Synthesis and X-ray Crystal Structure Analysis of a Cp-Substituted Phosphaferrocene

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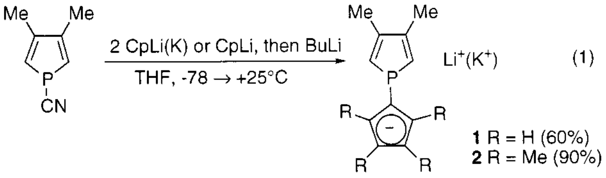
Summary: At 140 °C in THF, a 2,3,4,5-tetramethyl-1-cyclopentadienylide anionic substituent migrates from phosphorus to the α-carbon of the corresponding P-substituted 3,4-dimethylphosphole ***2****. The resulting 2-cyclopentadienyl-3,4-dimethylphospholide ion (****3****) reacts with a [CpFe]*$^+$ *source to give the corresponding 2-cyclopentadienyl-3,4-dimethyl-1-phosphaferrocene (****5****) as a mixture of two diastereomers, one of which has been characterized by X-ray crystal structure analysis.*

Fulvalene bis-η^5-complexes have been the subject of numerous studies aimed at the understanding of ligand-mediated interactions between two transition metal centers.[1] The emergence of η^5-phospholyl complexes as a new class of species combining the chemistry of sp^2-phosphorus ligands with a metallocenic structure[2] led us to wonder what would be the influence of the replacement of one carbon by one phosphorus in the backbone of these fulvalene complexes. From a synthetic standpoint, this means that a convenient access to the still unknown cyclopentadienyl−phospholide ions must be devised. This report describes such an access and the characterization of the resulting anion as a 2-cyclopentadienyl-1-phosphaferrocene derivative.

Our synthetic strategy was based on a previously reported synthesis of 2-functional phospholide ions.[3] The functional substituent is grafted on the phosphorus atom, then a [1,5] sigmatropic migration of the substituent is induced by heat, and the resulting 2-functional-2*H*-phosphole is deprotonated in situ by a base. Three conditions must be fulfilled by the substituent: thermal stability, migratory aptitude, and compatibility with the base. We reasoned that an anionic cyclopentadienide substituent would be automatically stable toward both heat and bases. The only question concerned its migratory aptitude. Indeed, some sp^2-carbon substituentts are known to migrate with difficulty, e.g., the 1-methyl-2-pyrrolyl which migrates slowly at 160 °C,[3] and no data were available on the shift of anionic substituents.

As a first step, we synthesized two P-cyclopentadienide derivatives from 1-cyano-3,4-dimethylphosphole[4] as shown in eq 1.



These salts were characterized by ^{1}H, ^{13}C, and ^{31}P NMR and negative ion mass spectrometry. The ^{31}P resonances appear at relatively high field for a phosphole: δ^{31}P −10.6 (**1**) and −21.2 (**2**) in THF. The mass spectrum of **1** shows the molecular peak at *m*/*z* 175 and the phospholide as the base peak at *m*/*z* 111. No other peak is visible.

It soon appeared that the thermally induced migrations lead to rather unstable products in the case of **1**. On the contrary, reproducible results were obtained with **2**. The potassium salt was heated at 140 °C in THF for one night. The ^{31}P monitoring of the reaction mixture showed the clean transformation of **2** into a series of phospholide ions at δ 76.1 (68%), 71.9 (4%), 70.0 (5%), and 64.7 (22%). The ^{1}H-coupled spectrum showed the first three resonances as doublets and the last one as a triplet (^2J(H−P) ≈ 40−41 Hz in all cases). The triplet is produced by the 3,4-dimethylphospholide ion[5] and the three doublets by the three possible isomers of the Cp-substituted phospholide **3** (eq 2). The ^{1}H spectrum of the mixture (C_4D_8O) is, of course, somewhat complex, but it is possible to check the presence of the resonances associated with **4**,[5] δ (CH_3) 2.09, δ (CHP) 6.40, $^2J_{(H-P)}$ = 40.2 Hz, and to extract the main resonances corre-

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[1] Some recent references: Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. Kovacs, I.; Shaver, A. *J. Organomet. Chem.* **1999**, *586*, 31. Boese, R.; Cammack, J. K.; Matzger, A. J.; Pflug, K.; Tolman, W. B.; Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 6757. Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. *Organometallics* **1996**, *15*, 2354. Kang, Y. K.; Shin, K. S.; Lee, S.-G.; Lee, I. S.; Chung, Y. K. *Organometallics* **1999**, *18*, 180.

[2] Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998. Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1 (reviews).

[3] Holand, S.; Jeanjean, M.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 98. Holand, S.; Maigrot, N.; Charrier, C.; Mathey, F. *Organometallics* **1998**, *17*, 2296.

[4] Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796. Synthesis of **2**(Li$^+$): A solution of tetramethylcyclopentadiene (1.22 g, 1 × 10^{-2} mol) in THF (25 mL) at −5 °C was allowed to react with a 1.6 M solution of ^{n}BuLi in hexane (1 × 10^{-2} mol). After stirring for one night at RT, the reaction mixture was cooled to −78 °C, and 1-cyano-3,4-dimethylphosphole (1.3 g, 9.5 × 10^{-3} mol) was added dropwise. After stirring for 2 h at RT, THF was evaporated and the resulting 1-cyclopentadienylphosphole was extracted from the residue with hexane. To this cyclopentadienylphosphole (0.29 g, 1.25 × 10^{-3} mol) in THF (10 mL) was added at −78 °C a hexane solution of ^{n}BuLi (1.6 M, 0.78 mL, 1.25 × 10^{-3} mol). The solution became deep red. The reaction mixture was warmed to RT, and THF was evaporated. Anion **2** was obtained as a beige powder (0.27 g, 91%). ^{31}P NMR (C_4D_8O): δ −21.2. ^{1}H NMR (C_4D_8O): δ 1.76 and 1.79 (2s, Me(Cp)), 2.04 (d, $^4J_{H-P}$ = 4.0 Hz, Me(phosphole)), 6.44 (d, $^2J_{H-P}$ = 34.3 Hz, CH−P); ^{13}C NMR (C_4D_8O): δ 11.36 (s, Me(Cp)), 11.72 (d, $^3J_{C-P}$ = 7.6 Hz, Me(Cp)), 17.49 (d, $^3J_{C-P}$ = 4.4 Hz, Me(phosphole)), 86.04 (d, $^1J_{C-P}$ = 13.6 Hz, C-P(Cp)), 112.41 (d, $^3J_{C-P}$ = 8.7 Hz, C_γ(Cp)), 117.53 (d, $^2J_{C-P}$ = 16.9 Hz, C_β(Cp)), 133.81 (d, $^1J_{C-P}$ = 5.4 Hz, CH-P), 140.28 (d, $^2J_{C-P}$ = 13.4 Hz, C_β(phosphole)).

[5] Charrier, C.; Mathey, F. *Tetrahedron Lett.* **1987**, *28*, 5025.

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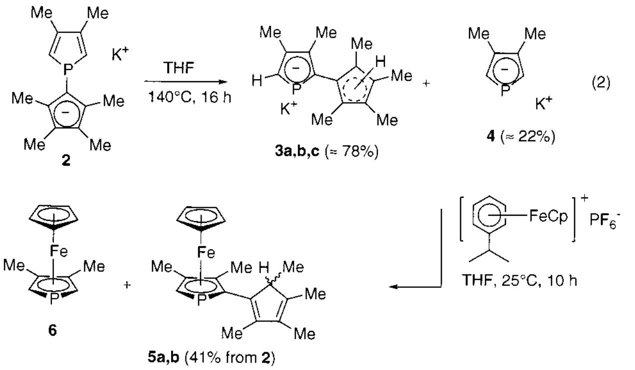
sponding to **3a**: δ (CH_3−CH) 0.82 (d, $^3J_{(H-H)} = 7.65$ Hz), δ (CH$_3$ phosphole) 2.08 and 2.11 (s), δ (CH$_3$CH) 2.86 (q), δ (CH−P) 6.47 (d, $^2J_{(H-P)} = 40.2$ Hz). The negative ion mass spectrum shows the molecular ions corresponding to **3a** (*m*/*z* 231, base peak) and to **4** (*m*/*z* 111). All the other peaks are of minor intensities. The reaction of this mixture with a source of [CpFe]$^+$ according to the method of Roberts and Wells[6] gives the phosphaferrocene **5** as a mixture of two diastereomers and the 3,4-dimethyl-1-phosphaferrocene (**6**) (eq 2).



According to the ^{31}P spectrum (CDCl$_3$), the prepurified mixture contains ca. 37% of **5a** (δ^{31}P −72.0, d, $^2J_{(H-P)} =$ 34.6 Hz), 55% of **5b** (δ^{31}P −78.1, d, $^2J_{(H-P)} = 35.0$ Hz), and 8% of **6** (δ^{31}P −82.3, t, $^2J_{(H-P)} = 36.4$ Hz). The identity of **6** is confirmed by the ^{1}H spectrum: δ (CH$_3$) 2.20 (s), δ (CHP) 3.77 (d, $^2J_{(H-P)} = 36.4$ Hz). After chromatography, the final product is a mixture of **5a** (ca. 40%) and **5b** (ca. 60%).[7] The mass spectrum shows the molecular and base peak at *m*/*z* 352. Upon crystallization at −20 °C in hexane, one of the isomers was obtained in the pure state and characterized by X-ray crystal structure analysis (Figure 1).[8] The Cp-substitution induces some dissymmetry in the phosphole ring as seen on the C−P bonds: P(2)−C(1) 1.774(2) and P(2)−C(4) 1.798(2) Å. The phosphole and C$_5$Me$_4$H planes make an angle of 62.1°. The phosphole and Cp rings are eclipsed and their two planes are almost parallel: C$_4$P centroid−Fe−C$_5$ centroid 174.3°. The methyl on the sp^3-carbon is located on the *exo* side of the phosphaferrocene.

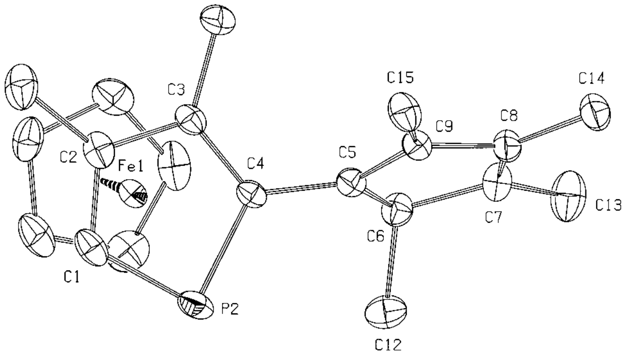


Figure 1. X-ray crystal structure of one diastereomer of **5**. Selected bond lengths (Å) and angles (deg): P(2)−C(1) 1.774(2), P(2)−C(4) 1.798(2), C(1)−C(2) 1.420(2), C(2)−C(3) 1.433(2), C(3)−C(4) 1.428(2), C(4)−C(5) 1.479(2), C(5)−C(9) 1.357(2), C(5)−C(6) 1.517(2), C(6)−C(7) 1.511(2), C(6)−C(12) 1.529(2), C(7)−C(8) 1.344(2), C(8)−C(9) 1.474(2), P(2)−Fe(1) 2.286(1), Fe(1)−C(1) 2.067(2), Fe(1)−C(2) 2.054(2), Fe(1)−C(3) 2.056(2), Fe(1)−C(4) 2.091(2), Fe(1)−C(16)···Fe(1)−C(20) 2.044−2.054(2); C(1)−P(2)−C(4) 89.26(7), P(2)−C(1)−C(2) 114.1(1), C(1)−C(2)−C(3) 111.5(1), C(2)−C(3)−C(4) 113.0(1), C(3)−C(4)−C(5) 124.2(1), C(5)−C(4)−P(2) 123.5(1), C(3)−C(4)−P(2) 112.1(1).

The syntheses of **3** and **5** open a simple route to the still unknown phosphafulvalene heterobimetallic complexes. The only related work concerns the syntheses of a 2-cyclopentadienylmethyl-1-phosphaferrocene and its η^5-Ru(Cl)(PPh$_3$) complex.[9]

Supporting Information Available: Listings of atomic coordinates, including H atoms and equivalent isotropic displacement parameters, bond lengths, and bond angles of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[6] Roberts, R. M. G.; Wells, A. S. *Inorg. Chim. Acta* **1986**, *112*, 171.

[7] **5**: purified by chromatography on silica gel with 90:10 hexane/CH$_2$Cl$_2$ as the eluent. **5a** (minor): selected NMR data: ^{31}P NMR (CDCl$_3$) −72.0; ^{1}H NMR (CDCl$_3$) 0.80 (d, $^3J_{H-H} = 7.6$ Hz, CH_3-CH), 2.28 (s, CH$_3$ phosphole), 3.12 (q, CH$_3$-CH), 3.89 (d, $^2J_{H-P} = 34.8$ Hz, CHP), 4.16 (s, C$_5$H$_5$); ^{13}C NMR (CDCl$_3$) 51.61 (s, *C*HMe), 73.19 (s, C$_5$H$_5$) , 95.35 (d, $^1J_{CP} = 58.2$ Hz, C-P) (CH-P masked). **5b** (major): ^{31}P NMR (CDCl$_3$) −78.1; ^{1}H NMR (CDCl$_3$) 1.34 (d, $^3J_{(H-H)} = 7.6$ Hz, CH_3-CH), 2.27 (s, CH$_3$ phosphole), 2.69 (q, CH$_3$-CH), 3.85 (d, $^2J_{(H-P)} = 35.2$ Hz, CHP), 4.17 (s, C$_5$H$_5$); ^{13}C NMR (CDCl$_3$) 54.81 (s, *C*HMe), 72.94 (s, C$_5$H$_5$) , 77.92 (d, $^1J_{(C-P)} = 59.2$ Hz, CH-P), 97.47 (d, $^1J_{(C-P)}= 57.9$ Hz, C-P); MS *m*/*z* 352 (M$^+$, 100), 337 (M$^+$ − CH$_3$, 17), 232 (M$^+$ − CpFe + H, 42). Anal. Calcd for C$_{20}$H$_{25}$FeP: C, 68.20; H, 7.15. Found: C, 67.85; H, 7.20.

[8] Crystallographic_data for **5**, C$_{20}$H$_{25}$FeP: $M = 352.22$ g/mol; triclinic; space group $P\bar{1}$; $a = 8.792(5)$ Å, $b = 10.681(5)$ Å, $c = 11.190(5)$ Å, $\alpha = 112.350(5)°$, $\beta = 111.470(5)°$, $\gamma = 95.680(5)°$, $V = 869.1(7)$ Å^3; $Z = 2$; $D = 1.346$ g cm^{-3}; $\mu = 0.954$ cm^{-1}; $F(000) = 372$. Crystal dimensions 0.20 × 0.20 × 0.20. Total reflections collected 6729 and 4328 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.013; $R(I > 2\sigma(I)) = 0.0325$, wR2 = 0.0847 (all data); maximum/minimum residual density 0.472(0.060)/−0.393(0.060) e Å^{-3}. Data were collected on a KappaCCD diffractometer at 150.0(1) K with Mo Kα radiation ($\lambda = 0.71073$ Å). Full details of the crystallographic analysis are described in the Supporting Information.

[9] Kaulen, C.; Pala, C.; Hu, C.; Ganter, C. *Organometallics* **2001**, *20*, 1614.