2$) and 1.6475(1) (P$_1$); C(1)–P(1)–C(4) = 89.42(5), P(1)–C(1)–C(2) = 113.88(8), C(1)–C(2)–C(3) = 112.0(1), C(2)–C(3)–C(4) = 111.77(9), P(1)–C(4)–C(3) = 112.70(8), P(1)–C(4)–C(5) = 121.55(8), C(3)–C(4)–C(5) = 124.33(9), C(4)–C(5)–C(6) = 112.0(1), C(5)–C(6)–C(7) = 111.59(9), C(6)–C(7)–C(8) = 123.7(1), C(6)–C(7)–P(2) = 122.36(8).

magnesium in THF. The reaction provides the coupled product **4** in high yield.[7] It is interesting to note that, when the P=O analogue of **3** is used, the reaction almost fails probably because magnesium is deactivated by coordination with the phosphoryl group. The reduction of the disulfide **4** by an excess of P(CH$_2$CH$_2$CN)$_3$ in boiling xylene afforded the corresponding diphosphole **5** in 60% isolated yield as a 1:1 mixture of the two possible diastereomers. In contrast to the case for **2**–**4**, the characterization of **5** was minimal because it proved to be extremely sensitive toward oxidation.[8] The cleavage of the two P–Ph bonds of **5** was then classically carried out with lithium in THF. The two diastereomers of **5** afford the diphospholide **6** as a single product (δ-(^{31}P) +51). The dianion was then reacted with FeCl$_2$ in the presence of AlCl$_3$ by following an optimized synthetic procedure.[9] The [2]ferrocenophane **7** was obtained as a *single isomer*.[10] The structure is shown in Figure 1.[11] The two phospholyls are in a head-to-tail disposition. The angle between the two mean planes is 20.00 ± 0.03°. The strain within **7** is apparently very similar to that existing in its all-carbon analogues.[12] The polymerization of **7** and other possible applications of **5** and **6** are currently under active investigation.

Supporting Information Available: Tables giving X-ray crystallographic data for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] **7**: after filtration on a deoxygenated Florisil column with hexane, the residue was crystallized in EtOH. ^{31}P NMR (CH$_2$Cl$_2$): δ −34. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.08 (s, 6H, CH$_3$), 2.56 (d, 6H, $^{4}J_{\text{H-P}} = 2.1$ Hz, CH$_3$), 2.51–2.58 (m, 4H, CH$_2$), 3.57 (d, 2H, $^{2}J_{\text{H-P}} = 36.5$ Hz, CH–P). ^{13}C NMR (CD$_2$Cl$_2$): δ 15.46 (m, CH$_3$), 16.12 (s, CH$_3$), 32.35 (pseudo t, $J_{\text{C-P}} = 24.0$ Hz, CH$_2$), 81.58 (d, $^{1}J_{\text{C-P}} = 61.0$ Hz, CH–P), 96.66 and 97.44 (2 pseudo s, *C*Me), 99.94 (d, $^{1}J_{\text{C-P}} = 63.2$ Hz, C–P). MS: *m/z* 304 (M$^+$, 100). UV/vis (ethanol): $\lambda_{\max}$ 440 and 511 nm (for comparison: 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene: $\lambda_{\max}$ 438 nm). Anal. Calcd for C$_{14}$H$_{18}$FeP$_2$: C, 55.30; H, 5.97. Found: C, 55.42; H, 6.06.

[11] Crystallographic data for C$_{14}$H$_{18}$P$_2$Fe: $M_r = 304.09$; triclinic; space group $P\bar{1}$; $a = 7.947(2)$ Å, $b = 8.961(2)$ Å, $c = 9.378(4)$ Å, $\alpha = 91.61(3)°$, $\beta = 91.31(3)°$, $\gamma = 98.36(3)°$; $V = 660.2(7)$ Å^3; $Z = 2$; $d = 1.53$ g cm^{-3}; $\mu = 1.358$ cm^{-1}; $F(000) = 316$, crystal dimensions 0.32 × 0.25 × 0.22 mm, 4055 total reflections collected ($I > 3\sigma(I)$), goodness of fit on F 0.998; $R = 0.027$, $R_w = 0.039$; maximum/minimum residual density 0.517/−0.426 e Å^{-3}. Data were collected on a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Full details of the crystallographic analysis are described in the Supporting Information.

[12] Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035.