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Mechanistic Insight into the Formation of Phosphaferrocene

Joachim Bitta, Stefan Fassbender, Guido Reiss,[†] and Christian Ganter*

Institut für Anorganische Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1,
D-40225 Düsseldorf, Germany

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Summary: The thermal reaction between $[CpFe(CO)_2]_2$ and 1-tert-butyl-3,4-dimethylphosphole leading to phosphaferrocene has been studied with respect to its mechanistic characteristics. Isobutene was identified as the only product originating from the ^tBu group, suggesting a nonradical pathway which involves β-H elimination from the intermediately formed $[CpFe(CO)_2$-$^tBu]$.

Introduction

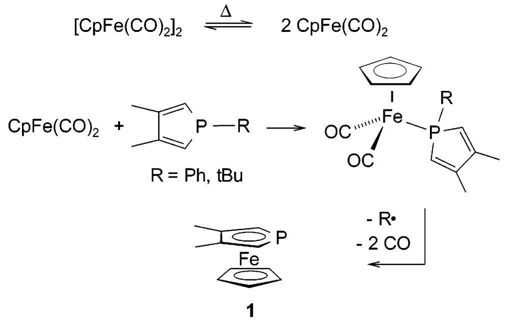
Phosphaferrocenes are among the best investigated heterometallocenes. The first compound of this familiy, 3,4-dimethylphosphaferrocene (**1**), was prepared as early as 1977 by Mathey.[1] Since then, phosphaferrocene derivatives have been studied intensely, due to their interesting properties.[2] The propensity to coordinate to metal fragments via the P atom makes them unique ligands with strong π-acceptor characteristics. Recently, substituted phosphaferrocenes with planar chirality were incorporated into chelate ligand structures which have found application in asymmetric catalysis.[3]

Two main synthetic routes are available for the preparation of phosphaferrocenes, one of them involving the reaction of a phospholide anion with a reagent delivering a $CpFe^+$ synthon and the other being the thermal reaction between a neutral phosphole and $[CpFe(CO)_2]_2$ (=Fp_2) in a high-boiling-point solvent such as xylene. Although the latter method was the first one to be discovered and is frequently used, little is known about the mechanism of this transformation. We have therefore studied this reaction regarding its mechanistic features, and the results are presented in this paper.

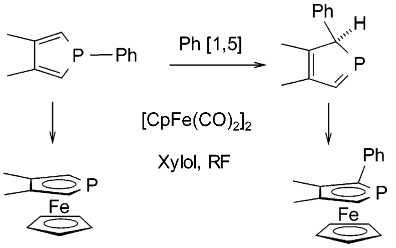
Results and Discussion

A possible mechanism for the formation of phosphaferrocene from a phosphole and Fp_2 was proposed by Mathey (Scheme 1).[1] It involves a thermal dissociation of Fp_2 as the initial step and a subsequent coordination of the phosphole to the Fe atom to form the 19-electron species $[CpFe(CO)_2(1\text{-}R\text{-phosphole})]$. A homolytic scission of the exocyclic P−C bond is postulated as the next step, leading to the radical $R^•$ and the 18-electron complex $[CpFe(CO)_2(phospholyl)]$, which leads to phosphaferrocene on thermal elimination of two molecules of CO. The formation of 2-phenyl-3,4-dimethylphosphaferrocene as a byproduct in the synthesis of 3,4-dimethylphosphaferrocene (**1**) from 1-phenyl-3,4-dimethylphosphole and Fp_2 was originally accounted for by the intermediate formation of free phenyl radicals, which bring about a substitution on the phosphaferrocene **1**.

Scheme 1



Scheme 2



However, it became clear later that the phenyl-substituted product arises from a sigmatropic phenyl shift at the phosphole prior to the reaction with Fp_2 (Scheme 2).[4] This sigmatropic shift occurs typically at elevated temperatures with aromatic groups bound to the phosphorus in the phosphole and has been exploited in an elegant way for the synthesis of phosphametallocenes carrying respective groups at the 2-position.[5] On the other hand, P-bound alkyl groups show no appreciable migratory aptitude; therefore, 1-*tert*-butyl-3,4-dimethylphosphole is the preferred starting material for the synthesis of phosphaferrocene **1**.[6]

The enthalpy required for the homolytic dissociation of Fp_2 has been estimated by various methods to be in the range of 110 ± 20 kJ/mol, and therefore, a small concentration of monomeric $[CpFe(CO)_2]$ radicals exists at elevated temperature.

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* To whom correspondence should be addressed. E-mail: christian.ganter@uni-duesseldorf.de.

[†] X-ray structure determination.

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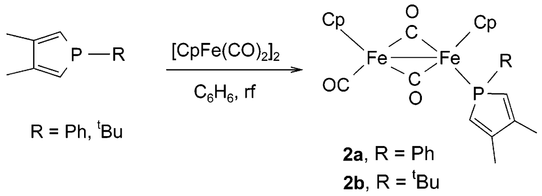
10.1021/om060025s CCC: $33.50

Scheme 3



At room temperature in cyclohexane the equilibrium constant for the dissociation of Fp_2 is $K = 2 \times 10^{-17}$ mol/L.[7] The sterically demanding derivative $[(C_5{}^iPr_5)Fe(CO)_2]$ is a stable monomeric species in solution but a dimer in the solid state.[8] The photochemical dissociation of Fp_2 is also a well-known process.[9] To the best of our knowledge, 19-electron species of the type $[CpFe(CO)_2L]$ have not been isolated, due to their strong reducing character. However, they are considered to play a role as transient species in the disproportionation reaction of Fp_2 with various donor ligands.[10] It was shown that the rate of recombination of photochemically generated $[CpFe(CO)_2]$ radicals in solution is not affected by the presence of added PPh_3,[11] while the reaction of Fp radicals with $P(OMe)_3$ proceeds via the short-lived substitution product $[CpFe(CO)\{P(OMe)_3\}]$ to form the mono- and disubstituted dimers $[Cp_2Fe_2(CO)_3P(OMe)_3]$ and $[Cp_2Fe_2(CO)_2\{P(OMe)_3\}_2]$ as the final products.[9b] The quoted experimental observations render the original mechanistic suggestion for the formation of phosphaferrocene unlikely, and we suggest a more plausible pathway based on the following experimental results.

Fp_2 and *tert*-butyl- and phenylphospholes react in benzene under reflux to give the monosubstituted dimers **2a**,**b** (Scheme 3). ^{31}P NMR spectra of the reaction mixtures indicate a virtually complete conversion of the phenylphosphole after 10 h, whereas the conversion of the *tert*-butylphosphole is ca. 50% after the same reaction time. The selectivity of the transformation toward the complexes **2a**,**b** is greater than 90% in both cases, and the products are isolated as deep green powders after chromatography.[12]

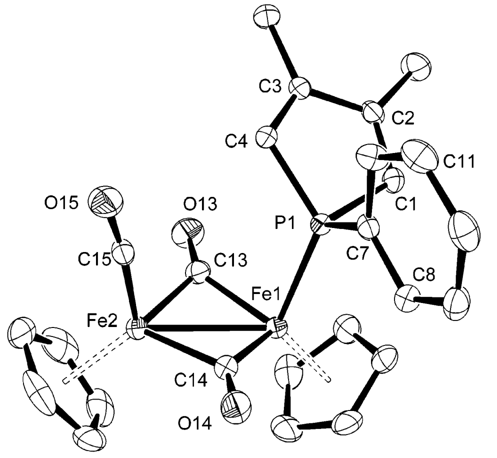


Figure 1. ORTEP view of the molecular structure of **2a**. H atoms have been omitted for clarity. Selected bond lengths (pm): Fe1−Fe2 = 253.75(7), Fe1−P1 = 220.8(1), Fe1−C13 = 189.9 (3), Fe1−C14 = 188.1(4), Fe2−C13 = 195.0(4), Fe2−C14 = 195.6(3), Fe2−C15 = 174.2(4), C13−O13 = 117.8(4), C14−O14 = 118.4(4), C15−O15 = 114.7(4). Selected angles (deg): C13−Fe1−C14 = 98.1(2), C13−Fe2−C14 = 93.9(1), Fe1−C13−Fe2 = 82.5(1), Fe1−C14−Fe2 = 82.8(1), Fe1−Fe2−C15 = 104.3(1), Fe2−Fe1−P1 = 103.7(1), C15−Fe2−Fe1−P1 = 7.1(1).

The phenyl derivative **2a**, which has been prepared earlier by Mathey,[1] could be characterized by X-ray diffraction. The molecular structure of the complex is depicted in Figure 1 together with selected bond lengths and angles. The structure is quite typical for a monosubstituted Fp_2 derivative, featuring a cis arrangement of the two CpFe fragments with two bridging carbonyl groups. The structural parameters all lie within the range typically observed for related derivatives such as the parent compound *cis*-$[CpFe(CO)_2]_2$[13] (**A**), $[Cp_2Fe_2(CO)_3(PPh_2Bz)]$[14] (**B**), $[Cp_2Fe_2(CO)_3\{P(OPh)_3\}]$[15] (**C**), and $[Cp_2Fe_2(CO)_2$(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole)][16] (**D**). In detail, the Fe−Fe distance of 253.75(7) pm is almost identical with the values found in **A** (253.1 pm), **B** (254.0 pm), and the P,P-bridged complex **D** (252.0 pm). The Fe−CO bonds to the bridging carbonyl ligands are slightly shorter for the P-substituted iron atom Fe1 (189.9(3) and 188.1(4) pm) than for the other atom Fe2 (195.0(4) and 195.6(3) pm). A similar asymmetry was found in complex **B** (averaged values 187.3 and 193.6 pm), while the related value in the parent compound **A** is 191.7 pm. There is only a small deviation of 7° from an ideal eclipsed arrangement of the terminal CO and the phosphole P atom. The two Fe1−Fe2−C planes containing C13 or C14, respectively, form an interplanar angle of 163°, identical with the value in Fp_2 and close to those of the derivatives **B** (157°) and **C** (159°).

If the above reaction is carried out in refluxing xylene (160 °C), phosphaferrocene **1** is formed. There is no evidence for a disubstituted Fp_2 dimer where both terminal CO ligands have been replaced by phosphole. Indeed, such disubstituted dimers are rare but some examples are known, including $[CpFe(CO)\{P(OMe)_3\}]_2$[17] and the 2,2′-diphosphole-bridged dimer **D**.[16] Interestingly, the latter complex does not yield diphosphaferrocene on heating.

Heating the pure ᵗBu compound **2b** in boiling xylene yields selectively phosphaferrocene **1**, Fp_2, and isobutene. A slow stream of nitrogen was passed through the reaction flask during the heating period, and low-boiling-point volatiles were isolated from the gas stream in a cooling trap at liquid-nitrogen temperature. Isobutene was the only isolated species and was identified by GC-MS and NMR analysis. In particular, there

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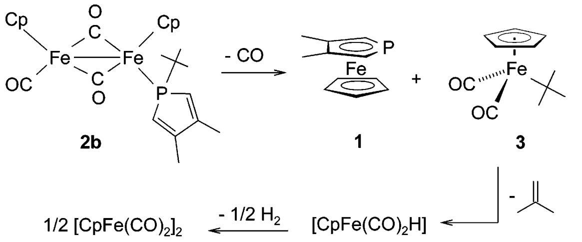
Scheme 4



was no isobutane and no other butene isomers. This result makes the intermediate presence of free *tert*-butyl radicals very unlikely, because they certainly would not selectively decay to isobutene but also to isobutane by H-atom abstraction. Under the conditions of the preparative phosphaferrocene synthesis, i.e., Fp_2 and *tert*-butylphosphole in a 1:2 ratio in refluxing xylene, isobutene is again the only detectable species in the volatiles. (The identification of H_2 was not attempted.) Under optimized conditions, phosphaferrocene can be isolated in 65% yield.[3a]

To account for the selective formation of isobutene during the reaction, we propose the reaction pathway given in Scheme 4: the initial step is the substitution of one CO ligand in Fp_2 by *tert*-butylphosphole, leading to the substituted dimer **2b**, which is unstable under the reaction conditions (160 °C) and reacts further under simultaneous fragmentation of the two CpFe fragments and the P$-$CMe$_3$ bond. Transfer of the ^{t}Bu group from phosphorus to the second Fe atom thus generates [CpFe(CO)$_2$^{t}Bu] (**3**) and—after elimination of another CO group—1 equiv of phosphaferrocene **1**. β-H elimination of isobutene from the ^{t}Bu complex **3** offers a straightforward explanation as to why this is the only observed product originating from the *tert*-butyl group and strongly supports the mechanistic suggestion. The resulting hydride complex [CpFe(CO)$_2$H] is known to be thermally labile and to form Fp_2 under concomitant release of H_2, even below room temperature.[18] In contrast, the phosphine hydride derivatives [CpFe(CO)(PR$_3$)H] are stable species.[19]

β-H elimination is a well-known process for the decomposition of metal alkyl complexes, which may or may not be isolable, depending on the nature of the metal, the coligands, and the alkyl group. Various complexes of the type [CpFe(CO)$_2$R] have been prepared, isolated, and characterized, including the methyl, ethyl, *n*-propyl, long-chain alkyl, and *tert*-butyl derivatives.[20] Under photochemical conditions in a molecular beam, scission of the Fe$-$R bond in [CpFe(CO)$_2$R] proceeds by both β-elimination and homolytic cleavage, producing free radicals.[21] The irradiation of [CpFe(CO)$_2$Et] in hexane solution produces Fp_2 and both ethylene and ethane. However, the formation of ethane presumably does not proceed via ethyl radicals.[22]

To corroborate the assumption of the ^{t}Bu complex **3** being an intermediate in the reaction which decays via β-elimination, compound **3** was independently prepared according to the literature by starting from Na[CpFe(CO)$_2$] and methallyl chloride[23] and its behavior in refluxing xylene was investigated: the only products observed under these conditions were Fp_2 and isobutene, confirming that β-elimination to [CpFe(CO)$_2$H] and subsequent release of H_2 were indeed operative under preparative conditions. The identification of H_2 in the volatiles was not attempted.

An alternative potential pathway from the phosphole-substituted dimer **2b** to the phosphaferrocene **1** might involve fragmentation of **2b** to give the two 17-electron species [CpFe(CO)$_2$] and [CpFe(CO)(*tert*-butylphosphole)], respectively. While dimerization of the former fragment could straightforwardly account for the formation of Fp_2, the selective transformation of the latter species into phosphaferrocene and isobutene does not seem very convincing, due to its radical character. Instead, the formation of products expected to arise from ^{t}Bu radicals would be anticipated: e.g., isobutane or dimeric ^{t}Bu$-$^{t}Bu. Since those species could not be detected, we consider the mechanism outlined in Scheme 4 the more plausible.

Obviously, it is more difficult to rationalize the formation of phosphaferrocene from 1-phenylphosphole. Very likely, the reaction similarly proceeds via the monosubstituted dimer **2a**. However, β-elimination does not provide a suitable pathway, due to the highly unfavorable release of benzyne.

In conclusion, we have provided a meaningful mechanistic pathway for the formation of phosphaferrocene from 1-*tert*-butylphosphole and Fp_2 under thermal conditions.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dry nitrogen by means of conventional Schlenk techniques. Solvents were dried and purified by standard methods. Alumina was heated at 220 °C for 12 h, cooled to room temperature under high vacuum, deactivated with 5% water, and stored under nitrogen. NMR spectra were recorded on a Bruker Avance DRX 500 (^{1}H, 500 MHz; ^{31}P{^{1}H}, 202 MHz; ^{13}C{^{1}H}, 126 MHz) and a Bruker Avance DRX 200 spectrometer (^{1}H, 200 MHz; ^{31}P{^{1}H}, 81 MHz). ^{1}H spectra are referenced to the residual solvent signal and ^{31}P spectra to external H_3PO_4 (85%). Mass spectra were recorded on a Varian MAT 311A spectrometer (EI, 70 eV electron energy). [CpFe(CO)$_2$^{t}Bu] (**3**) was prepared according to literature procedures, starting from NaFp and methallyl chloride.[23,24]

Synthesis of 2b. A mixture of 1-*tert*-butyl-3,4-dimethylphosphole[25] (1.45 g, 8.6 mmol) and [CpFe(CO)$_2$]$_2$ (3.05 g, 8.6 mmol) in 50 mL of benzene was refluxed for 1 day. ^{31}P NMR inspection of the crude mixture indicated a 50% conversion of starting phosphole to product **2b**. Purification by chromatography on alumina with hexane/diethyl ether (8:1) afforded the pure product as a deep green powder (1.04 g, 25%). ^{1}H NMR (500 MHz, acetone-d_6): 0.97 (d, $^3J_{HP}$ = 14.2 Hz, 9H, ^{t}Bu), 2.02 (s, 6H, CH$_3$), 4.54 (s, 5H, Cp), 4.72 (s, 5H, Cp), 5.96 (d, 2H, ^2J(HP) = 32.6 Hz, phospholyl α-H). ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$): 83.50 ppm (s). MS: 429 [M$^+$ $-$ Cp], 401 [M$^+$ $-$ Cp $-$ CO]. Anal. Calcd: C, 55.91; H, 5.51. Found: C, 55.72; H, 5.25.

Synthesis of 2a. 2a (2.37 g) was obtained in a manner analogous to that for **2b** from 1-phenyl-3,4-dimethylphosphole[26] and Fp_2 in 66% yield after chromatography. Crystals suitable for X-ray diffraction were obtained by cooling a hexane solution to 4 °C. ^{1}H

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NMR (500 MHz, acetone-d_6): 1.81 (s, 6H, 2 × CH_3), 4.34 (s, 5H, Cp), 4.61 (s, 5H, Cp), 6.04 (d, 2H, ^2J(HP) = 33,1 Hz, phospholyl α-H), 7.56 (m, 5H, phenyl). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): 72.70 (s). Anal. Calcd: C, 58.41; H, 4.51. Found: C, 58.53; H, 4.90.

Thermal Treatment of 2a,b. 2b (1 mmol) was heated in xylene under reflux for 1 h, and the volatiles were removed under vacuum. Chromatography of the residue on alumina yielded 0.9 mmol (90%) of phosphaferrocene **1** (hexane) and 0.45 mmol (90%) of Fp_2 (hexane/ether 2/1). The NMR data of the compounds are in agreement with the literature data. Refluxing the phenyl derivative **2a** in xylene leads quantitatively to a mixture of **1** and 2-phenyl-3,4-dimethylphosphaferrocene (9:1), as shown by in situ ^{31}P NMR spectroscopy.

Volatile Products Formed from Fp_2 and *tert*-Butylphosphole. A mixture of 1-*tert*-butyl-3,4-dimethylphosphole[25] (10.8 g, 64.6 mmol) and $[CpFe(CO)_2]_2$ (12.4 g, 35.2 mmol) in 100 mL of xylene was refluxed for 4 h with a cooling trap attached to the reflux condenser and kept at −78 °C to collect volatile products. About 2 mL of liquid was collected during the reaction and identified as isobutene (36 mmol) by GC-MS and ^1H NMR. Evaporation of the solvent from the reaction mixture in the flask under vacuum and purification of the crude product by chromatography gave 9.1 g (39.2 mmol, 60.5%) of analytically pure **1**.

Thermal Treatment of $[CpFe(CO)_2{}^tBu]$ (3). $[CpFe(CO)_2{}^tBu]$ (**3**; 150 mg, 0.64 mmol) was heated under reflux in 5 mL of xylene for 1 h (until gas evolution had ceased). Ca. 35 μL of volatile material was collected in a cooling trap (−78 °C) and identified by GC-MS to be a mixture of xylene and isobutene. No isobutane or 2,2,3,3-tetramethylbutane could be detected. Fp_2 was identified as the reaction product in the flask by ^1H NMR and EI-MS, being formed in almost quantitative yield.

X-ray Structure Determination of Complex 2a. Crystal data: $C_{25}H_{23}Fe_2PO_3$, $M_r = 514.10$, red platelet, 0.8 × 0.5 × 0.1 mm^3, $T = 293$ K, STOE CCD, Mo Kα radiation, $\lambda = 0.710\,73$ Å, triclinic, space group $P\bar{1}$, $a = 8.2305(13)$ Å, $b = 8.7775(14)$ Å, $c = 16.3203(19)$ Å, $\alpha = 74.432(12)°$, $\beta = 79.150(12)°$, $\gamma = 79.994(13)°$, $V = 1106.0(3)$ Å^3, $Z = 2$, $D_c = 1.544$ Mg/m^3, μ(Mo Kα) = 1.409 mm^{-1}, $F(000) = 528$, total of 12 687 reflections, 4075 unique reflections, $R(\text{int}) = 0.0481$, 3421 reflections with $I > 2\sigma(I)$, structure solution by direct methods[27] and subsequent ΔF syntheses, full-matrix least-squares refinement[28] on F^2, 281 parameters, final results R1 = 0.0427, wR2 = 0.0895 ($I > 2\sigma(I)$), R1 = 0.0523, wR2 = 0.0946 (all data), GOF = 1.046, maximum/minimum residual electron density +0.66 /−0.46 e Å^{-3}. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-298729. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. +1223/336−033; E-mail, teched@chemcrys.cam.ac.uk) or via the Internet at http://www.ccdc.cam.ac.uk.

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Supporting Information Available: A CIF file giving X-ray structural information for compound **2a**. This material is available free of charge via the Internet at http://www.acs.org.

OM060025S

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