Reaction of 1-Alkyl-1,1′-diphosphaferrocene Monoanions with Acyl Chlorides. Synthesis and Zwitterionic Structure of Stable λ^3,λ^5-Diphosphaferrocenes

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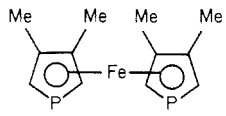
Reaction of *tert*-butyllithium with 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (1) affords the 1-*tert*-butyl P anion **2a** which reacts in situ with acyl chlorides to give the corresponding stable 1-*tert*-butyl-1-acyl-1,1′-diphosphaferrocenes **4** (acyl = MeCO) and **5** (acyl = PhCO). The X-ray crystal structure analysis of **5** shows that the pentavalent phosphorus atom is not bonded to iron and that these λ^3,λ^5-diphosphaferrocenes are better represented as (η^5-phospholyl)(η^4-phospholium)iron zwitterions. The rather short Fe···λ^5-P distance (2.565 Å) nevertheless indicates a strong through-space interaction which seems to be responsible for the unusual stability of these species. Pyrolysis of **5** under vacuum at 170 °C affords diphosphaferrocene **1**, 1-*tert*-butylphosphole **7**, probably through a migration of the benzoyl group from phosphorus to iron, and 1′-phenyl-1-phosphaferrocene **8**, by a mechanism certainly related to a phosphole to cyclopentadiene conversion described earlier.

Following their discovery in 1978, improved synthetic procedures have increased the availability of 1,1′-diphosphaferrocenes. The 3,3′,4,4′-tetramethyl derivative **1** is now available on a kilogram scale. This has allowed us to launch a thorough investigation of their chemistry which has revealed many unique features for compounds of this type. Thus, they are acylated,[3] formylated,[3] and carboxylated to the ring carbons through electrophilic substitutions in strict analogy to ferrocenes. On the contrary, reactive alkyl halides liberate the phosphole rings through alkylation at phosphorus.[4] Similarly, their phosphorus lone pairs behave as donors and will coordinate to an additional metal center.[4] In another vein, preliminary electrochemical studies[5] have shown that 1,1′-diphosphaferrocenes are reversibly oxidized to 1,1′-diphosphaferricinium ions less readily than ferrocenes. Finally, in a previous paper,[6] we demonstrated that alkyllithiums attacked these species at phosphorus to give monoanions such as **2**, but we were unable to isolate the expected λ^3,λ^5-diphosphaferrocenes **3** by alkylation of **2**. The search for stable species such as **3** is the subject of this paper.



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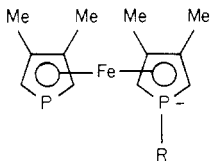
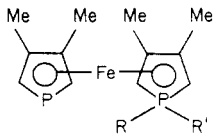


2a, R = *t*-Bu



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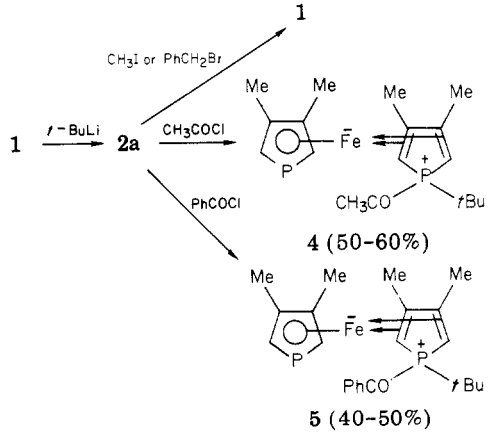
Results and Discussion

Synthesis. In our preliminary experiments we reacted **2a** with methyl iodide and benzyl bromide. In both cases, after the usual workup, we recovered the starting diphosphaferrocene **1** because of spontaneous reductive elimination of the two alkyl groups on the λ^5-phosphorus of **3**. Similar reductive eliminations from λ^5-phosphorus have been previously reported for λ^5-phosphorins[7] but only at high temperature (≃300 °C). We then sought to improve the stability of the desired λ^3,λ^5-diphosphaferrocenes by replacing the alkyl P substituents by other groups. Thus, we discovered that the reaction of **2a** with acetyl and benzoyl chlorides afforded the stable compounds **4** and **5** which were purified by column chromatography on silica gel. We attributed to them a partly zwitterionic structure



on the basis of the X-ray crystal structure analysis of **5** (vide infra). These compounds show numerous interesting spectral features. First, their mass spectra indicate a tendency to loose the λ^5-P substituents, producing the starting diphosphaferrocene **1**. Indeed, in both cases the *m/e* 278 peak (1) is the base peak. It also seems quite clear that the main decomposition path involves the primary departure of the *tert*-butyl group in both cases. Accordingly, the structure of **5** shows that the *t*-Bu–P bond is

(1) (a) Laboratoire CNRS-SNPE. (b) Institut Le Bel.
(2) G. De Lauzon, F. Mathey, and M. Simalty, *J. Organomet. Chem.*, **156**, C33 (1978).
(3) G. De Lauzon, B. Deschamps, J. Fischer, F. Mathey, and A. Mitschler, *J. Am. Chem. Soc.*, **102**, 994 (1980).
(4) G. De Lauzon, B. Deschamps, and F. Mathey, *Nouv. J. Chim.*, **4**, 683 (1980).
(5) P. Tordo, personal communication.
(6) B. Deschamps, J. Fischer, F. Mathey, and A. Mitschler, *Inorg. Chem.*, **20**, 3252 (1981).
(7) G. Märkl, *Phosphorus Sulfur*, **3**, 77 (1977).

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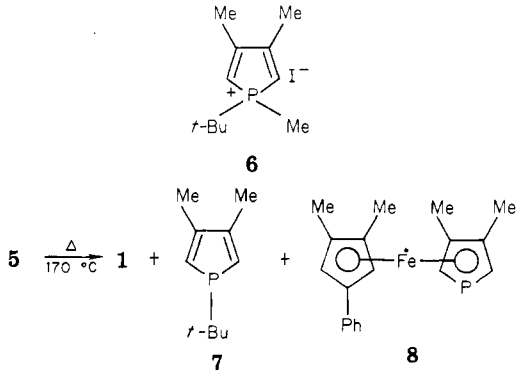
longer and weaker (1.876 Å) than the PhCO–P bond (1.858 Å). The ^{1}H NMR spectra also give some insight into the electronic structure of these compounds. Indeed, the *tert*-butyl groups of **4** and **5** are very shielded: **4**, δ(*t*-Bu) 0.70 ($CDCl_3$); **5** δ(*t*-Bu) 0.72 (CD_2Cl_2). These values can be compared to that recorded for a normal phospholium salt such as **6**: δ(*t*-Bu) 1.38 ($CDCl_3$). This shielding seems to indicate the presence of a direct through-space interaction between Fe^- and P^+–*t*-Bu, partly "neutralizing" the positive charge on phosphorus. Consistent with this suggestion, it should be stressed that the λ^5-phosphorus of **4** and **5** resonates at high field but in the low part of the range normally associated with the pentacoordinate species: −2.4 ppm ($CDCl_3$) for **4** and −8.5 ppm (C_6D_6) for **5** vs. +50.3 ppm ($CDCl_3$) for **6**.

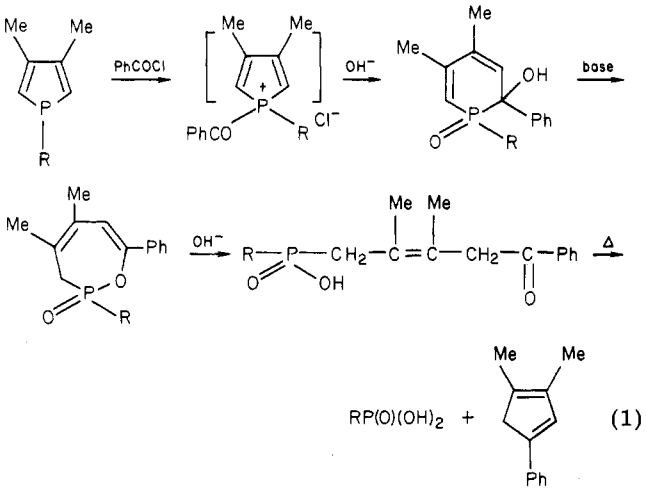
Another curious feature has been noted for the ^{1}H NMR spectrum of **5**. Whereas the *t*-Bu signal appears as one sharp doublet, all other methyl or CH groups of the phosphole rings give rise to two equal and independent signals (we have checked that this is not due to J(H–P) couplings). This doubling does not occur in the spectrum of **4**. The X-ray crystal structure of **5** gives a clue for explaining this phenomenon. Indeed, the phenyl ring of the benzoyl group crosses the plane of the λ^3-phospholyl moiety, and the distance between the λ^3-phosphorus (P_1) and the plane of the phenyl (PL_4) is very short (0.60 Å). Thus the rotation of the λ^5-phospholyl ring about the ring Fe vector is very probably hindered, with P_2 only oscillating between the verticals of C_2 and P_1 (see Figure 1) due to P_1 and Me–C_2 interactions with the phenyl ring. Thus the two sides of both phosphole rings become inequivalent and the λ^3-phospholyl C_1H is very shielded: δ(C_1H in **5**) 2.85 vs. δ 3.01 (C_4H in **5**), 3.31 (λ^3-phospholyl CH in **4**), and 3.71 (CH in **1**). The short distance between P_1 and PL_4 also explains why it is impossible to attack the second phosphorus atom of **5** even with a great excess of *tert*-butyllithium and benzoyl chloride to obtain a product similar to **11** which was described in our previous paper[6] when using MeI instead of PhCOCl. Finally it must be noted that, in the ^{13}C NMR spectra, the carbonyl carbons of **4** and **5** appear in the normal region with a very strong ^1J(C–P) coupling similar to what was noted in acylphosphonium zwitterions.[8] δ(CO in **4**) 186.2 (^1J(C–P) = 90.3 Hz ($CDCl_3$), δ(CO in **5**) 175.2 (^1J(C–P) = 100.4 Hz (C_6D_6)).

In view of the mass spectral data of **5**, we wanted to determine if **5** would regenerate **1** upon pyrolysis. At 170 °C under vacuum, **5** decomposed and indeed gave some λ^3,λ^3-diphosphaferrocene **1** but also yielded two other unexpected products **7** and **8**. The structure of **7** was



established by comparing its ^{1}H and ^{31}P NMR spectra with those of an authenticated sample[9] and by converting it into its P sulfide which was analyzed (correct melting point and ^{1}H NMR spectrum). The mechanism for the formation of **7** probably includes a migration of the benzoyl group from phosphorus to iron followed by the decomplexation of the tervalent phosphole.

The structure of **8** was established by mass, ^{1}H NMR, and ^{31}P NMR spectroscopy. Since **8** was not very stable, it was difficult to obtain a perfectly correct C, H, Fe, and P analysis as with other monophosphaferrocenes. Nevertheless, the experimental ratio Fe/P was found to be 1.01. Moreover, in the mass spectrum (70 eV, 80 °C), the molecular peak (m/e 336) was also the base peak as usual for these species.[10] No other peak exceeded a 6% intensity. The ^{31}P spectrum ($CDCl_3$) showed a very shielded phosphorus at δ(^{31}P(**8**)) −75 as expected. The ^{1}H NMR spectrum was also in perfect agreement with the proposed formula. Although **8** was only obtained in 13% yield, the two-step conversion of a diphosphaferrocene into a monophosphaferrocene (**1** → **5** → **8**) remains noteworthy. The mechanism for this pyrolysis is certainly complicated, but previous work in our laboratory throws some light on this problem. Indeed, we have established the sequence shown in eq 1.[11] There is an obvious relationship between this



(1)

sequence which converts an acylphospholium salt into a substituted cyclopentadiene and the formation of **8** from **5**, although, according to preliminary experiments (thermolysis of **5** in the presence of hydrated basic alumina), it does not seem that OH^- anions are necessary in the present case.

Crystal Structure of 5

$C_{23}H_{30}FeOP_2$ (**5**): monoclinic, space group $P2_1/n$, a = 17.564 (6) Å, b = 12.254 (4) Å, c = 10.346 (4) Å, β = 96.39 (2)°, Z = 4. Atomic coordinates and thermal parameters with their estimated standard deviations are listed in Tables I and II. Intermolecular contacts less than 3 Å are given in Table III.

The crystal structure of **5** consists of discrete molecules in which an iron atom is sandwiched between two phosphole rings. The individual molecules are linked only by hydrogen bonds and van der Waals type interactions.

Figure 1 shows an ORTEP[12] plot of a molecule together with the labeling scheme used. Hydrogen atoms are omitted for clarity, and the other atoms are represented

(8) R. Appel and M. Montenarh, *Chem. Ber.*, **110**, 2368 (1977).

(9) F. Mathey, *Tetrahedron*, **28**, 4171 (1972).
(10) F. Mathey, *J. Organomet. Chem.*, **139**, 77 (1977).
(11) F. Mathey, *Tetrahedron*, **29**, 707 (1973); *Bull. Soc. Chim. Fr.*, 2783 (1973).
(12) C. K. Johnson, Report ORNL 3794, Oak Ridge, Tenn., 1965.

Table III. Intermolecular Contacts (Å) Less Than 3 Å and Intermolecular Contacts around P2 Less Than 3.5 Å

A···B		equiv positns[a]
C3···H1C15	2.82	1/001
C9···HC21	3.00	2/101
C12···HC21	3.00	2/101
O···HC10	2.75	2/011
O···HC19	2.78	2/011
C20···H2C6	2.98	2/001
C21···H3C11	2.70	2/000
C21···H2C12	2.93	2/000
H1C5···H1C16	2.96	2/011
H1C5···H2C16	2.90	2/001
H2C5···H3C14	2.99	2/001
H1C6···HC20	2.89	2/100
H2C6···H1C15	2.91	1/001
H2C6···HC20	2.70	2/100
H1C11···H1C16	2.64	1/001
H2C12···HC22	2.52	2/101
H2C14···HC23	2.66	2/001
H2C15···H3C16	2.86	1/001
H3C15···HC21	2.77	2/101
H3C15···HC22	2.73	2/001
H3C15···HC23	2.66	2/001
H2C16···HC20	2.99	2/011
P2···C18	2.938 (9)	
P2···C19	3.277 (9)	
P2···HC19	2.90	

[a] The relative coordinates of the atom in column A are listed in Table I. The atoms in column B have their atom atomic parameters specified by I/uvw which denotes how the parameters can be derived from the corresponding atoms in the crystal unit: $1, x, y, z; \bar{1}, \bar{x}, \bar{y}, \bar{z}; 2, {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z; \bar{2}, {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. u, v, and w code a lattice transition as $u\vec{a} + v\vec{b} + w\vec{c}$.

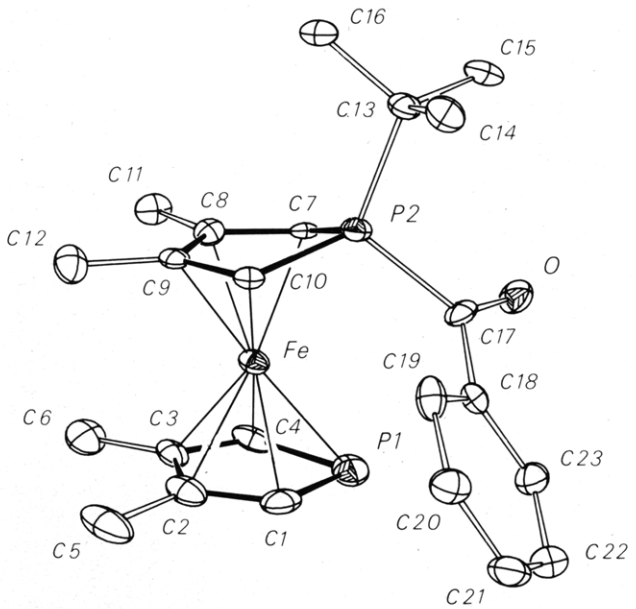


Figure 1.

by their ellipsoids of thermal motion scaled to enclose 50% of the electron density. Figure 2 shows the projection of one phosphole ring on the plane of the other. Table IV gives selected bond lengths (Å), angles (deg), and average values. Table V gives the least-squares planes of interest.

The key point to be discussed here is the bonding mode of the λ^5-phospholyl moiety with the iron atom. The Fe···P_2 distance [2.565 (2) Å] is clearly outside of the normal length range associated with phosphorus–iron bonds. Indeed, one of the longest previously determined Fe···P bonds was found in the structure of t-$Bu_3P \rightarrow Fe(CO)_4$: 2.364 (1) Å.[13] Thus, the structure is certainly partly

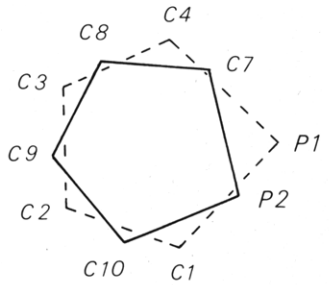


Figure 2.

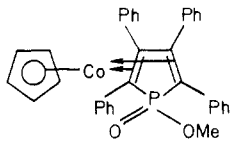
Table IV. Selected Bond Lengths (Å) and Angles (Deg) with Their Estimated Standard Deviation

Bond Lengths			
Fe-P1	2.289 (3)	C7-C8	1.41 (1)
Fe-C1	2.042 (8)	C8-C9	1.41 (1)
Fe-C2	2.075 (9)	C9-C10	1.43 (1)
Fe-C3	2.089 (8)	av C-C	1.418 (6)
Fe-C4	2.092 (7)		
av Fe-C	2.074 (4)	C8-C11	1.51 (1)
		C9-C12	1.52 (1)
Fe-P2	2.565 (2)	P2-C13	1.876 (7)
Fe-C7	2.078 (7)	P2-C17	1.858 (8)
Fe-C8	2.018 (7)	C13-C14	1.53 (1)
Fe-C9	2.011 (7)	C13-C15	1.53 (1)
Fe-C10	2.087 (8)	C13-C16	1.52 (1)
P1-C1	1.74 (1)	C17-O	1.217 (9)
P1-C4	1.76 (1)	C17-C18	1.52 (1)
av P-C	1.752 (7)	C18-C19*	1.40 (1)
		C19-C20*	1.39 (1)
C1-C2	1.39 (1)	C20-C21*	1.38 (1)
C2-C3	1.39 (1)	C21-C22*	1.37 (1)
C3-C4	1.42 (1)	C22-C23*	1.38 (1)
av C-C	1.402 (7)	C23-C18*	1.40 (1)
C2-C5	1.52 (1)	av C-C*	1.388 (4)
C3-C6	1.50 (1)		
P2-C7	1.746 (8)		
P2-C10	1.763 (8)		
av P-C	1.754 (6)		

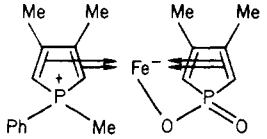
Bond Angles			
C1-P1-C4	87.1 (4)	C7-C8-C11	123.0 (7)
P1-C1-C2	115.8 (7)	C10-C9-C12	120.6 (7)
P1-C4-C3	114.3 (7)	C9-C8-C11	124.7 (7)
av P-C-C	115.0 (5)	C8-C9-C12	126.9 (7)
		C7-P2-C13	117.1 (3)
C1-C2-C3	111.6 (9)	C10-P2-C13	118.3 (3)
C4-C3-C2	111.0 (9)	C13-P2-C17	105.6 (3)
av C-C-C	111.3 (6)	C7-P2-C17	108.8 (4)
		C10-P2-C17	116.2 (4)
C1-C2-C5	125 (1)	P2-C17-O	116.4 (6)
C3-C2-C5	123 (1)	P2-C17-C18	120.2 (7)
C4-C3-C6	123.3 (9)		
C2-C3-C6	125.5 (9)		
C7-P2-C10	90.5 (4)		
P2-C7-C8	110.6 (6)		
P2-C10-C9	109.0 (6)		
av P-C-C	109.8 (4)		
C7-C8-C9	112.3 (7)		
C10-C9-C8	112.4 (7)		
av C-C-C	112.3 (5)		

zwitterionic as represented in formula **5**. Nevertheless, both the folding of the λ^5-phospholyl ring around the C_7–C_{10} axis (20.8°) and the Fe···P_2 distance are much smaller than those in other known η^4-complexed λ^5-phosphole rings such as in **9**, **10**, and **11**. Thus, it is quite

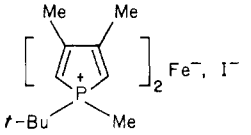
(13) J. Pickardt, L. Rösch, and H. Schumann, *J. Organomet. Chem.*, **107**, 241 (1976).
(14) K. Yasufuku, A. Amada, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, **102**, 4363 (1980).



9[14] (folding 30.3°)

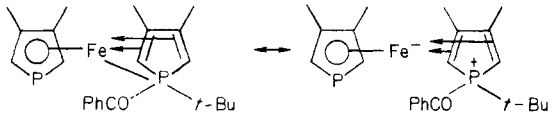


10[6] (folding 34.3° (P^+ moiety), Fe···P^+ = 2.732 (1) Å)



11[6] (folding 31°, Fe···P = 2.688 (1) Å)

clear that there is a rather strong through-space interaction between iron and the P_2 phosphorus in agreement with what has been suggested on the basis of ^1H and ^{31}P NMR spectroscopy, such that **5** is probably best represented as a bond–no bond resonance hybrid.



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This through-space interaction is probably responsible for the stability of these compounds. The question then is how can an acyl group facilitate such an Fe···P interaction whereas it does not exist in compounds with only alkyl or aryl groups on phosphorus. A direct interaction between the iron atom and the carbonyl carbon being excluded [Fe···C = O 3.17 Å], we suggest that the acyl group increases the positive charge on phosphorus, thus creating a stronger Coulombic attraction between iron and P_2 phosphorus. As a whole the λ^5-phospholyl becomes more electron attracting and, consequently, the λ^3-phospholyl–iron bond is weakened as monitored by Fe···P_1 [2.289 (3) Å] and Fe···PL_1 [1.670 (1) Å] distances (see Table V) which are abnormally long when compared with other (η^5-phospholyl)iron complexes.[3,15] Due to this longer Fe···PL_1 distance, the λ^3-phospholyl ring is now strictly planar whereas it is significantly folded (0.67–3.84°) around its Cα–Cα' axis in **1**.[3] Finally, the endo position of the acyl group explains why it migrates easily to iron in the thermal decomposition of **5**. This facile migration of the benzoyl group between phosphorus and iron together with the lack of steric control on the relative positions of *tert*-butyl and benzoyl groups (according to the structural data the *tert*-butyl group could not interact strongly with the λ^3-phospholyl ring if it were endo) suggests that the initial attack of benzoyl chloride onto **2a** takes place at iron.

Experimental Section

NMR spectra [chemical shifts in parts per million from internal Me_4Si for ^1H and ^{31}C and from H_3PO_4 (external reference) for ^{31}P; δ positive for downfield shifts in all cases] were recorded for proton on a Bruker WP 80 instrument at 80 MHz and on a Varian XL 100 A instrument at 100 MHz and for carbon and phosphorus on a Bruker WP 80 instrument at 20.15 and 32.44 MHz, respectively. We thank Mrs. M. J. Pouet and M. P. Simonnin (ENSCP Laboratory) for the ^{31}P decoupled proton spectra. Mass spectra were recorded on a MS 30 AEI spectrometer at 70 eV.

(15) F. Mathey, A. Mitschler, and R. Weiss, *J. Am. Chem. Soc.*, **99**, 3537 (1977).

Table V. Significant Mean Planes

no.		dist,[a] Å	equations[b]	χ^2
PL1	P1°	−0.002 (3)	$a = -0.0334$, $b = 0.0958$,	14
	C1°	0.023 (9)	$c = -0.9948$, $d = -10.9740$	
	C2°	−0.015 (8)		
	C3°	−0.003 (8)		
	C4°	0.014 (8)		
	C5	−0.151 (10)		
	C6	−0.088 (10)		
	Fe	1.670 (1)		
PL2	P2°	0	$a = -0.3315$, $b = 0.3688$,	0
	C7°	0	$c = -0.8684$, $d = -6.3009$	
	C10°	0		
PL3	C7°	−0.002 (7)	$a = -0.0723$, $b = 0.1461$,	0
	C8°	0.003 (8)	$c = -0.9866$, $d = -7.5108$	
	C9°	−0.003 (7)		
	C10°	0.002 (8)		
	P2	0.439 (2)		
	Fe	−1.629 (1)		
	C11	0.017 (9)		
	C12	0.049 (9)		
PL4	C18°	0.000 (9)	$a = 0.5620$, $b = -0.4703$,	4
	C19°	−0.008 (9)	$c = -0.6805$, $d = -4.1348$	
	C20°	0.013 (9)		
	C21°	−0.012 (10)		
	C22°	0.002 (10)		
	C23°	0.003 (9)		
	C17	0.021 (8)		
	O	0.457 (6)		
	P2	−0.602 (2)		
	P1	−2.964 (3)		

Dihedral Angles

PL1/PL2 = 24.5° PL2/PL3 = 20.8°
PL1/PL3 = 3.7°

[a] Atom labels marked with a degree sign are used for computing the mean plane. [b] Least-squares planes are computed according to D. M. Blow, *Acta Crystallogr.*, 13, 168 (1960).

All reactions were carried out under argon. Chromatographic separations were performed on a silica gel column (70–230 mesh Merck).

(η^4-1-*tert*-Butyl-1-benzoyl-3,4-dimethylphospholium)(η^5-3,4-dimethylphospholyl)iron (5). To a stirred solution of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**1**)[3] (1.39 g, 5×10^{-3} mol) in THF (100 cm^3) was added at −80 °C 5×10^{-3} mol of *t*-BuLi in pentane. After 30 min, 0.5 cm^3 (5×10^{-3} mol) of freshly distilled benzoyl chloride was added to this solution. After 1 h, the reaction mixture was allowed to come to room temperature. The THF was evaporated and the residue was chromatographed with ether. The green fraction was rechromatographed with ether–pentane (10–90): $R_f \approx 0.5$; yield 0.9–1.1 g (40–50%); mp 205 °C dec (ether–pentane at low temperature); ^1H NMR (CD_2Cl_2) δ 0.72 (d, ^3J(H–P) = 14 Hz, 9 H, *t*-Bu), 1.27 (m, 2 H, CH–P_2), 1.60 and 1.77 (2s, 3 + 3 H, Me–C_8 and Me–C_9), 1.97 and 2.01 (2s, 3 + 3 H, Me–C_2 and Me–C_3), 2.85 (d, ^2J(H–P) = 36 Hz, 1 H, H–C_1), 3.01 (d, ^2J(H–P) = 36 Hz, 1 H, H–C_4), 7.6 (m, 3 H, Ph meta and para), 8.2 (m, 2 H, Ph ortho); ^{31}P NMR (C_6D_6) δ −8.5 and −63.7 (J(P–P) = 2.5 Hz); IR (KBr) ν(CO) 1592–1612 cm^{-1}; mass spectrum (70 eV, 180 °C), m/e 440 (M, 17%), 383 (M − *t*-Bu, 13%), 355 (383 − CO, 21%), 2 78 (1, 100%). In ether solution, **5** shows an absorption at 740 mm in the visible part of the spectrum which is not present in the spectra of either **1** or **4**; this absorption is probably responsible for the green color of **5** whereas **1** and **4** are red.

(η^4-1-*tert*-Butyl-1-acetyl-3,4-dimethylphospholium)(η^5-3,4-dimethylphospholyl)iron (4). The procedure is the same as above except with 0.35 cm^3 (5×10^{-3} mol) of acetyl chloride: $R_f \approx 0.6$; yield 0.9–1.1 g (50–60%); red crystals; mp 80 °C; ^1H NMR ($CDCl_3$) δ 0.70 (d, ^3J(H–P) = 13.7 Hz, 9 H, *t*-Bu), 1.07 (d, ^2J(H–P) = 23.9 Hz, 2 H, CH–P–λ^5), 1.77 (s, 6 H, Me), 1.97 (d, J = 0.9 Hz, 6 H, Me), 2.82 (dd, J = 4.9 and 1.5 Hz, 3 H, Me–CO), 3.31 (d, ^2J(H–P) = 35.9 Hz, 2 H, CH–P–λ^3); ^{31}P NMR ($CDCl_3$) δ −2.4 and −65.5 (J(P–P) $\simeq$ 0 Hz); IR (KBr) ν(CO) 1650 cm^{-1}; mass spectrum (70 eV, 200 °C), m/e 378 (M, 13%), 335 (M − COMe, 1%), 321

(M − t-Bu, 11%), 306 (321 − Me, 4%), 293 (321 − CO, 5%), 278 (1, 100%).

Thermolysis of 5

1 (0.5 g) is thermolyzed at 170 °C in a Büchi GKR 50 tubular furnace under vacuum. 7 distils slowly: yield 0.07 g (36%); $\delta(^{31}P(7))$ 24.1 ($CDCl_3$) (lit.[9] 27.5 ppm ($CDCl_3$)), correct ^1H NMR spectrum. P sulfide of 7 (through reaction with S_8 in benzene): mp 156 °C (lit.[9] 160 °C); correct ^1H NMR spectrum and C, H, and P elemental analysis.

The residue of the thermolysis is recovered in hexane and chromatographed after filtration of the insoluble products (hexane–benzene (90–10)). The first red band is 1 and the second red band 8: yield 0.05 g (13%); ^1H NMR ($CDCl_3$) δ 1.77 (s, 6 H, Me), 1.88 (s, 6 H, Me), 3.22 (d, ^2J(H–P) = 36 Hz, 2 H, CH–P), 4.37 (s, 2 H, CH of the Cp ring), 7.10 (m, 5 H, Ph).

X-ray Data Collection and Processing

Suitable single crystals of 5 were obtained by recrystallization in a mixture of CH_2Cl_2–pentane at −20 °C. Preliminary crystal data of 5 were determined by a systematic search in reciprocal space using a Philips PW1100/16 automatic diffractometer and Cu Kα radiations; crystals of 5 are monoclinic. The lattice parameters were refined at 18 ± 2 °C by using 25 high-angle reflections evenly distributed in reciprocal space and standard Philipps programs.[16] Final results are as follows: a = 17.564 (6) Å, b = 12.254 (4) Å, c = 10.346 (4) Å, β = 96.39 (2)°, V = 2213 Å^3. With four molecules of $C_{23}H_{30}FeOP_2$ per unit cell (mol wt 440.29), ρ_{calcd} = 1.32 g·cm^{-3}, and ρ_{obsd}(measured by flotation in an aqueous KI solution) = 1.30 ± 0.02 g·cm^{-3}. The space group is $P2_1/n$ (C_h^5), F_{000} = 928, and μ = 69.87 cm^{-1}.

A parallelepiped crystal of dimensions 0.26 × 0.11 × 0.10 mm was related in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW1100/16 four-circle diffractometer controlled by a P852 computer using graphite-monochromated Cu Kα radiation and the standard software. Intensity data were collected by using the flying $\theta/2\theta$ step–scan technique with a scan rate of 0.020° s^{-1}, a total scan width of [1.20 + (Cu Kα_1,α_2 splitting)]°, and a step width of 0.050°. An attenuator was inserted in the diffracted beam whenever the scan count exceeded 60 000 counts·s^{-1}. The intensities of three standard reflections were monitored throughout the data collection at intervals of 2 h; they did not vary by more than 2% during the entire data collection period. All 3194 hkl and $hk\bar{l}$ independent reflections within 0.045° < sin θ/λ < 0.544° were recorded. The raw step–scan data were converted to intensities by using the Lehman–Larson algorithm[17] which were then corrected for Lorentz, polarization, and absorption factors, the latter being computed by numerical integration[18] (transmission factors between 0.2596 and 0.4226). For each reflection, the estimated variance from counting statistics was $\sigma^2(I) = \sigma^2_{count} + (pI)^2$.

For all computations the Enraf-Nonius SDP/V17 package[19] was used on a PDP 11/60 computer.

The structure was solved by using direct methods; the most probable phase set of MULTAN[20] was the correct one, and the E map permitted the location of all nonhydrogen atoms. A difference map computed at the end of isotropic refinement revealed electron density close to the computed positions for hydrogen atoms. These were included in all subsequent calculations with anisotropic temperature factors of 8 Å and with their computed coordinates using a C–H distance of 0.95 Å, but they were not refined.

Atomic coordinates and individual anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least squares minimizing $\sum w(|Fo| - |Fc|)^2$ and using 1457 independent reflections having $F^2 \geq 3\sigma(F^2)$ with p = 0.08. Refinement converged to $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$ = 0.061 and $R_2 = (\sum w||Fo| - |Fc||^2/\sum w|Fo|^2)^{1/2}$ = 0.077. The standard deviation of a unit weight observation was 1.55.

Registry No. 1, 67887-86-9; 4, 79664-03-2; 5, 79664-04-3; 6, 38066-27-2; 7, 38066-25-0; 7 sulfide, 38066-26-1; 8, 79664-05-4.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters (Tables I and II) and a listing of observed and calculated structure factors (×10) (Table VI) (12 pages). Ordering information is given on any current masthead page.

(16) "Computer Controlled Single Crystal X-ray Diffractometer PW1100, Users manual", N.V. Philips Gloeilampenfabricken, Eindhoven, The Netherlands, 1974.

(17) M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, **A30**, 580 (1974).

(18) W. R. Busing "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 319.

(19) B. A. Frenz, "Computing in Crystallography", H. Schenk, R. Olthof-Hazenkamp, H. Van Konigsveld, and G. C. Bassi, Eds.; Delft University Press, Delft, Holland, 1978, p 64.

(20) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B* **B26**, 274 (1970); *Acta Crystallogr., Sect. A* **A27**, 368 (1971).