# Synthesis of a 1,2-Diphosphaferrocene under Participation of Carbonyl Ligands *via* Silyl Group-shift

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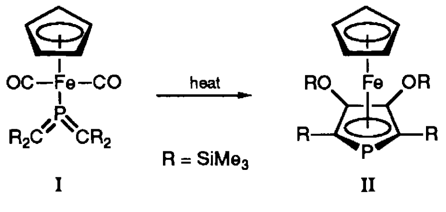
The reaction of the silylated phosphinomethylenephosphane **1** with $Cp(CO)_2FeBr$ gives the novel 1,2-diphosphaferrocene-system **5** (Cp = cyclopentadienyl).

Cyclopentadienides in which threefold coordinated carbon centres are replaced by one or more phosphorus atoms play an important role in transition metal chemistry and a great number of ligands containing one[1] or more[2] phosphorus atoms are known.

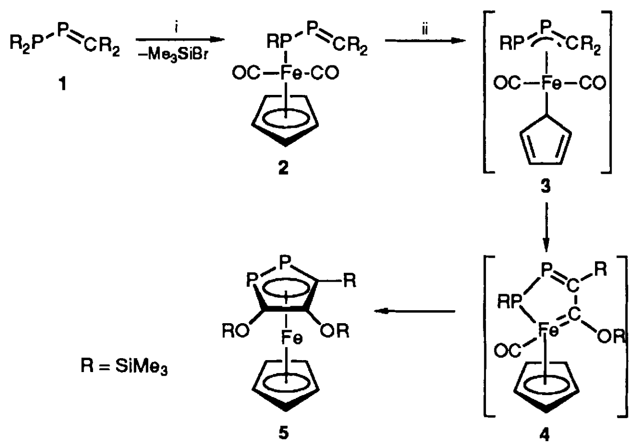
Recently, we reported[3] a novel synthetic route to phosphaferrocenes **II** *via* isomerization of a ferrio-bis(methylene)-phosphorane **3**, which has been obtained by reacting the silylated chloro(bismethylene)phosphorane with $[(Cp)Fe(CO)_2]Li$ **I** (Scheme 1). In order to get further insight into this type of CO insertion reaction with concomitant coupling of a pπ-bonded phosphorus(III) containing fragment, we investigated the reaction of the persilylated phosphinomethylenephosphane **1** with $(Cp)Fe(CO)_2Br$. With this we wanted to explore whether the reaction might be extended to other systems containing reactive elemental-silicon bonds, especially, in order to synthesise the unknown 1,2-diphospholyl ligand, in the coordination sphere of a transition metal.[4]

Treatment of 2.52 g (6.8 mmol) of $(Me_3Si)_2P\text{–}P{=}C(SiMe_3)_2$ **1**, dissolved in 10 ml of toluene, with an equimolar quantity of $CpFe(CO)_2Br$ and catalytic amounts of hexamethylphosphorous triamide (HMPT) immediately produced a deep red solution. After stirring for 4 h at *ca.* 60 °C the product was isolated by solvent separation and fractional vacuum distillation in the form of a thermally stable, oily liquid, b.p. 137–139 °C ($10^{-2}$ Torr) in 33% yield.

Identification of the product as the 1,2-diphosphaferrocene **5** was established by analytical and spectroscopic methods. The $^{31}P$ NMR spectrum exhibits an AB system at high field (δ −66.2, −67.2), which is indicative of phosphorus containing cyclopentadienides.[3,5] The value for $J_{PP}$ (379 Hz) corresponds to a one bond coupling as is found for the sandwich complexes containing the triphospholyl ligand.



Scheme 1



**Scheme 2** *Reagents and conditions*: i, $(Cp)(CO)_2FeBr$ (1 equiv.), −78 °C to room temp., toluene, HMPT; ii, 60 °C, 4 h

The presence of an unsymmetrically substituted 1,2-diphospholyl ligand is in accord with two characteristic downfield multiplets for the siloxy carbon atoms (δ 134.5, $^1J_{CP}$ 55.2, $^2J_{CP}$ 38.5 Hz; δ 131.4, $^2J_{CP}$, $^3J_{CP}$) as well as a doublet of doublets at higher field (δ 78.0, $^1J_{CP}$ 55.8, $^2J_{CP}$ 38.0 Hz)† in the $^{13}$C NMR spectrum. The five ring carbon atoms of the cyclopentadienide ligand show a similar shielding (δ 73,5). The presence of the unsymmetrical diphospholyl ligand is also clear from the $^1$H NMR spectrum‡ consisting of three chemically non-equivalent silyl groups.

The mass spectrum, with the molecular ion as the base peak, as well as the absence of a CO vibrational band in the IR spectrum are further evidence for the sandwich structure of **5**.

For the formation of **5** the following mechanism was established for the interaction of **1** with $CpFe(CO)_2Br$ (Scheme 2). $^{31}$P NMR spectroscopic monitoring at −78 °C indicated a formation of a phosphinomethylenephosphane complex **2** (δ −95.0, 494.2, $^1J_{PP}$ 256 Hz) in the primary reaction step. Rearrangement should give a highly reactive $\eta^3$-1,2-diphosphaallylic species **3**, which initiates the silyl group shift to give a carbenic type intermediate **4**. Subsequent silyl group shift from phosphorus to carbonyl oxygen produces then the final product **5**. Further investigations in this field are in progress.

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† Additional $^{13}C\{^1H\}$ NMR-data (20 MHz, ext. $Me_4Si$): **5** (20 °C, $C_6D_6$) δ 0.17 (dd, $^3J_{CP}$ 3.5, $^4J_{CP}$ 2.5 Hz $C_3SiC$), 0.76 (d, $^4J_{CP}$ 2.0 Hz $C_3SiO$), 1.77 (s, $C_3SiO$).

‡ $^1$H NMR (80 MHz, int. $Me_4Si$): **5** (20 °C, $CDCl_3$) δ 0.03 (s, $SiMe_3$), 0.18, 0.28 (s, $OSiMe_3$), 4.42 (s, $C_5H_5$).

## References

1. F. Mathey, A. Mitschler and R. Weiss, *J. Am. Chem. Soc.*, 1977, **99**, 3537; review: F. Mathey, J. Fischer and J. H. Nelson, *Struct. Bonding (Berlin)*, 1983, **55**, 153.
2. $\eta^5$-$C_2Bu^t{}_2P_3$, $\eta^5$-$C_3Bu^t{}_3P_2$: R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 1146; *J. Organomet. Chem.*, 1988, **340**, C37; 1988, **356**, Cl; $\eta^5$-$P_5$: O. J. Scherer and T. Brück, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 59; M. Baudler and T. Etzbach, *Angew. Chem.*, 1991, **103**(5), 590.
3. H. J. Metternich and E. Niecke, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 312.
4. An $\eta^5$- and $\eta^1$(P)-coordinated 1,2-diphosphoyl ligand has been observed recently by L. Weber, personal communication.
5. R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1988, 819.