F573, and R.E.D., Grant No. F233).

Registry No. 1, 57139-08-9; **2**, 19599-68-9; **9a**, 100700-54-7; **9b**, 100700-57-0; **9c**, 100700-60-5; **10a**, 100837-22-7; **10b**, 100837-25-0; **10c**, 100837-27-2; **11a**, 100700-55-8; **11b**, 100700-58-1; **12a**, 100700-56-9; **12b**, 100700-59-2; **13a**, 100837-23-8; **13b**, 100895-70-3; **14a**, 100837-24-9; **14b**, 100837-26-1; nonacarbonyldiiron, 15321-51-4; *o*-bis(phenylphosphino)benzene, 38023-29-9.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional crystallographic coordinates, thermal parameters, and full listings of bond lengths and angles (77 pages). Ordering information is given on any current masthead page.

Ligand Exchange Reaction of Ferrocene with 2,4,6-Triphenylphosphabenzene. Synthesis and Structural Study of Isomeric (η^5-Phosphacyclohexadienyl)(η^5-cyclopentadienyl)iron(II) Complexes Containing a η^5-Phosphadienyl Unit

François Nief*[1a] and Jean Fischer[1b]

Equipe CNRS-SNPE, BP 28, 94320 Thiais, France, and Laboratoire de Cristallochimie, Institut Le Bel,
Université Louis Pasteur, 67070 Strasbourg Cedex, France

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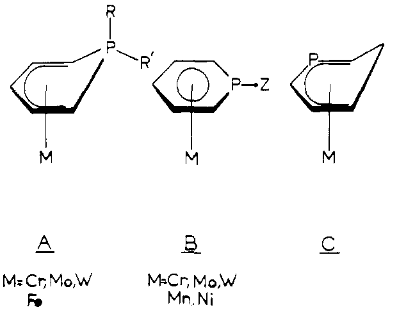
The reaction of 2,4,6-triphenylphosphabenzene with ferrocene and aluminum chloride gives a transient (η^6-2,4,6-triphenylphosphabenzene)(η^5-cyclopentadienyl)iron cation which reacts with water to give (η^5-2,4,6-triphenyl-1-hydrophosphabenzene 1-oxide)(η^5-cyclopentadienyl)iron, a secondary phosphine oxide complex. Reduction of this complex with trichlorosilane affords, depending on the conditions used, four isomeric (η^6-2,4,6-triphenylhydrophosphabenzene)(η^5-cyclopentadienyl)iron compounds, three of which possess the unprecedented η^5-phosphadienyl ligand. The X-ray crystal structure of one of these complexes is presented. The interconversion of the isomeric η^5-2,4,6-triphenylhydrophosphabenzene complexes has been studied by using 2,4,6-triphenylphosphabenzene-*1,3*-d_2 as ligand. The aforementioned (η^6-phosphabenzene)(η^5-cyclopentadienyl)iron cationic complex could be obtained by hydride abstraction from (η^5-2,4,6-triphenyl-2-hydrophosphabenzene)(η^5-cyclopentadienyl)iron.

Introduction

Several organometallic complexes in which a π-ligand has the phosphabenzene structure are now known. The π-complexes that have been prepared so far can be classified according to two types, A and B (Chart I). In structure A[2] a metal is coordinated by a η^5-dienyl ligand. In this type of compound, the phosphorus atom is not coordinated to the metal and has no specific role in the metal–ligand interaction. Indeed, compounds have been isolated in which the phosphorus atom had the structural properties of a phosphine,[2f] a phosphine oxide or sulfide,[2g] or a phosphonium salt.[2a-e]

In structure B,[3] a metal is complexed by the η^6 aromatic phosphabenzene ligand. In this case, the phosphorus atom is bonded to the metal. It still possesses a lone pair and can act as a two-electron ligand.

Chart I



Another interesting complex would be type C (Chart I). This type of complex would be similar to structure A in the sense that, in structure C, a η^5-dienyl ligand would also be present, but bonding of the phosphorus atom to the metal would be similar to that in structure B. No compound of type C (η^5-phosphadienyl) has been previously reported in the literature.

So far, complexes of type B have been synthetized with the chromium triad,[3a-d,g] manganese,[3f] and nickel.[3e] In order to expand this series, we wanted to prepare a (cyclopentadienyl)(phosphabenzene)iron(II) cation by the well-known ligand exchange reaction with ferrocene.[4] We now wish to report on this and on the synthesis and structure of some of the previously unknown complexes of type C as well.

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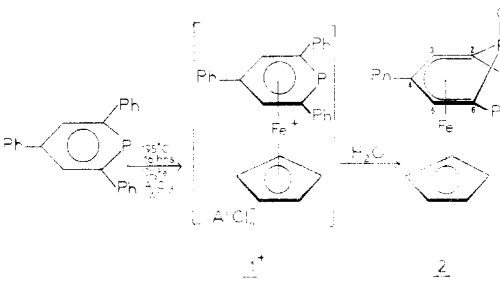
(1) (a) Equipe CNRS-SNPE. (b) Laboratoire de Cristallochimie.

(2) (a) Debaerdemaeker, T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1686. (b) Dimroth, K.; Kaletsch, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 871. (c) Dimroth, K.; Luckhoff, K. *Chem. Ber.* **1980**, *113*, 313. (d) Dimroth, K.; Berger, S.; Kaletsch, H. *Phosphorus Sulfur* **1981**, *10*, 295. (e) Debaerdemaeker, T. *Cryst. Struct. Commun.* **1982**, *11*, 1209. (f) Lehmkuhl, H.; Paul, R.; Krüger, C.; Tsay, Y. H.; Benn, R.; Mynott, R. *Liebigs Ann. Chem.* **1981**, 1147. (g) Deschamps, E.; Mathey, F.; Knobler, C.; Jeannin, Y. *Organometallics* **1984**, *3*, 1144.

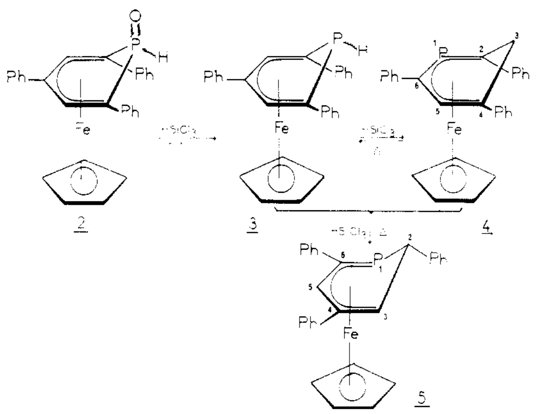
(3) (a) Deberitz, J.; Nöth, H. *Chem. Ber.* **1970**, *103*, 1970. (b) Deberitz, J.; Nöth, H. *Chem. Ber.* **1973**, *106*, 2222. (c) Vahrenkamp, H.; Nöth, H. *Chem. Ber.* **1972**, *105*, 1148. (d) Nainan, K. C.; Sears, C. T. *J. Organomet. Chem.* **1978**, *148*, C31. (e) Lehmkuhl, H.; Paul, R.; Mynott, R. *Liebigs Ann. Chem.* **1981**, 1139. (f) Nief, F.; Charrier, C.; Mathey, F.; Simalty, M. *J. Organomet. Chem.* **1980**, *187*, 227. (g) Nief, F.; Charrier, C.; Mathey, F.; Simalty, M. *Nouv. J. Chim.* **1981**, *5*, 187. (h) Fischer, J.; De Cian, A.; Nief, F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1067.

(4) For a recent review, see: Astruc, D. *Tetrahedron* **1963**, *24*, 4027.

Scheme I



Scheme II



Results and Discussion

Ligand Exchange Reaction. The (arene)(cyclopentadienyl)iron cations are easily made by direct reaction of the arene with ferrocene in the presence of a Lewis acid such as $AlCl_3$ and of Al powder acting as an antioxidant, provided that the arene is sufficiently electron-rich. Since the readily available 2,4,6-triphenylphosphabenzene easily forms π-complexes and is a good π-base,[2a-c,e,f,h] we tried to react it with ferrocene, $AlCl_3$, and Al in a 1:1:2:1 molar ratio. When these reactants were heated in refluxing heptane for 48 h, no reaction was observed. Under more forcing conditions (heating a mixture of those reactants neat at 195 °C for 16 h), a brown oil was obtained as a crude product. ^{31}P NMR investigation of a dichloromethane solution of this reaction mixture revealed, besides a low-field signal at 186 ppm corresponding to the starting material, a new peak at −7.5 ppm. However, when the reaction mixture was hydrolyzed, the organic phase turned dark red and, on addition of NH_4PF_6 to the aqueous phase, no precipitate was obtained. This means that no cationic complex of type **1** (Scheme I) was present in the aqueous phase. A ^{31}P NMR spectrum of an aliquot taken from the organic phase showed the disappearance of the initial resonance at −7.5 ppm and the appearance of a new peak at −27 ppm. Chromatography of the organic phase afforded orange-red crystals for which all spectral data indicated structure **2** (Scheme I).

The infrared spectrum reveals the presence of P=O and P—H bonds at frequencies of 1150 and 2325 cm^{-1}, respectively. The presence of a secondary phosphine group is also consistent with the NMR spectra: the proton attached to phosphorus resonates at 8.22 ppm with a characteristic $^1J_{P-H}$ equal to 515 Hz. The formula was established from the elemental analysis and mass spectra, and the other data deserve no special comment. We propose the following explanation for the formation of **2**: reaction of the triphenylphosphabenzene with ferrocene did give $1^+{\cdot}AlCl_4^-$ as the primary product, and the ^{31}P resonance at −7.5 ppm corresponds to this product; but $1^+{\cdot}AlCl_4^-$ then underwent nucleophilic attack at the phosphorus atom by water and was eventually transformed into **2**. The driving force for the formation of **2** would then be the strength of the P=O bond.

Phosphadienyl Complexes. In order to get the cationic complex 1^+ reasonably pure, and in view of the expected difficulty of isolating this complex directly from the reaction mixture, we tried to circumvent this problem in two steps: (a) reduction of complex **2** into a secondary phosphine and (b) abstraction of a hydride from this secondary phosphine complex with the trityl cation.

The reduction of phosphine oxides classically involves reaction with excess of a silane in an inert solvent.[5] Therefore, we reacted secondary phosphine oxide **2** with an excess of $HSiCl_3$ in toluene. ^{31}P NMR monitoring of this reaction mixture revealed an unexpected set of transformations. First, when $HSiCl_3$ was added to a solution of **2** in toluene at room temperature, the reaction mixture turned dark red within 5 min. A ^{31}P NMR spectrum of the solution revealed total disappearance of the starting material and appearance of another single peak at −84 ppm. When this reaction mixture was heated to reflux, two other resonances appeared, at respectively −18 and −173 ppm. The resonance at −18 ppm reached a maximum intensity after about 45 min of reflux in toluene. After 3 h of reflux, the peaks at −18 and −84 ppm had disappeared and only the peak at −173 ppm remained. No more changes occurred in the ^{31}P spectrum of the reaction mixture when it was further heated. We were able to isolate and structurally identify the products corresponding to these three ^{31}P resonances (Scheme II). These three isolated complexes were isomers of the secondary phosphine **3** as indicated by their mass spectra. Indeed, the product corresponding to the ^{31}P chemical shift of −84, which was obtained by hydrolysis of the reaction mixture after 5 min without heating, was assigned the secondary phosphine structure **3**: the presence of a P–H bond in this compound was evidenced by IR (ν(P–H) 2240 cm^{-1}) and NMR (δ 5.30 ($^1J_{P-H}$ = 153 Hz). The product which had a ^{31}P resonance at −18 ppm was isolated by stopping the reaction after it had about reached its maximum concentration. The reaction mixture was cooled, hydrolyzed, and chromatographed. It was assigned structure **4** on the following bases. The presence of a CH_2 group was inferred from the ^1H NMR spectrum; the high-field proton at 2.08 ppm should be an exo proton because, in (cyclohexadienyl)(cyclopentadienyl)iron complexes, this is the most shielded position.[6,7] The value of 13.7 Hz fits with a geminal coupling constant with the proton at 3.79 ppm which would then be the 3-endo proton. The presence of a CH_2 group is established by ^{13}C NMR; the resonance at 32.6 ppm is a singlet on the broad-band {^{31}P, ^1H} spectrum, a doublet ($^3J_{P-C}$ = 5 Hz) in the broad-band {^1H} spectrum, and a triplet in the broad-band {^{31}P}, off-resonance {^1H} spectrum. The other ^{13}C and ^1H NMR data fit well with the proposed structure. The thermodynamic product which was isolated after 3 h of reflux in toluene, was assigned structure **5**; the proton at 1.95 ppm very likely corresponds to an exo proton and presents a small coupling with H_3, which also resonates at high field because it is at a terminal position on the dienyl structure.[7] The proton H_3 is long-range-coupled with H_5, which could be detected in the aromatic H multiplet by decoupling experiments.

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[5] E.g., see: Quin, L. D.; Caster, K. C.; Kisalus, J. G.; Mesch, K. A. *J. Am. Chem. Soc.* **1984**, *106*, 7021 and references cited herein.

[6] Khand, U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2257.

[7] Ittel, S. D. *J. Organomet. Chem.* **1980**, *195*, 331.

Scheme III

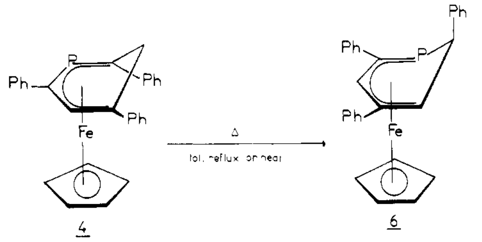
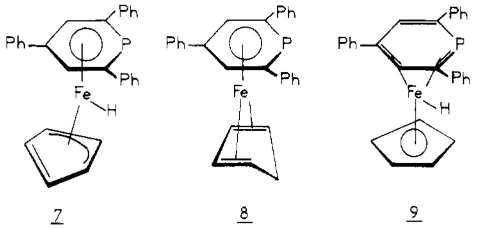
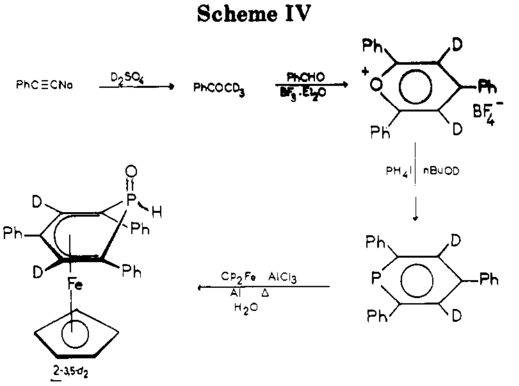


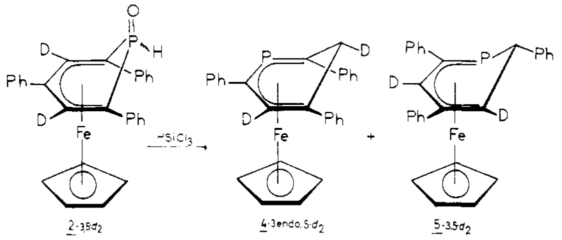
Chart II



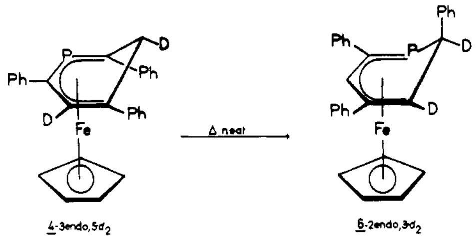
Scheme IV



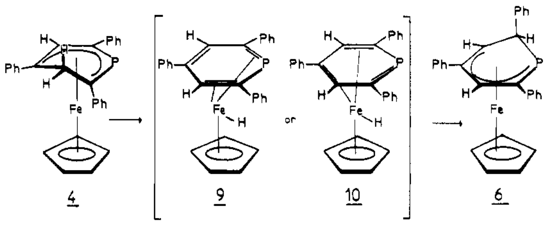
Scheme V



Scheme VI



Scheme VII



The high-field position of the ^{31}P resonance is not surprising since the resonances of terminal carbons in the cyclohexadienyl group appear at very high field.[2g]

Next, we wanted to study the reactivity of the kinetic products **3** and **4** when isolated in a pure state. The secondary phosphine **3** was dissolved in toluene and heated to reflux, and the reaction mixture was checked by ^{31}P NMR. This compound appears to transform slowly into a complex mixture of products, none of which had a chemical shift similar to those of **4** and **5**. On the other hand, when **4** was heated in refluxing toluene or as a neat liquid, it cleanly transformed into a single product which could be assigned structure **6**, i.e., a diastereoisomer of **5** (Scheme III), having an endo proton at position 2 of the ring instead of an exo proton as in compound **5**. This structure was inferred from the NMR data and was confirmed by an X-ray crystallographic study (this structure will be discussed in a following section). Finally, when a solution of isolated **4** was heated in the presence of $HSiCl_3$, a ^{31}P NMR spectrum of the solution showed peaks at −18 and −173 ppm and also at −84 ppm (corresponding to **3**), indicating that **3** and **4** are in equilibrium in the presence of $HSiCl_3$. Under these conditions, either isomer irreversibly transforms into **5**. The rearrangement [**3** ⇄ **4**] → **5** is clearly not an unimolecular process since it is dependent on the presence or absence of the external agent $HSiCl_3$. This equilibrium could possibly involve transfer of hydrogen as a hydride ion: Semmelhack[8] has shown that (η^5-cyclohexadienyl)chromium carbonyl anions that were substituted at the exo position could equilibrate at this position by anionic exchange. But we cannot exclude a radical mechanism: reductions with $HSiCl_3$ under radical conditions are well-known.[9]

As for the **4** → **6** interconversion, an attractive mechanism would involve hydrogen transfer to the metal or to the cyclopentadienyl ring in the first step, followed by transfer of this hydrogen to phosphorus in the endo position. Ligand-to-metal[10] and ligand-to-ligand[11] hydrogen shifts are known processes. Possible intermediates could therefore be (η^6-phosphabenzene)(η^4-cyclopentadiene)iron (**7**), (η^6-phosphabenzene)(η^5-cyclopentadienyl)iron hydride (**8**), and (η^4-phosphabenzene)(η^5-cyclopentadienyl)iron hydride (**9**) (Chart II).

Deuterium-Labeling Experiments. In order to gain more insight into these unexpected rearrangements, we decided to use deuterium-labeling experiments; we could easily prepare **2**-*3,5*-d_2 with 85% isotopic purity (Scheme IV). When this compound was reacted with $HSiCl_3$ in refluxing toluene, we were able to isolate **4**-*3*(*endo*),*5*-d_2 and **5**-*3,5*-d_2 as shown by their respective ^1H and ^2H spectra. In particular, the ^2H spectra of **4**-*3*(*endo*),*5*-d_2 and **5**-*3,5*-d_2 showed that there was no detectable resonance at the 3-exo- and 2-positions, respectively. This shows that the $HSiCl_3$ mediated transformation of **2** into **4** and **5** does not involve the deuterium-labeled positions (Scheme V). This is consistent with exo transfer of hydrogen. Next, the isolated **4**-*3*(*endo*),*5*-d_2 was heated without $HSiCl_3$. NMR investigation of the product that was isolated showed that it had deuteriums at positions 2 and 3 and therefore the structure of **6**-*2*(*endo*),*3*-d_2 (Scheme VI): its ^2H spectrum showed resonances only at the chemical shifts

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(8) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535.

(9) Rochow, E. G. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Jr.; Emeleus, H. J.; Nyholm, R.; Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford 1973; Vol. I, p 1377.

(10) Humphties, A.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans* **1975**, 1710.

(11) Green, M. L. H.; Newman, P. A. *J. Chem. Soc., Chem. Commun.* **1984**, 816.

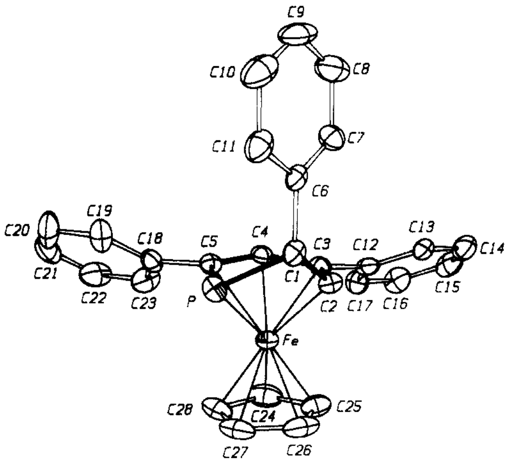
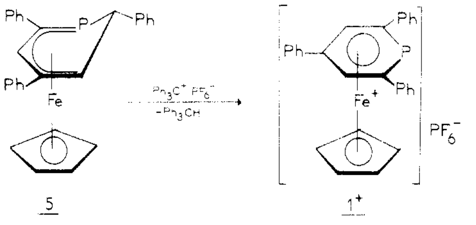


Figure 1. ORTEP plot of one molecule of **6** together with the labeling scheme used. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

Scheme VIII



of positions 2 and 3. We believe that this [1,4] hydrogen shift is consistent with an (η^4-phosphabenzene)(η^5-cyclopentadienyl)iron hydride like **9** or **10** as an intermediate (Scheme VII), where the hydrogen is transferred from one terminal position to the other of the complexed diene unit: if an intermediate such as **7** or **8** containing a η^6-phosphabenzene was involved, then there very likely would have been scrambling of the deuterium between positions 2 and 6 because the symmetry of the bonding of 2,4,6-triphenylphosphabenzene with iron in intermediates **7** and **8** renders positions 2 and 6 equivalent.

Hydride Abstraction Reaction. The desired (cyclopentadienyl)(phosphabenzene)iron cation should now result from an oxidation of derivatives **4** and **5** with trityl cation, because this reaction is known to proceed mostly by exo hydride abstraction.[4] Therefore we decided to react equimolecular quantities of **5** (which is the most easily available of the isomers) and trityl hexafluorophosphate in methylene chloride (Scheme VIII). We could not isolate $1^+{\cdot}PF_6^-$ as crystals, and it did not have a correct carbon analysis. However, we could assign the $1^+{\cdot}PF_6^-$ structure to the product we isolated on the following bases.[12] (a) Hydride has been abstracted from **5**, as indicated by a 73% recovery of triphenylmethane during the workup. (b) The ^1H and ^{13}C NMR spectra indicate that the 2,4,6-triphenylphosphabenzene structure is present in the molecule and is symmetrically bonded to iron. The ^1H NMR spectrum shows a deshielding of the Cp hydrogens from the starting **5**; this deshielding matches the observed deshielding of Cp (arene) cations from the corresponding Cp (cyclohexadienyl) neutral iron complexes (ca. 1.0 ppm in both cases).[6] (c) The ^{31}P NMR spectrum shows a peak at −10 ppm and a PF_6^- resonance as a septet at high field (−140 ppm). Integrations of these two resonances is approximately 1:1. In addition, the ^{31}P NMR resonance of isolated $1^+{\cdot}PF_6^-$ is very similar to the one we assigned to $1^+{\cdot}AlCl_4^-$, which supports the hypothesis of its formation as the primary reaction product of 2,4,6-triphenylphosphabenzene with ferrocene in the presence of $AlCl_3$.

Table I. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
Fe	0.81394 (5)	0.32860 (5)	0.43857 (7)	1.72 (1)
P	1.0292 (1)	0.33958 (8)	0.5617 (1)	2.02 (2)
C1	0.9813 (4)	0.4049 (3)	0.7516 (5)	1.9 (1)
C2	0.8420 (4)	0.3954 (3)	0.6883 (5)	1.93 (9)
C3	0.7997 (4)	0.2974 (3)	0.6380 (5)	1.77 (9)
C4	0.8731 (4)	0.2070 (3)	0.5562 (5)	1.76 (9)
C5	0.9762 (4)	0.2172 (3)	0.5096 (4)	1.69 (9)
C6	1.0664 (4)	0.3659 (3)	0.9007 (5)	2.0 (1)
C7	1.0215 (4)	0.3205 (4)	0.9856 (5)	2.5 (1)
C8	1.1045 (5)	0.2866 (4)	1.1219 (6)	3.7 (1)
C9	1.2320 (5)	0.2977 (4)	1.1751 (6)	4.0 (1)
C10	1.2774 (5)	0.3420 (4)	1.0939 (6)	3.8 (1)
C11	1.1947 (4)	0.3766 (4)	0.9560 (5)	2.8 (1)
C12	0.6761 (4)	0.2885 (3)	0.6580 (5)	2.1 (1)
C13	0.6402 (4)	0.3512 (4)	0.7948 (5)	2.5 (1)
C14	0.5278 (4)	0.3429 (4)	0.8196 (6)	3.2 (1)
C15	0.4514 (4)	0.2733 (4)	0.7074 (6)	3.4 (1)
C16	0.4860 (4)	0.2107 (4)	0.5710 (6)	3.1 (1)
C17	0.5977 (4)	0.2193 (4)	0.5469 (5)	2.6 (1)
C18	1.0358 (4)	0.1242 (3)	0.4007 (5)	2.1 (1)
C19	1.1668 (4)	0.1043 (4)	0.4227 (6)	3.1 (1)
C20	1.2255 (5)	0.0161 (4)	0.3283 (6)	3.9 (1)
C21	1.1523 (5)	−0.0522 (4)	0.2082 (5)	3.8 (1)
C22	1.0219 (6)	−0.0331 (4)	0.1820 (6)	3.8 (1)
C23	0.9635 (5)	0.0543 (4)	0.2776 (6)	3.2 (1)
C24	0.6680 (5)	0.2868 (4)	0.2311 (5)	3.3 (1)
C25	0.6244 (5)	0.3842 (4)	0.3293 (6)	3.8 (1)
C26	0.7027 (5)	0.4559 (4)	0.3474 (6)	3.7 (1)
C27	0.7923 (5)	0.4036 (4)	0.2602 (5)	3.5 (1)
C28	0.7706 (5)	0.2984 (4)	0.1885 (5)	3.3 (1)
CS1	0.6071 (6)	0.9565 (6)	0.0951 (8)	6.1 (2)*
CS2	0.6124 (8)	0.9815 (7)	−0.036 (1)	7.8 (2)*
CS3	0.4935 (7)	0.9741 (6)	0.1291 (9)	7.1 (2)*
CS4	0.701 (1)	0.9187 (8)	0.174 (1)	7.0 (2)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] Occupancy = 0.5.

Table II. Selected Bond Lengths (Å), Bond Angles (deg), and Averages with Their Estimated Standard Deviations

	Bond Lengths		
Fe–Cp	2.310 (1)	P–C1	1.862 (3)
Fe–C2	2.101 (3)	P–C5	1.775 (3)
Fe–C3	2.037 (3)	C1–C2	1.497 (4)
Fe–C4	2.064 (3)	C1–C6	1.509 (5)
Fe–C5	2.080 (3)	C2–C3	1.414 (4)
Fe–C24	2.060 (4)	C3–C4	1.428 (4)
Fe–C25	2.055 (4)	C4–C5	1.416 (4)
Fe–C26	2.052 (4)	C3–C12	1.502 (4)
Fe–C27	2.072 (4)	C5–C18	1.492 (4)
Fe–C28	2.072 (4)	⟨C–C⟩Cp	1.408 (3)
		⟨C–C⟩phe	1.382 (1)
	Bond Angles		
C1–P–C5	100.0 (1)	P–C1–C6	116.1 (2)
P–C1–C2	99.2 (2)	P–C5–C18	118.3 (2)
C1–C2–C3	122.8 (3)	C2–C1–C6	120.1 (3)
C2–C3–C4	118.2 (3)	C2–C3–C12	121.4 (3)
C3–C4–C5	121.2 (3)	C4–C3–C12	120.2 (3)
C4–C5–P	122.2 (2)	C4–C5–C18	119.2 (3)
		⟨C–C–C⟩Cp	108.0 (1)
		⟨C–C–C⟩phe	120.0 (1)

Structure of (η^5-Cyclopentadienyl)(η^5-2,4,6-triphenyl-2-*endo*-hydrophosphabenzene)iron (6). Table

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[12] One reviewer pointed out that, since reaction with Ph_3C^+ probably proceeds by electron transfer, depending on the reversibility of the 18e ⇄ 17e oxidation, one could obtain a mixture of C–C and C–H bond cleavage. However, we have no spectral evidence of compounds occurring from C–C bond cleavage in the products we isolated.

I gives the final atomic parameters for all non-hydrogen atoms. Each unit-cell contains two molecules of **6** in general positions and one $CH_3C_6H_5$ solvent molecule located on an inversion center and therefore disordered. There are no unusual intermolecular contacts. Table II lists selected bond lengths and angles with averages, and Figure 1 displays an ORTEP plot of one molecule. Each iron atom is sandwiched between an η^5-cyclopentadienyl ring (R1) and an η^5-phosphacyclohexadienyl unit (R2). The iron–C(R1) bond lengths are not significantly different from each other with a mean value of 2.062 (2) Å leading to an Fe···C_5H_5 mean plane distance of 1.680 (1) Å. This distance is somewhat lengthened compared to those found in free phosphaferrocene[13] (1.655 (1) Å, in complexed phosphaferrocene[14] (1.664) (1) Å), or in (η^5-cyclohexadienyl)(η^5-cyclopentadienyl)iron complexes (1.66 Å).[15] The phosphorus atom and carbon atoms C2 to C5 of R2 are η^5-bonded to iron; C1 is not bonded to the metal, the Fe···C1 distance being 2.859 (3) Å.

The P, C2 to C5 unit is not planar; the deviations from the least-squares plane through these atoms range from 0.038 (4) to −0.027 (4) Å: P and C3 to C5 are toward the iron atom and C2 to C4 toward C1. The iron atom is 1.527 (1) Å out of this plane and C1 is 0.888 (4) Å. The dihedral angle between this mean plane and the plane defined by P/C1/C2 is equal to 54.6°. The Fe–C2 to C5 bond distances vary from 2.037 (3) Å for C3 to 2.101 (3) Å for C2; in contrast, the C–C bond lengths (C2 to C5) of R2 are equivalent within 2σ (mean 1.419 (2) Å), somewhat shorter than the 1.446-Å distance found in η^6-phosphabenzene rings[3h] but rather in the range of those found in η^5-phospholyls.[13,16] The two P–C bond lengths of R2 are different, P–C1 being typical for a P–C σ-bond, whereas the P–C5 distance is close to that found in η^6-phosphabenzene rings (1.764 (3) Å).[3h] Thus, the electronic density of R2 is delocalized over atoms P, C2, C3, C4, and C5. The three phenyl rings are planar within experimental error and have normal geometries with a mean C–C bond length of 1.382 (1) Å and a mean C–C–C bond angle of 120.0 (1)°.

Experimental Section

General Data. All manipulations were performed under a protective atmosphere of argon. ^1H (80.13 MHz), $^{31}P\{^1H\}$ (32.44 MHz), and $^{13}C\{^1H\}$ (20.15 MHz) NMR spectra were recorded on a Bruker WP80 SY spectrometer. Chemical shifts are expressed in δ units relative to Me_4Si (^1H and ^{13}C) and external H_3PO_4 (^{31}P). Coupling constants are expressed in hertz. $^2H\{^1H\}$ NMR spectra were recorded in C_6H_6 at 61.4 MHz with a Bruker AM 400 instrument. Chemical shifts are internally referenced to the natural abundance signal of C_6H_5D at 7.20 ppm. ^{31}P NMR monitoring of the reactions was performed by measuring the spectrum of ca. 2 mL of the crude reaction mixtures in a 10-mm tube fitted with a coaxial capillary tube filled with D_2O, which acted as a lock substance. In the ^{13}C NMR spectra, the multiplicity of the carbon atoms was verified by ^1H off-resonance-decoupling experiments. Mass spectra (70 eV) and elemental analyses were performed by the "Service Central d'Analyses du CNRS". IR spectra were measured with a Perkin-Elmer Model 297 spectrometer. Column chromatography separations were made with silica gel (Kieselgel 60, 70–270 mesh ASTM, Macherey-Nagel, Düren, Germany).

(η^5-2,4,6-Triphenyl-1-hydrophosphabenzene 1-oxide)(η^5-cyclopentadienyl)iron (2). A mixture of 2,4,6-triphenylphosphabenzene[17] (2.0 g, 6.17 mM), ferrocene (1.15 g, 6.18 mM), aluminum chloride (1.65 g, 12.36 mM), and aluminum powder (0.17 g, 6.30 mM) was heated in a sealed tube for 18 h at 195 °C. The dark brown reaction mixture was then dissolved in dichloromethane (50 mL) and cooled to 0 °C. Water (20 mL) was then carefully added, whereupon the reaction mixture turned bright red. The organic phase was filtered, dried ($MgSO_4$), and chromatographed (CH_2Cl_2/THF, 9/1). After a brown band containing mainly unreacted ferrocene and phosphabenzene was obtained, an orange band was collected and evaporated to dryness, yielding crude **2** as an orange-red air-stable amorphous solid (1.10 g, 2.38 mM, 47%) which was crystallized in toluene. Unreacted triphenyl-2,4,6-phosphabenzene (350 mg) could be recovered from the first fraction by further chromatography (hexane/benzene, 80/20); mp 147 °C. Anal. Calcd for $C_{28}H_{23}FeOP$: C, 72.72; H, 4.97; *m/e*, 462.0833. Found: C, 72.78; H, 5.17; *m/e*, 462.0846. Mass spectrum, *m/e* (relative intensity) 462 (M^+, 46), 396 ($M - C_5H_6^+$, 37), 324 (L, 100). ^1H NMR ($CDCl_3$): δ 4.07 (s, Cp), 6.12 (dd, $^3J_{PH} = 14.5$, $^4J_{HH} = 2.0$ Hz, H_3 and H_5), 7.1–7.8 (m, CH arom), 8.22 (dt, $^1J_{PH} = 515$, $^4J_{HH} = 2.0$ Hz, H_1). ^{31}P NMR ($CDCl_3$): −27.0 ppm. ^{13}C NMR ($CDCl_3$): δ 61.4 (d, $^1J_{PC} = 93$ Hz, C_2 and C_6), 77.0 (s, Cp), 84.0 (s, C_3 and C_5), 96.0 (d, $^3J_{PC} = 12$ Hz, C4), 125–129 (m, CH arom), 140.3 (d, $^2J_{PC} = 17$ Hz, C ipso C_3 and C ipso C_5), 140.5 (s, C ipso C_4).

(η^5-2,4,6-Triphenyl-1-hydrophosphabenzene)(η^5-cyclopentadienyl)iron (3). To a solution of **2** (150 mg, 0.32 mM) in toluene (2 mL) was added $HSiCl_3$ (0.1 mL, 1 mM). After 5 min of stirring at room temperature, the solution was cooled to 0 °C and carefully hydrolyzed with a degassed 10% NaOH solution (2 mL). The organic phase was separated, dried ($MgSO_4$, 50 mg), and evaporated to dryness, yielding **3** as a very air-sensitive dark red oil (110 mg, 0.25 mM, 77%). MS calcd for $C_{28}H_{23}FeP$: *m/e* 446.0884. Found: *m/e* 446.0879. MS: *m/e* (relative intensity) 446 (M^+, 100), 445 ($M - 1^+$, 44), 380 ($M - CpH^+$, 61), 324 (L, 87). IR (KBr): $\nu_{PH} = 2240$ cm^{-1}. ^1H NMR (C_6D_6): δ 3.52 (s, C_5H_5), 5.30 (d, $J_{PH} = 153$ Hz, H_1), 6.06 (d, $^3J_{PH} = 2.7$ Hz, H_3 and H_5), 7–8 (m, CH arom). ^{31}P NMR (C_6D_6): −83.8 ppm. ^{13}C NMR (C_6D_6): δ 78.7 (s, Cp), 86.3 (d, $^2J_{CP} = 7$ Hz, C_3 and C_5), 101.8 (s, C_4), 123–133 (m, CH arom), 147.3 (d, $^2J_{PC} = 25.5$ Hz, C ipso C_2 and C ipso C_6), 143.9 (s, C ipso C_4). Resonances of C_2 and C_6 were not observed.

(η^5-2,4,6-Triphenyl-3-hydrophosphabenzene)(η^5-cyclopentadienyl)iron (4). A solution of **2** (730 mg, 1.58 mM) and 0.5 mL (5 mM) of $HSiCl_3$ in toluene (15 mL) was heated at 105 °C for 55 min. The reaction mixture was cooled to 0 °C and hydrolyzed with a degassed 10% solution of NaOH (15 mL). The organic phase was dried ($MgSO_4$) evaporated to dryness and chromatographed (pentane/benzene, 80/20). A red band was collected, which was evaporated to dryness, yielding 200 mg of crude **4** as a moderately air-sensitive red oil (0.45 mM, 28%). An analytical sample was crystallized in pentane at −20 °C; mp 134 °C. Anal. Calcd for $C_{28}H_{23}FeP$: C, 75.34; H, 5.16; *m/e*, 446.0884. Found: C, 75.41; H, 5.36; *m/e*, 446.0853. MS: *m/e* (relative intensity) 446 (M^+, 100), 445 ($M - 1^+$, 53), 380 ($M - CpH^+$, 51), 324 (L, 100). ^1H NMR (C_6D_6): δ 2.18 (dd, $^2J_{HH} = 13.7$, $^3J_{HP} = 3.7$ Hz, H_3 endo), 3.82 (dd, $^2J_{HH} = 13.7$, $^3J_{HP} = 7.6$ Hz, H_3 exo), 3.71 (s, Cp), 5.68 (d, $^3J_{HP} = 5.1$ Hz, H_6), 7–8 (m, CH arom). ^{31}P NMR (C_6D_6): −20.4 ppm. ^{13}C NMR (C_6D_6): δ 32.6 (d, $^2J_{CP} = 5$ Hz, C_3), 35.5 (d, $^1J_{CP} = 60$ Hz, C_2), 40.9 (s, C_4), 80.5 (s, Cp), 88.2 (d, $^2J_{CP} = 6$ Hz, C_5), 108.4 (d, $^1J_{CP} = 65$ Hz, C_6), 123–132 (m, CH arom), 146.3 (d, $^2J_{CP} = 19.5$, C ipso C_2 or C ipso C_6), 147.4 (s, C ipso C_4), 151.3 (d, $^2J_{PC} = 19.5$ Hz, C ipso C_6 or C ipso C_2).

(η^5-2,4,6-Triphenyl-2-*exo*-hydrophosphabenzene)(η^5-cyclopentadienyl)iron (5). To a solution of **2** (600 mg, 1.3 mM) in toluene (10 mL) was added 0.5 mL (5 mM) of trichlorosilane. The reaction mixture was refluxed for 3 h and then cooled to room temperature and filtered on a short (5 × 2 cm) column of silica gel. The red filtrate was evaporated to dryness whereupon **5** crystallized. The air-sensitive red crystals were rinsed with cold ether and cold hexane and dried (455 mg, 1.03 mM, 79%). An analytical sample was recrystallized in toluene/hexane; mp 166 °C. Anal. Calcd for $C_{28}H_{23}FeP$: C, 75.34; H, 5.16; P, 6.95. Found: C, 75.16; H, 5.03; P, 6.53. MS: *m/e* (relative intensity) 446 (M^+, 100), 445 ($M - H^+$, 32), 380 ($M - CpH^+$, 43). ^1H NMR (C_6D_6):

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δ 1.95 (t, $^3J_{HH} \simeq {}^2J_{HP}$ = 2.2 Hz, H_2), 2.98 (quintet, $^3J_{HH}$ = 2.2, $^4J_{HH} \simeq {}^3J_{HP}$ = 1.2 Hz, H_3), 3.93 (d, J_{PH} = 0.8 Hz, Cp), 7.36 ($^3J_{PH}$ = 3.4, $^4J_{HH}$ = 1.2 Hz, H_5), 7–8 (m, CH arom). ^{31}P NMR (C_6D_6): −173.0 ppm. ^{13}C NMR (C_6D_6): δ 23.0 (d, $^2J_{CP}$ = 2.5 Hz, C_3), 33.3 (d, $^1J_{CP}$ = 22 Hz, C_2), 79.5 (s, Cp), 91.8 (d, $^2J_{CP}$ = 6 Hz, C_5), 93.4 (d, $^3J_{CP}$ = 2.5 Hz, C_4), 100.2 (d, $^1J_{CP}$ = 72 Hz, C_6), 126–130 (m, CH arom), 143 (s, C ipso C_4), 145.3 (d, $^2J_{CP}$ = 17, C ipso C_6 or C ipso C_2), 145.7 (d, $^2J_{CP}$ = 12 Hz, C ipso C_2 or C ipso C_6).

(η^5-2,4,6-Triphenyl-2-*endo*-hydrophosphabenzene)(η^5-cyclopentadienyl)iron (6). Crude 4 (250 mg) was refluxed in 10 mL of toluene for 15 h. The mixture was evaporated to dryness, and **6** was quantitatively obtained as an air-sensitive red oil, which later crystallized; mp 90 °C. MS calcd for $C_{28}H_{23}FeP$: *m/e* 446.0884. Found: 446.0905. MS: *m/e* (relative intensity) 446 (M^+, 100), 445 ($M - H^+$, 66), 380 ($M - CpH^+$, 70). ^{1}H NMR (C_6D_6): δ 2.76 (dd, $^3J_{HH}$ = 8.0, $^2J_{HP}$ = 15.0 Hz, H_2), 3.43 (ddd, $^3J_{HH}$ = 8.0, $^3J_{HP}$ = 3.0, $^4J_{HH}$ = 1.8 Hz, H_3), 3.95 (s, Cp), 7–7.7 (m, CH arom), 7.10 (m, H_5). ^{31}P NMR (C_6D_6): −150.1 ppm. ^{13}C NMR (C_6D_6): δ 26.5 (s, C_3), 35.0 (d, $^1J_{CP}$ = 24.7 Hz, C_2), 78.8 (s, Cp), 92.7 (s, C_4), 92.9 (d, $^2J_{CP}$ = 6 Hz, C_5), 97.7 (d, $^1J_{CP}$ = 72 Hz, C_6), 122–132 (m, CH arom), resonances at 143.8, 145.1, 146.1, 147.0 (C ipso).

(η^5-2,4,6-Triphenylphosphabenzene)(η^5-cyclopentadienyl)iron (II) Hexafluorophoshate ($1^+ \cdot PF_6^-$). On a high vacuum lime, 10 mL of dichloromethane was condensed at −78 °C onto a mixture of **5** (224 mg, 0.5 mM) and trityl hexafluorophosphate (194 mg, 0.5 mM). The reaction mixture was stirred at room temperature for 15 min. It was then filtered while still on the vacuum line and evaporated to dryness. The resulting solid was then thoroughly extracted with diethyl ether (10 × 10 mL). This extract was evaporated to dryness, and a solid (178 mg) was obtained which was identified as triphenylmethane by NMR[18] (0.37 mM, 73%). The residue was then dissolved in a minimum quantity of dichloromethane, precipitated with ether, and filtered (twice) to give 192 mg (0.33 mM, 65%) of a hygroscopic greenish brown amorphous solid. Anal. Calcd for $C_{28}H_{22}F_6FeP_2$: C, 56.95; H, 3.73; F, 19.32; Fe, 9.49; P, 10.51. Found: C, 58.69; H, 4.12; F, 19.14; Fe, 9.58; P, 11.27. ^{1}H NMR (CD_2Cl_2): δ 4.97 (s, Cp), 7.27 (d, J_{HP} = 4 Hz, H_3 and H_5), 7.4–8.1 (m, CH arom). ^{31}P NMR ($CDCl_3$): −10.4 (P_1), −147.1 ppm (septet, $^1J_{PF}$ = 713 Hz, PF_6^-). ^{13}C NMR ($CDCl_3$): δ 80.7 (s, Cp), 89.2 (d, $^2J_{CP}$ = 6 Hz, C_3 and C_5), 105.1 (d, $^3J_{CP}$ = 2 Hz, C_4), 118.3 (d, $^1J_{CP}$ = 68.5 Hz, C_2 and C_6), 120.5–130 (m, CH arom), resonances at 135.3, 136.9, 138.0, 143.7 (C ipso).

Deuterated Compounds. The starting material for the preparation of the deuterated phosphadienyl complexes was the deuterated ligand 2,4,6-triphenylphosphabenzene-*1,3*-d_2. It was prepared in two steps: first, 2,4,6-triphenylpyrylium-*1,3*-d_2 tetrafluoroborate was prepared from acetophenone-ω-d_3[19] benzaldehyde, and $BF_3 \cdot Et_2O$ as previously described for the protio compound.[20] Then, the desired phosphabenzene was prepared[17] from this deuterated pyrylium salt (3 g) and phosphonium iodide (4 g) in 50 mL of *n*-BuOD:[21] yield 1.2 g; % D 85.

***2-3,5-d*$_2$.** This compound was prepared from 400 mg of 2,4,6-triphenylphosphabenzene-*1,3*-d_2, 230 mg of Cp_2Fe, 350 mg of $AlCl_3$, and 30 mg of Al and was isolated as described for **2** (250 mg). ^{1}H NMR ($CDCl_3$): δ 4.10 (5 H), 5.10 (br s, 0.5 H), 6.12 (br d, *J* = 14 Hz, 0.4 H), 11.20 (br s, 0.5 H). % D: 80.

***4-3(endo),5-d*$_2$:** prepared from **2**-*3,5*-d_2 (150 mg) and $HSiCl_3$ (0.3 mL) in 3 mL of toluene at 95 °C for 1 h. After hydrolysis and chromatography (hexane/toluene 80/20), 40 mg of the compound was obtained. ^{1}H NMR (C_6D_6): δ 2.15 (d, superimposed on a dd, J_{PH} = 4 Hz, 1 H), 3.70 (s, Cp), 5.68 (d, J_{PH} = 5.1 Hz, 0.2 H). The resonance at about 3.8 ppm due to H_{3exo} could not be accurately integrated. % D: 80. ^{2}H NMR (C_6H_6): δ 5.74 (br s, 1 D), 3.82 (br s, 1 D).

***6-2,3-d*$_2$.** 4-*3*(*endo*),*5*-d_2 (40 mg) was heated at 110 °C for 16 h. The resulting oil was dissolved in toluene, filtered on a short column of silica gel (in the drybox), and evaporated to dryness to give 20 mg of the compound. ^{1}H NMR (C_6D_6): δ 2.75 (br d, J_{HP} = 15 Hz, 0.2 H), 3.40 (br s, 0.2 H), 3.95 (s, 5 H). ^{2}H NMR (C_6H_6): δ 3.37 (br s, 1 D), 2.77 (br s, 1 D) % D: 80.

***5-3,5-d*$_2$:** prepared from **2**-*3,5*-d_2 (50 mg) and $HSiCl_3$ (0.1 mL) in 3 mL of toluene at 110 °C for 24 h, isolated by silica gel filtration (toluene) and evaporation to dryness (35 mg). ^{1}H NMR (C_6D_6): δ 1.95 (s, 1 H), 3.00 (d, J_{HH} = 2 Hz, 0.2 H), 3.93 (s, 5 H). ^{2}H NMR (C_6H_6):[22] δ 3.00 (br s, 1 D), 7.37 (br s, 1 D) % D: 80.

X-ray Data Collection and Processing. Suitable single crystals of **6** were obtained by slow evaporation of toluene solutions at room temperature.

A systematic search in reciprocal space using a Philips PW 1100/16 automatic diffractometer showed that crystals of **6** belong to the triclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu Kα radiation (λ = 1.5405 Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{23}H_{28}PFe \cdot {}^1/_2\, C_7H_8$, mol wt 492, a = 11.246 (4) Å, b = 13.484 (4) Å, c = 9.046 (3) Å, α = 107.98 (2), β = 110.31 (2), γ = 74.53 (2), V = 1204 Å^3, Z = 2, d(calcd) = 1.358 g cm^{-3}, d(obsd) = 1.34 ± 0.02 g cm^{-3}, μ = 57.93 cm^{-1}, F_{000} = 515, space group $P\bar{1}$.

A parallelepipedic single crystal of 0.12 × 0.26 × 0.30 mm was cut out of a cluster of crystals, sealed in a Lindemann glass capillary, and mounted on a rotation free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite-monochromated radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step–scan used was $\Delta\theta = (1.0 + 0.143 \tan \theta)°$ with a step width of 0.05° and a scan speed of 0.020° s^{-1}. A total of 3381 hkl, $h\bar{k}l$, $hk\bar{l}$, and $h\bar{k}\bar{l}$ reflections were recorded (4° < θ < 57°). The resulting data set was transfered to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 package was used,[23] with the exception of a local data-reduction program.

Three standard reflections measured every hour during the entire data-collection period showed no significant trend.

The raw step–scan data were converted to intensities by using the Lehmann–Larsen method[24] and then corrected for Lorentz–polarization and absorption factors, the latter computed by the empirical method of Walker and Stuart,[25] since face indexation was not possible (transmission factors between 0.16 and 0.53). A unique data set of 2733 reflections having $I > 3\,\sigma(I)$ was used for determining and refining the structure.

The structure was solved by direct methods using MULTAN[26] in space group $P\bar{1}$ on the basis of E_{hkl} statistics. After refinement of the heavy atoms, a difference Fourier map revealed maximas of residual electronic density close to the positions expected for hydrogen atoms; they were introduced into structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors of $B_{eqv}(c)$ + 1 Å^2 but not refined. The occupancy factors of the disordered methyl group of the $C_6H_5CH_3$ molecule were fixed at 0.5 on the basis of the relative peak height in a Fourier difference synthesis of C1S, C2S, C3S, and C4S. These factors were not refined. Full least-squares refinement converged to $R(F)$ = 0.060 and $R_w(F)$ = 0.082 ($\sigma(F^2) = (\sigma^2(\text{counts}) + (pI)^2)$. An attempt to refine the isotropic extinction coefficient c led to $c = 1.6 \times 10^{-6}$ with an error of 1.0×10^{-6}; therefore extinction was ignored. The unit-weight observation was 1.45 for p = 0.08. A final difference map revealed no sig-

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[18] ^{1}H NMR ($CDCl_3$): δ 5.52 (s, 1 H), 7.15 (br s, 15 H).

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[22] Small peaks at 3.37 and 2.77 ppm (estimated to about 0.05 D) were present and were attributed to **6**-*2,3*-d_2. In a ^{1}H NMR spectrum of **5** as a crude product obtained from reduction of **2**, resonances of **6** were also detected.

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nificant maxima. The scattering factors coefficients and anomalous dispersion coefficients come respectively from ref 27 and 28.

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Registry No. $1^+ \cdot PF_6^-$, 100945-90-2; **2**, 100993-21-3; **2**-*3,5*-d_2, 100945-92-4; **3**, 100945-87-7; **4**, 100993-22-4; **4**-*3*(*endo*),*5*-d_2, 100945-93-5; **5**, 100945-88-8; **5**-*3,5*-d_2, 101052-75-9; **6**, 101052-74-8; **6**-*3,5*-d_2, 100945-94-6; 2,4,6-triphenylphosphabenzene, 13497-36-4; 2,4,6-triphenylphosphabenzene-*1,3*-d_2, 100945-91-3; ferrocene, 102-54-5; trityl hexaflourophosphate, 437-17-2; 2,4,6-triphenylpyrylium-*1,3*-d_2 tetrafluroborate, 100945-95-7; acetophenone-ω-d_3, 17537-31-4.

Supplementary Material Available: Table III, thermal factors (U_{ij}) for anisotropic atoms, Table IV, hydrogen atoms parameters, and Table V, observed and computed structure factor amplitudes (×10) for all observed reflections (16 pages). Ordering information is given on any current masthead page.

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(28) Cromer, D. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England; 1974; Vol. IV, Table 2.3.1.

Derivatives of the (Arene)M(CO)$_2$ (M = Mn or Re) Fragment. The Molecular Structure of (η^6-C$_6$Me$_6$)Mn(CO)$_2$Cl

Randal J. Bernhardt, Marie A. Wilmoth, Jerry J. Weers, Daniel M. LaBrush, and
Darrell P. Eyman*

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242

John C. Huffman

Department of Chemistry, The University of Indiana, Bloomington, Indiana 47405

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The compounds $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2X$ (X = I (**3a**), Br (**3b**), and Cl (**3c**)) have been prepared by the photolysis of the cation $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3^+$ in water saturated with NaX. These compounds as well as $(\eta^6\text{-}C_6H_n(CH_3)_{6-n})Mn(CO)_2I$ (n = 1 (**3d**), 3 (**3e**), and 6 (**3f**)), $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2(PR_3)PF_6$ ($R = C_6H_5$, OCH_3), $(\eta^6\text{-}C_6H(CH_3)_5)Mn(CO)_2(P(C_6H_5)_3)PF_6$, and $(\eta^6\text{-}C_6(CH_3)_6)Re(CO)_2I$ have been synthesized in CH_2Cl_2, from the corresponding $(\eta^6\text{-arene})M(CO)_3PF_6$ (M = Mn, Re), by the $(CH_3)_3NO$-induced displacement of CO, in the presence of $(n\text{-}C_4H_9)_4NX$ or the phosphine. Compounds **3b** and **3f** undergo rapid halide displacement with CH_3Li to form $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2CH_3$ (**6a**) and $(\eta^6\text{-}C_6H_6)Mn(CO)CH_3$. Reaction of NaCN with **3b** or **3f** gives $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2CN$ or $(\eta^6\text{-}C_6H_6)Mn(CO)_2CN$. Treatment of **3a** with $NaBH_4$ in THF gives the hydride $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2H$ (**8**). Deprotonation of **8**, with CH_3Li, gives the anion $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2^-$, which is also produced by the reaction of **3a** with $NaC_{10}H_8$ in THF. This anion is methylated by CH_3I to form **6a**. These compounds have been characterized by analytical and spectroscopic techniques, and the structure of **3c** has been determined by single-crystal X-ray diffraction studies. This compound crystallizes in the space group $P2_1/c$ with unit-cell dimensions a = 8.701 (3) Å, b = 13.618 (5) Å, c = 13.266 (4) Å, β = 120.82 (1)°, Z = 4, V = 1349.8 Å^3, R = 0.0332, and R_w = 0.0391. The "piano stool" structure involves an η^6-arene with the carbonyls and chloride staggered relative to the arene carbons.

Introduction

(Arene)manganese tricarbonyl cations, $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_3^+$ (**1**), have been and continue to be the topic of extensive investigation.[1,2] This is due in part to the rich chemistry associated with nucleophilic attack at the aromatic ring leading to the formation of cyclohexadienylmanganese tricarbonyl compounds.[3] In contrast, little is known about the compounds $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2N$, where N is not carbonyl and the compound is neutral. All compounds in this class, reported to date, have been formed from **1**.

Coffield and Clossen[3a] observed that increasing methylation of **1** increases steric inhibition of nucleophilic attack at the arene ring in deference to formation of products arising from attack at the carbonyl. Addition of the nucleophiles Me^-, $C_6H_5^-$, MeO^-, and RNH^- to $(\eta^6\text{-}C_6Me_6)Mn(CO)_3^+$ gave products arising from attack at the carbonyl carbon.[2d] When H^- is used as the nucleophile,[3b] reduction occurs at the ring to yield the cyclohexadienyl derivative *endo*-$(\eta^5\text{-}C_6H_{7-n}Me_n)Mn(CO)_3$ and at the carbonyl to give $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2Me$ (**6**). The latter compound has also been synthesized[4] from **1** and Me_2CuLi as well as by photolysis of $(\eta^6\text{-}C_6H_nMe_{6-n})Mn(CO)_2C(O)Me$.[3b] The latter technique has also led to the formation of the phenyl analogue from the benzoyl derivative. Hy-

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