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Synthesis of 2,5-Difunctional Phosphaferrocenes

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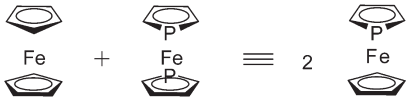
*Summary: The reaction of FeCl$_2$ with a 1:1 mixture of 2,5-diacylphospholides and Cp*Li in the presence of ZnCl$_2$ affords 2,5-bis(RCO)phosphaferrocenes when R = OEt, Ph and the tetrafunctional 1,1′-diphosphaferrocene when R = ^{t}Bu. We explain these results by a combination of two effects: the push−pull stabilization of the ferrocene structure by Cp* (donor) and phospholide (acceptor) and the classical steric protection of the η^5 complexes by bulky α-substituents.*

Together with phosphinines, phosphaferrocenes are one of the two fundamental classes of aromatic species featuring an sp^2 phosphorus center. They are readily functionalizable, and they have already found a certain number of catalytic applications.[1] At the present time, however, essentially no 2,5-difunctional phosphaferrocene is known aside from the silyl derivatives,[2] thus preventing the easy incorporation of the phosphaferrocene unit into rings or polymers. This point has been raised by Ganter,[2] who unsuccessfully tried to prepare 2,5-diacylphosphaferrocenes. We show hereafter how it is possible to circumvent this limitation.

Results and Discussion

Our initial reasoning was that the failure reported by Ganter was due to the very poor π-donating ability of 2,5-diacylphospholides. Indeed, it is well established, on the basis of comparative IR studies of cymantrene and phosphacymantrene, that the nonfunctional η^5-phospholyl is already a poorer π-donor than the η^5-cyclopentadienyl ligand.[3] From another standpoint, this fact seems to contradict the observation that the Friedel−Crafts acylation of phosphaferrocenes selectively takes place at the phospholyl ring.[4] This contradiction is suppressed if we admit that a sizable electronic transfer from cyclopentadienyl to phospholyl takes place through iron in phosphaferrocenes. This transfer must induce a stabilization of the phosphaferrocene by a classical push−pull effect. In order to evaluate this effect, we decided to compute the energies of the two members of the formal equation (1) by DFT at the 6-31G(d)-Lanl2dz (Fe) level.[5]



(1)

The results are ambiguous. The two molecules of phosphaferrocene appear to be more stable than the 1 + 1 mixture of ferrocene and 1,1′-diphosphaferrocene by only 0.9 kcal mol^{-1} (ZPE included). Even though this effect is limited, we could expect to enhance it on replacing Cp by Cp* and the nonfunctional phospholyl by a phospholyl substituted with an electron-withdrawing group. Two practical consequences can be expected: (1) if we react a 1:1 mixture of cyclopentadienide and phospholide with FeCl$_2$, we must get more phosphaferrocene than the statistical mixture; (2) we can envisage compensating the very poor π-complexing ability of 2,5-diacylphospholyl by using the strong Cp* donor as the coligand of iron. This led us to investigate the reaction of a 1:1 mixture of the pentamethylcyclopentadienide **1** and 2,5-diethoxycarbonyl-3,4-dimethylphospholide (**2**)[6] with FeCl$_2$ in the presence of ZnCl$_2$ as acidic coreagent.[7] We were delighted to

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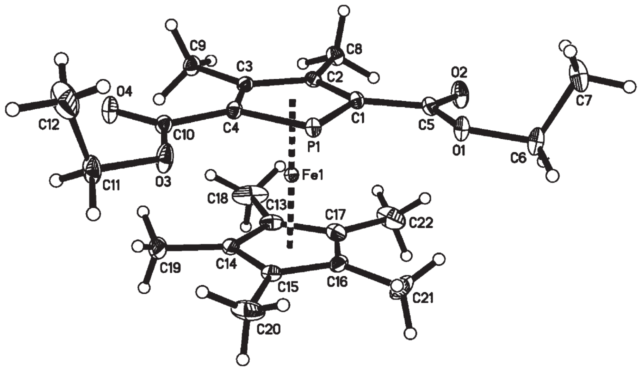


Figure 1. X-ray crystal structure of phosphaferrocene **3**. Main distances (Å) and angles (deg): Fe1−P1 = 2.2780(3), Fe1−C1 = 2.0643(11), Fe1−C13 = 2.0773(12), P1−C1 = 1.7868(12), P1−C4 = 1.7832(12), C1−C2 = 1.4384(16), C2−C3 = 1.4254(16), C3−C4 = 1.4386(16); C1−P1−C4 = 87.88(5).

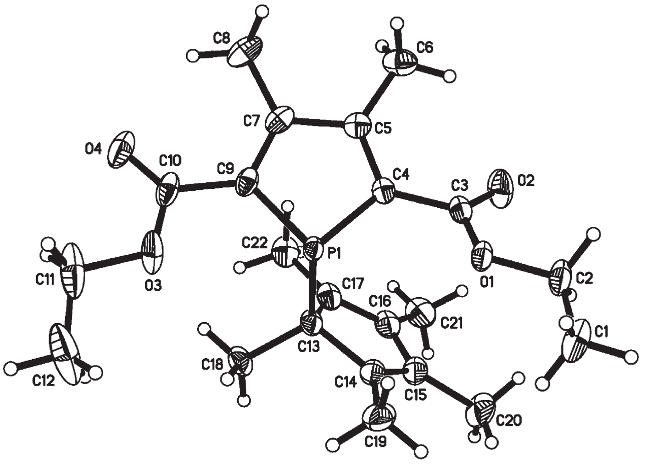
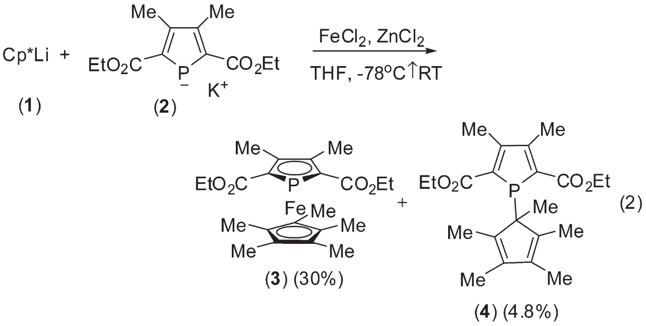


Figure 2. X-ray crystal structure of phosphole **4**. Main distances (Å) and angles (deg): P1−C13 = 1.8967(16), P1−C9 = 1.8033(17), P1−C4 = 1.8011(16), C4−C5 = 1.362(2), C5−C7 = 1.464(2), C7−C9 = 1.367(2), C4−C3 = 1.474(2), C9−C10 = 1.479(2); C4−P1−C9 = 89.86(8), C4−P1−C13 = 103.57(7), C9−P1−C13 = 109.16(7).

find that this reaction provides a very simple access to the 2,5-difunctional phosphaferrocene **3** (eq 2).



This result is remarkable because we have shown previously that the reaction of **2** with $FeCl_2$ leads exclusively to the tetrafunctional P−P coupling product.[7] In line with this previous result, we just get a small quantity of the Cp*-substituted phosphole **4**. Both products were characterized by X-ray crystal structure analysis (Figures 1 and 2). In phosphaferrocene **3**, both rings are in a staggered conformation. The phosphole ring is quasi planar, the bending around C1···C4 being only 1.67°. The Cp* and phospholyl planes are almost parallel (angle 1.33°). The phospholyl plane is closer to iron than the Cp* plane (1.637 vs 1.670 Å). As expected, the phospholyl ring shows practically no alternation between the C−C bonds. In phosphole **4**, the steric bulk of the Cp* substituent induces a lengthening of the P−C exocyclic bond at 1.8967(16) Å but the phosphorus pyramid is not flattened ($\sum$(angles at P) = 302.6°, the same as in 1-benzylphosphole[8]). The intracyclic P−C bonds are long, and the alternation between C−C and C═C bonds is high. The bending of the ring around C4−C9 is significant at 9.65°. Using the same experimental protocol, but replacing the 2,5-bis(ethoxycarbonyl) by 2,5-dibenzoylphospholide,[9] we obtained the 2,5-dibenzoylphosphaferrocene **5** in 33% yield. The surprise came when we used the 2,5-bis(pivaloyl)phospholide.

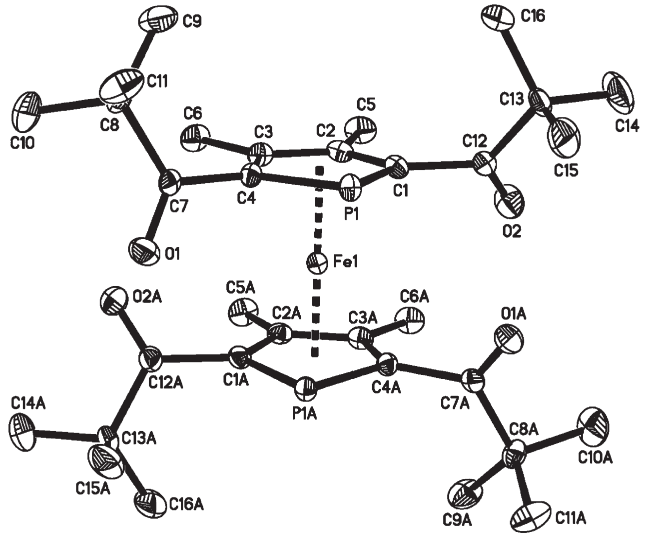
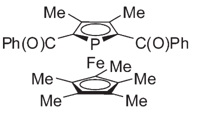
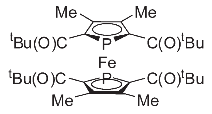


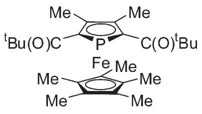
Figure 3. X-ray crystal structure of 1,1′-diphosphaferrocene **6**. Main distances (Å) and angles (deg): Fe1−P1 = 2.2746(9), Fe1−C1 = 2.092(3), Fe1−C2 = 2.086(3), P1−C1 = 1.782(3), C1−C2 = 1.430(5), C2−C3 = 1.426(5), C3−C4 = 1.423(5), P1−C4 = 1.795(3); C1−P1−C4 = 88.72(15).



(**5**) (33%)



(**6**) (80%)



(**7**) (2%)

In the presence of a stoichiometric amount of Cp*Li, only traces of the expected phosphaferrocene **7** are obtained. By far the main product of the reaction is the tetrafunctional 1,1′-diphosphaferrocene **6**. In the absence of Cp*Li, we got an impressive 80% yield of this product. The identity of **6** was unambiguously established by X-ray crystal structure analysis (Figure 3). The conformation of the molecule lies halfway between staggered and eclipsed. One ring is rotated with respect to the other by 23.24°. The two phospholyl planes are almost parallel (interplane angle 1.26°). The two rings are

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[8] Coggon, P.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1973**, 1888.

[9] Toullec, P.; Mathey, F. *Synlett* **2001**, 1977.

slightly folded around their Cα−Cα′ axis, both by 1.78°. The two planes are equidistant from iron at 1.655 Å. The preferential formation of **6** vs **7** is somewhat mysterious. It might have something to do with the relative stabilities of the intermediate σ-complexes.

Experimental Section

2,5-Bis(ethoxycarbonyl)phosphaferrocene 3 and 1-pentamethylcyclopentadienylphosphole 4. 1-Phenyl-3,4-dimethylphosphole[10] (1 g, 5.32 mmol) in dry THF (15 mL) was allowed to react with an excess of lithium wire for 5 h at room temperature. After excess lithium was removed, the solution was treated with *tert*-butyl chloride (0.6 mL, 5.32 mmol) and heated to 60 °C for 1 h. Ethyl chloroformate (0.55 mL, 5.85 mmol) was added dropwise at −78 °C. The solution was heated at 65 °C for 2 h. tBuOK was added (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was heated at 60 °C for 2 h. Another 1 equiv of ethyl chloroformate (0.6 mL, 5.85 mmol) was added at −78 °C, immediately followed by addition of another 1 equiv of tBuOK (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was stirred at 40 °C for 18 h. The solution was cooled to 0 °C, $ZnCl_2$ (1.450 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. In a separate reaction flask, Cp*Li was prepared by adding *n*-BuLi (2.85 mL, 4.5 mmol) to 1,2,3,4,5-pentamethylcyclopentadiene (0.84 mL, 5.32 mmol) in dry THF (15 mL) at −78 °C. The solution was stirred at −78 °C for 30 min and warmed to room temperature for 1 h. The 2,5-bifunctionalized phospholide mixture was then added to the Cp*Li solution at −78 °C and stirred for 20 min at −78 °C. In a separate flask, $FeCl_2$ (0.725 g, 5.32 mmol) was stirred in dry THF at room temperature for 30 min. After the $FeCl_2$ solution was cooled to −78 °C, the 2,5-bifunctionalized phospholide/Cp*Li solution was added dropwise by cannula. The resulting mixture was stirred at −78 °C for 1 h and at room temperature for 18 h. The crude solution mixture was concentrated, dissolved in methylene chloride, filtered through silica, and concentrated. Purification was performed via cold column chromatography on silica using 1:1 dichloromethane−hexanes. An orange band was collected and, once concentrated, 570 mg (1.28 mmol) of an orange solid (**3**) was obtained in 30% yield. The product was crystallized by slow evaporation of methylene chloride. When the polarity of the eluent was increased to 2:1 dichloromethane−hexanes, a yellow band was recovered from the same column. On concentration, 100 mg (0.26 mmol) of a yellow solid (**4**) was obtained in 4.8% yield. The solid was crystallized by slow evaporation of methylene chloride.

Data for **3** are as follows. ^{1}H NMR (CD_2Cl_2): δ 1.31 (t, 6H, Me), 1.64 (s, 15H, Me), 2.24 (s, 6H, Me), 4.12 (q, 4H, OCH_2). ^{13}C NMR (CD_2Cl_2): δ 8.99 (s, Me Cp*), 11.90 (s, Me), 14.15 (s, Me), 60.00 (s, OCH_2), 82.78 (d, $^1J_{PC}$ = 56.8 Hz, C−P), 84.74 (s, C Cp*), 97.83 (d, $^2J_{PC}$ = 6.4 Hz, Cβ), 171.58 (d, $^2J_{PC}$ = 18.5 Hz, CO). ^{31}P NMR (CD_2Cl_2) δ −29.7. Exact mass: *m*/*z* calcd for $C_{22}H_{32}FeO_4P$ 447.1388, found 447.1386. Anal. Calcd for $C_{22}H_{31}FeO_4P$: C, 59.21; H, 7.00. Found: C, 60.08; H, 7.34.

Data for **4** are as follows. ^{1}H NMR (CD_2Cl_2): δ 1.23 (d, $^3J_{HP}$ = 15.6 Hz, Me Cp*), 1.31 (t, Me OEt), 1.60 (s, Me Cp*), 1.67 (s, Me Cp*), 2.21 (s, Me phosphole), 2.22 (s, Me phosphole), 4.08 and 4.21 (2 m, OCH_2). ^{13}C NMR (CD_2Cl_2): δ 10.63 (s, Me Cp*), 10.77 (d, J_{CP} = 5.8 Hz, Me Cp*), 14.09 (s, Me OEt), 15.30 (s, Me phosphole), 18.84 (d, $^2J_{CP}$ = 12.5 Hz, Me−C−P), 60.57 (s, OCH_2), 133.52 (s, =C Cp*), 135.98 (d, $^1J_{CP}$ = 9.6 Hz, C−P), 139.74 (s, =C Cp*), 153.38 (d, $^2J_{CP}$ = 8.6 Hz, Cβ), 166.07 (d, $^2J_{CP}$ = 19.2 Hz, CO). ^{31}P NMR (CD_2Cl_2) δ 29.7. Exact mass: *m*/*z* calcd for $C_{22}H_{32}O_4P$ 391.2038, found 391.2043.

2,5-Dibenzoylphosphaferrocene 5. 1-Phenyl-3,4-dimethylphosphole (1 g, 5.32 mmol) in dry THF (15 mL) was allowed to react with an excess of lithium wire for 5 h at room temperature. After excess lithium was removed, the solution was treated with *tert*-butyl chloride (0.6 mL, 5.32 mmol) and heated to 60 °C for 1 h. Benzoyl chloride (0.7 mL, 5.32 mmol) was added dropwise at −78 °C. The solution was warmed to room temperature and stirred for 20 min. tBuOK was added (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was heated at 60 °C for 2 h. Another 1 equiv of benzoyl chloride (0.7 mL, 5.32 mmol) was added at −78 °C, immediately followed by addition of another 1 equiv of tBuOK (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was stirred at 60 °C for 2.5 h. The solution was cooled to 0 °C, $ZnCl_2$ (1.450 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. The resulting 2,5-bifunctional phospholide solution was treated in the same manner as for **3**. Purification was performed via cold column chromatography on silica using 1:1 dichloromethane−hexanes. A red band was collected and, on concentration, 900 mg (1.76 mmol) of a red oil (**5**) was obtained in 33% yield.

Data for **5** are as follows. ^{1}H NMR (CD_2Cl_2): δ 1.61 (s, 15H, Me), 2.19 (s, 6H, Me), 7.38 (t, 4H *meta*), 7.48 (t, 2H *para*), 7.74 (d, 4H *ortho*). ^{13}C NMR (CD_2Cl_2): δ 9.24 (s, Me Cp*), 12.83 (s, Me phosphole), 85.27 (s, C Cp*), 92.45 (d, $^1J_{PC}$ = 61.2 Hz, C−P), 98.60 (d, $^2J_{PC}$ = 5.4 Hz, Cβ), 127.74 (s, CH *meta*), 128.81 (d, J_{PC} = 6.5 Hz, CH *ortho*), 131.47 (s, CH *para*), 141.88 (s, C *ipso*), 200.33 (d, $^2J_{PC}$ = 20.4 Hz, CO). ^{31}P NMR (CD_2Cl_2) δ −17.5. Exact mass: *m*/*z* calcd for $C_{30}H_{32}FeO_2P$ 511.1489, found 511.1475.

2,2′,5,5′-Tetrapivaloyl-1,1′-diphosphaferrocene 6. 1-Phenyl-3,4-dimethylphosphole (1 g, 5.32 mmol) in dry THF (15 mL) was allowed to react with an excess of lithium wire for 5 h at room temperature. After excess lithium was removed, the solution was treated with *tert*-butyl chloride (0.6 mL, 5.32 mmol) and heated to 60 °C for 1 h. Pivaloyl chloride (0.7 mL, 5.32 mmol) was added dropwise at −78 °C. The solution was warmed to room temperature and stirred for 20 min. tBuOK was added (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was heated at 60 °C for 2 h. Another 1 equiv of pivaloyl chloride (0.7 mL, 5.32 mmol) was added at −78 °C, immediately followed by addition of another 1 equiv of tBuOK (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was stirred at 60 °C for 2.5 h. The solution was cooled to 0 °C, $ZnCl_2$ (1.450 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. The resulting 2,5-bifunctional phospholide solution was treated in the same manner as for **3**. Purification was performed via cold column chromatography on silica using 3:1 dichloromethane−hexanes. An orange band was first collected. After concentration, 50 mg (0.11 mmol) of an orange solid (**7**) was obtained in 2% yield. A second red band corresponding to the diphosphaferrocene **6** was collected and, on concentration, 320 mg (0.52 mmol) of a red solid was obtained in 20% yield. The product was crystallized by slow evaporation of hexanes.

For the optimized synthesis of **6**, the initial preparation of the 2,5-diacylphospholide was identical. After the addition of $ZnCl_2$, $FeCl_2$ (0.335 g, 2.66 mmol) was added at room temperature. The solution was stirred for 18 h at room temperature. The crude solution mixture was filtered through silica and concentrated. Purification was performed via column chromatography on silica using 3:1 dichloromethane−hexanes. The red band was collected and, on concentration, 1.311 g (2.136 mmol) of a red solid (**6**) was obtained in 80% yield.

Data for **6** are as follows. ^{1}H NMR (CD_2Cl_2): δ 1.16 (s, 36H, Me tBu), 1.99 (s, 12H, Me phosphole). ^{13}C NMR (CD_2Cl_2): δ 12.99 (s, Me phosphole), 27.15 (s, Me tBu), 45.39 (s, C tBu), 98.79 (d, $^1J_{PC}$ = 72.5 Hz, C−P), 102.19 (d, $^2J_{PC}$ = 3.8 Hz, Cβ), 210.41 (d, $^2J_{PC}$ = 16.3 Hz, CO). ^{31}P NMR (CD_2Cl_2) δ −61.3. Exact mass: *m*/*z* calcd for $C_{32}H_{49}FeO_4P_2$: 615.2456, found 615.2466. Anal. Calcd for $C_{32}H_{48}FeO_4P_2$: C, 62.54; H, 7.87; Found: C, 62.85: H, 8.14.

Data for **7** are as follows. ^{1}H NMR (CD_2Cl_2): δ 1.21 (s, Me tBu), 1.62 (s, Me Cp*), 2.04 (s, Me phosphole). ^{13}C NMR (CD_2Cl_2): δ 9.52 (s, Me Cp*), 12.05 (s, Me phosphole), 27.63

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(10) Brèque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

and 27.71 (2s Me tBu), 45.69 (s, C tBu), 84.72 9 (s, C Cp*), 91.22 (d, $^1J_{PC}$ = 66.7 Hz, C−P), 99.50 (d, $^2J_{PC}$ = 4.8 Hz, Cβ), 211.78 (d, $^2J_{PC}$ = 16.8 Hz, CO). ^{31}P NMR (CD_2Cl_2) δ −66.3. Exact mass: *m*/*z* calcd for $C_{26}H_{40}FeO_2P$ 471.2115, found 471.2109.

Acknowledgment. Thanks are due to Nanyang Technological University in Singapore for financial support of this work and to Dr. Li Yong Xin for the X-ray crystal structure analyses.

Supporting Information Available: CIF files giving X-ray crystal structure analyses of compounds **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.