1,1′-Diphosphaferrocenes. Synthesis, Basic Chemistry, and Structure

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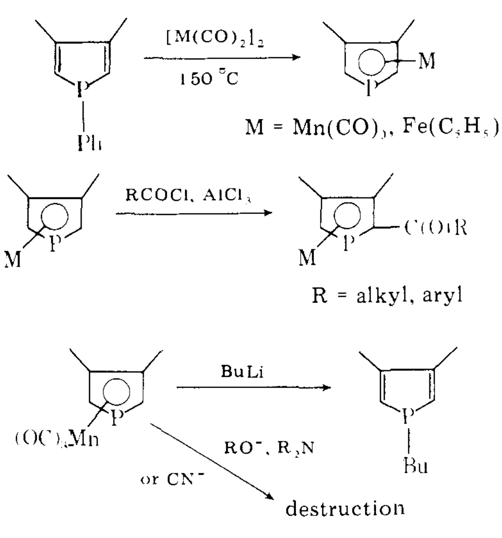
Abstract: The synthesis of 1,1′-diphosphaferrocenes by reaction of 1*H*-phosphol-1-yl anions with $FeCl_2$ is described. The 3,3′,4,4′-tetramethyl derivative **2** can be acylated on C_2 by reaction with $RCOCl-AlCl_3$ complexes in CH_2Cl_2 ($R = CH_3$, C_6H_5). With an excess of $CH_3COCl-AlCl_3$ a 2,2′-diacetylated compound is also obtained as a mixture of two diastereoisomers. The formylation of **2** and of 3,4-dimethyl-1-phosphaferrocene was achieved through a reaction with $POCl_3$ and *N*-methyl-*N*-phenylformamide. The various carbonyl derivatives thus obtained were reduced to the corresponding primary and secondary alcohols with $LiAlH_4$ or $NaBH_4$. The 2-acetyldiphosphaferrocene **7** was also reacted with CH_3MgI and $LiAlH_4-AlCl_3$ to yield respectively a tertiary alcohol and a 2-ethyl derivative. Rather unexpectedly an attempted lithiation of **2** by BuLi has failed whatever the conditions used. The crystal structure of **2** was determined from three-dimensional X-ray diffraction counter data. It consists of discrete molecules in which an iron atom is sandwiched between two π-bonded 1*H*-phosphol-1-yl anions. There are three such molecules in the asymmetric unit. The structural parameters of the 1*H*-phosphol-1-yl cycles are very similar to those found in other phosphametallocenes. When projected on the second cycle, the phosphorus atom of the first ring superposes with a β carbon.

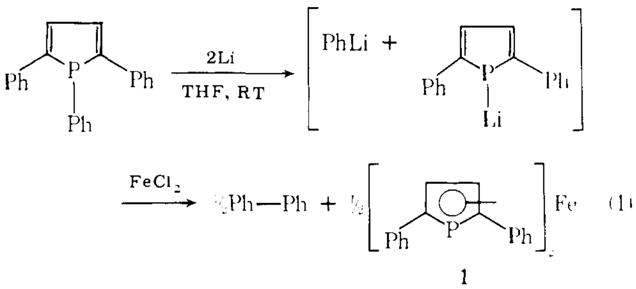
In previous papers we described the synthesis and chemistry of phosphacymantrenes[2,3] and phosphaferrocenes.[4,5] A brief outline of our main results is given in Scheme I. The most noteworthy feature of these compounds was their "aromatic" behavior.[6] However, neither phosphacymantrenes nor phosphaferrocenes were good model compounds for the study of the chemical aromaticity of the π-complexed 1*H*-phosphol-1-yl anions. Indeed the reactivity of the former compounds toward electrophiles was rather weak (direct alkylation, formylation, or carboxylation were impossible[3,7]) and their stability in nucleophilic media was very low.[3] On the other hand, the overall stability of the latter compounds was low and their synthesis was difficult. Moreover, the development of a potentially general synthesis of phosphametallocenes was highly desirable since the preparation of phosphacymantrenes and phosphaferrocenes which is based upon simultaneous P-Ph bond cleavage and π complexation of a *P*-phenylphosphole by an organometallic reagent obviously cannot be transposed in the general case. With these ideas in mind we started to study the synthesis, the chemistry, and the structural features of 1,1′-diphosphaferrocenes (bis[(η^5)-1*H*-phosphol-1-yl]irons). We have just published previously a preliminary paper on a low-yield synthesis of these species.[8]

Scheme I. Synthesis and Basic Chemistry of Phosphacymantrenes [M = $Mn(CO)_3$] and Phosphaferrocenes [M = $Fe(C_5H_5)$]



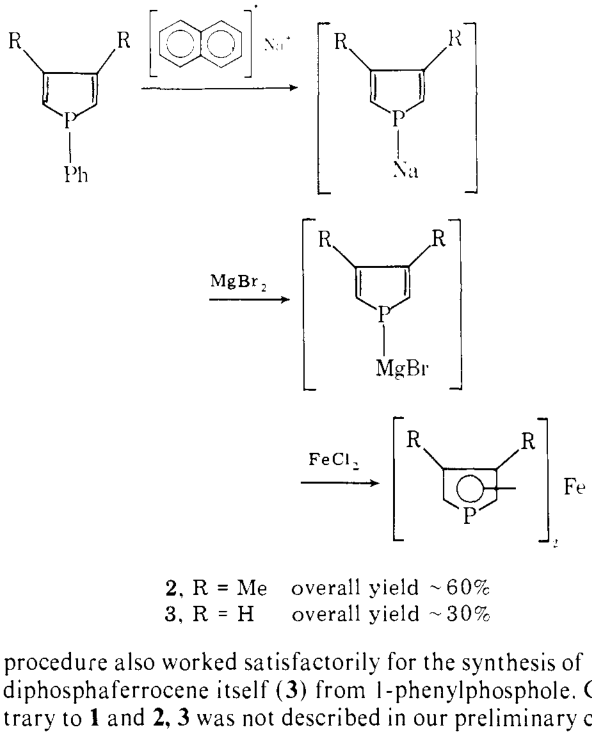
Results and Discussion

Synthesis. The basic scheme of the synthesis of 1,1′-diphosphaferrocenes relies upon a preliminary *P*-phenylphosphole P-Ph bond cleavage by alkali metals according to a work of Braye.[9] Among the various procedures described in the literature are Li in THF at room temperature,[9,10] K in boiling THF, dioxane, or toluene,[9] and Na in boiling THF;[11] the first one consistently gave us the best results. The 1*H*-phosphol-1-yl anion thus obtained was then reacted with anhydrous ferrous chloride as described in our preliminary communication.[8] After a careful optimization of the reaction conditions we obtained a satisfactory yield of 2,2′,5,5′-tetraphenyl-1,1′-diphosphaferrocene (**1**) when starting from 1,2,5-triphenylphosphole (eq 1). However, we did not use **1** for our further studies because its substitution pattern was not convenient and its solubility in classical organic solvents was very low. We concentrated our efforts on the synthesis of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**2**) from 3,4-dimethyl-1-phenylphosphole. Indeed **2** had a much higher solubility in organic solvents and its substitution pattern was better adapted to a study of C-electrophilic substitutions. Unfortunately the mere transposition of the synthesis of **1** afforded **2** in poor yield (~15%). This low yield was obviously not due to a low stability of the final product (in fact the π-complexing ability of 3,4-dimethyl-1*H*-phosphol-1-yl is certainly better than that of 2,5-diphenyl-1*H*-phosphol-1-yl) but to the synthetic scheme itself. Thus, in order to improve this yield, we tried at first to improve the



overall yield of **1** 53%

first step (cleavage of the exocyclic P-Ph bond). In a parallel work[12] we discovered that the 1:1 Na-naphthalene radical anion was a better reagent for this cleavage than alkali metals themselves. However, with $FeCl_2$ 3,4-dimethyl-1*H*-phosphol-1-ylsodium thus prepared always afforded **2** in poor yield (~15%). Since the samples of **2** prepared in this way were very oxidizable we suspected that some finely divided iron was produced by reduction of $FeCl_2$ by phosphol-1-ylsodium along with **2** itself. Besides, it seemed to us that the very high basicity of the P-Na derivative could be a drawback in such a synthesis. Thus, in order to lower both the reducing power and the basicity of the phosphol-1-ylsodium, we converted it into the magnesium derivative by in situ reaction with anhydrous $MgBr_2$. This magnesium derivative was then reacted with $FeCl_2$ and afforded **2** in good yield (eq 2).

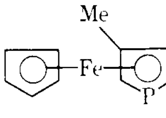


(2)

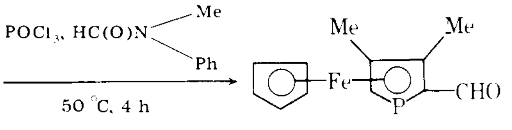
2, R = Me overall yield ~60%
3, R = H overall yield ~30%

This improved procedure also worked satisfactorily for the synthesis of 1,1'-diphosphaferrocene itself (**3**) from 1-phenylphosphole. Contrary to **1** and **2**, **3** was not described in our preliminary communication. When pure this is a rather stable, orange-red solid: mp ~145 °C; ^1H NMR ($CDCl_3$, internal Me_4Si) δ 4.05 (dm, $J_{H-P} = 36.5$ Hz, Hα), 5.30 (m, Hβ); ^{31}P NMR ($CDCl_3$, external H_3PO_4, δ positive for downfield shift) δ −59 ppm; ^{13}C NMR ($CDCl_3$, internal Me_4Si, ^1H decoupling) δ 79.3 (d, $J_{C-P} = 64.3$ Hz, Cα), 82.0 (Cβ); mass spectrum (70 eV, 100 °C) *m/e* 222 (*I* = 100%, M), 139 (*I* = 29%, M − C_4H_4P).

Chemical Reactivity. While optimizing the syntheses of **1-3** we were also trying to extend the chemistry of the closely related monophosphaferrocenes[4,5] further on. We thus discovered that, quite logically if we admit a parallelism between the relative behaviors of metallocenes and phosphametallocenes, phosphaferrocenes were much more reactive than phosphacymantrenes toward electrophiles; more precisely, we succeeded when attempting a Vilsmeier formylation of 3,4-dimethylphosphaferrocene, whereas all attempts to prepare 2-formyl-3,4-dimethylphosphacymantrene have failed so far (eq 3). The aldehyde **5** was characterized beyond any doubt by elemental analysis and spectroscopy. The fully selective formylation of the phosphol-1-yl nucleus is noteworthy. This aldehyde was of course an interesting starting point for the synthesis of other functional derivatives of phosphaferrocenes. Thus, the reduction of **5** afforded the corresponding primary alcohol in fair yield (eq 4). On the other hand, an attempted Cannizzaro reaction on **5** completely failed, whereas it has been successfully performed with ferrocenecarboxaldehyde.[13] Very probably the phosphaferrocene moiety does not withstand very basic conditions (KOH, EtOH, 90 °C, 3 h).

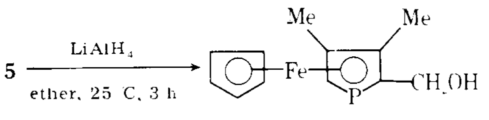


4



(3)

5 yield 43%

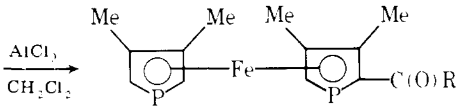


(4)

6 yield 53%

We did not pursue further our exploration of the properties of **5** mainly because of its limited availability. Nevertheless the results thus obtained were encouraging since they demonstrated that the synthetic potential of phosphaferrocenes was much higher than that of phosphacymantrenes. Therefore a thorough investigation of the chemical properties of the readily available diphosphaferrocenes was undertaken. All the reactions were performed with **2**. Some of the results are described hereafter. Our first aim was to evaluate the reactivity of **2** with classical electrophiles and with lithiating reagents. Friedel-Crafts acylations were performed with stoichiometric amounts of $CH_3COCl-AlCl_3$ and $C_6H_5COCl-AlCl_3$ in CH_2Cl_2 near room temperature. Both experiments succeeded (eq 5).

$2 + RCOCl$

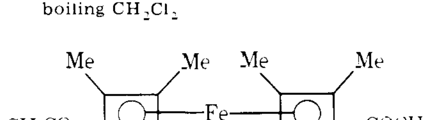


(5)

7, R = Me 74%
8, R = Ph 50%

Qualitatively it is obvious that **2** is much more reactive toward electrophiles than 3,4-dimethylphosphacymantrene since this last compound was benzoylated only at 110 °C.[3] On the other hand, since the yield of acetylation is much better with **2** than with **4** (only 17%[5]), **2** appears to be much more chemically stable than **4**. In line with this observation is the fact that **2** (as ferrocene) gave the diacetylated product **9** in good yield when reacted with an excess of the $CH_3COCl-AlCl_3$ complex, whereas **4** was completely destroyed when using the same reaction conditions (eq 6).

$$2 + 2CH_3COCl \xrightarrow[\text{boiling } CH_2Cl_2]{AlCl_3}$$



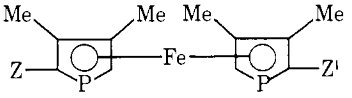
(6)

9a + 9b total yield 64%

Owing to their unsymmetrical substitution pattern, the phosphol-1-yl moieties of **9** were chiral centers[14] and thus **9** was a mixture of two diastereoisomers, **9a** and **9b**. Column chromatography on silica gel with benzene-ethyl acetate (90:10) yielded first **9a** and then **9b** (**9a**:**9b** ratio ≃60:40). We did not achieve a complete separation but we obtained pure samples of **9a** and **9b**.

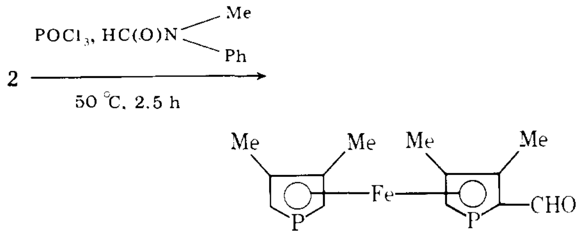
Encouraged by our success with **4** we then attempted a Vilsmeier formylation of **2** (eq 7). The monoaldehyde **10** was

Table I. ^{1}H and ^{31}P NMR Data of Functional Diphosphaferrocenes



Z	Z¹		^{1}H NMR[a] Me	CHP[c]	Z (JH-P)	^{31}P NMR[b] δ_P
H	H	**2**	2.08	3.71		−72
$COCH_3$	H	**7**	2.38, 2.11, 2.06, 1.99	4.02, 3.69	2.28 (2.9)	−54, −72
COC_6H_5	H	**8**	2.30, 2.13, 2.05, 2.0	3.93, 3.63	7.30 (*m*, *p*) 7.63(*o*)	−50, −69
$COCH_3$	$COCH_3$	**9a**	2.23, 2.0	3.70	2.26 (2)	−52
		9b	2.20, 2.0	4.02	2.23 (2)	−49
CHO	H	**10**	2.35, 2.10, 2.03, 2.0	4.10, 3.72	9.67 (4.5)	−51, −67
CH_2OH	H	**11**	2.12, 2.09	3.95, 3.58	CH_2: 4.19 OH: 1.56	−67.0, −73.7
$CH(OH)CH_3$	H	**12a**	2.11, 2.07, 2.01	4.15, 3.53, 3.42	CH: 4.43 OH: 2.50 CH_3: 1.29 $^3J_{H\text{-}H} = 6.1$	−79.6
		12b	2.24, 2.15, 2.07, 2.05	3.94, 3.53	CH: 4.53 OH: 1.26 CH_3: 1.48 $^3J_{H\text{-}H} = 6.3$	−71.6, −72.3
$C(OH)(CH_3)_2$	H	**13**	2.31, 2.16, 2.07, 2.05	4.29, 3.58, 3.44	CH_3: 1.41 (0) and 1.54 (3.4) OH: 2.43 (7.6)	−66, −83
C_2H_5	H	**14**	2.07, 2.02	3.57, 3.45	CH_3: 1.02[d]	

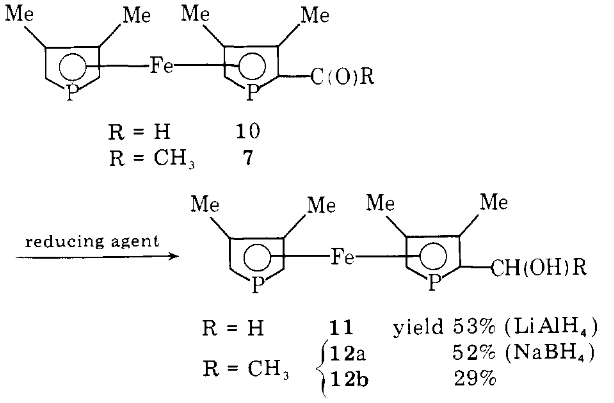
[a] δ in parts per million; J in hertz; $CDCl_3$, internal Me_4Si. [b] $CDCl_3$, external 85% H_3PO_4; δ positive for downfield shifts; $^2J_{P\text{-}P} = 10 \pm 2$ Hz for **7**, **8**, **10**, **11**, **12b**, and **13**. [c] $^2J_{H\text{-}P} = 36 \pm 1$ Hz in every case. [d] The CH_2 protons are masked by the peaks at δ 2.07–2.02.



(7)

10 yield 58%

obtained in fair to good yield but every attempt at obtaining the 2,2′-dialdehyde met with failure. The same phenomenon has been already noted with ferrocene.[13b] Having in hand the three possible types of carbonyl derivatives we started a study of their reduction. The primary and secondary alcohols were obtained by reaction of the suitable carbonyl compounds with $LiAlH_4$ or $NaBH_4$ (eq 8). Quite logically the secondary alcohol

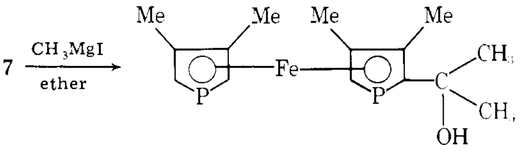


R = H 10
R = CH_3 7

(8)

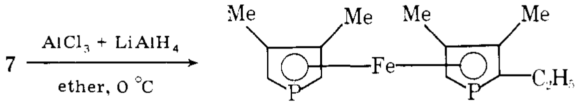
R = H 11 yield 53% ($LiAlH_4$)
R = CH_3 12a 52% ($NaBH_4$)
12b 29%

was a mixture of two diastereoisomers, **12a** and **12b**, which were easily and completely separated by chromatography (**12a** was eluted first on silica gel by benzene–ethyl acetate, 95:5). We also obtained a tertiary alcohol by reacting the acetyl derivative **7** with a Grignard reagent (eq 9). Even though this low yield was in part due to a lengthy purification procedure, it was also probably indicative of some sensitivity of the diphosphaferrocene system toward nucleophilic media, although to a much smaller extent than in the case of phosphacymantrenes.[3] Finally the reaction of **7** with $(AlH_3)_n$ afforded the ethyl derivative **14** also in modest yield (eq 10). We then decided to explore the reactivity of **2** toward butyllithium. Indeed the availability of a 2-lithio derivative would have given us access to a large variety of new functional complexes. Unfortunately all our experiments failed: (1) 1BuLi, THF, 2 h, −40 °C; (2) 1BuLi, ether, 4 h, 0 °C; (3) 2BuLi-TMEDA, hexane, 5 h, room temperature. In each case we attempted to trap the expected 2-lithiodiphosphaferrocene by CO_2 or Me_3SiCl. We never recovered anything in the organic phase (after acidification for reactions with CO_2) except **2** itself (the yield of recovery was better than 50% in each experiment). These failures are highly significant. Indeed, with the first set of conditions, 3,4-dimethylphosphacymantrene was completely destroyed,[3] whereas, with the last set, ferrocene was 1,1′-dilithiated in yields up to 94%.[15a] We have already noted some similarities between the behaviors of the phosphorus atom in phosphacymantrenes and phosphorins.[3] Thus we suspect that BuLi merely adds to the phosphorus atom of diphosphaferrocenes in the same way as it does with phosphorins.[15b] More work is currently being done in order to check this hypothesis.



(9)

13 yield 15.7%



(10)

14 yield 33%

Spectral Data. All the products described in this paper were fully characterized by elemental analysis and spectroscopy. The ^{1}H and ^{31}P NMR data are collected in Table I. 1,1′-Diphosphaferrocenes show the characteristic spectroscopic features of the phosphametallocene family, i.e., the absence of H···P and C···P couplings between β-methyl substituents and phosphorus (phospholes themselves do show such couplings[16,17]), the large ^2J(H-P) and ^1J(C-P) coupling constants within the cycle (ca. 36 and 60-65 Hz, respectively) (^2J(H-P) has the same order of magnitude in phospholes[16] but ^1J(C-P) is considerably smaller[17,18]), and the very large high-field shift of phosphorus by comparison either with more classical com-

Table VI. Bond Lengths (Å) and Angles (deg)

	molecule I	molecule II	molecule III	av
Fe-C1	2.057(5)	2.059(5)	2.054(5)	
Fe-C2	2.041(5)	2.086(6)	2.043(5)	
Fe-C3	2.084(5)	2.088(5)	2.073(5)	
Fe-C4	2.079(5)	2.075(5)	2.083(5)	
Fe-C7	2.050(5)	2.092(5)	2.058(5)	
Fe-C8	2.063(5)	2.068(6)	2.075(4)	
Fe-C9	2.075(5)	2.026(5)	2.058(5)	
Fe-C10	2.061(5)	2.041(5)	2.066(6)	2.064(1)
Fe-P1	2.277(1)	2.280(1)	2.272(1)	
Fe-P2	2.280(1)	2.274(1)	2.276(1)	2.276(4)
P1-C1	1.747 (6)	1.766 (7)	1.777(6)	
P1-C4	1.776(6)	1.772(6)	1.767(6)	
P2-C7	1.748(6)	1.781(6)	1.767(6)	
P2-C10	1.762(6)	1.752(6)	1.796(7)	1.767(1.7)
C1-C2	1.402(6)	1.465(8)	1.354(8)	
C2-C3	1.436(9)	1.391(9)	1.400(8)	
C3-C4	1.412(9)	1.421(8)	1.434(8)	
C7-C8	1.413(8)	1.390(9)	1.397(8)	
C8-C9	1.401(8)	1.420(8)	1.395(8)	
C9-C10	1.438(8)	1.397(8)	1.425(8)	1.410(2)
C2-C5	1.510(9)	1.500(10)	1.529(9)	
C5-C6	1.483(9)	1.518(8)	1.500(9)	
C8-C11	1.503(9)	1.504(9)	1.511(8)	
C9-C12	1.500(9)	1.527(9)	1.543(9)	1.510(2)
C1-P1-C4	87.7(0.2)	89.1(0.3)	87.4(0.2)	
C7-P2-C10	88.6(0.2)	87.7(0.2)	88.5(0.3)	88.22(8)
P1-C1-C2	115.7(0.3)	112.5(0.3)	115.0(0.3)	
P1-C4-C3	114.5(0.3)	113.6(0.3)	113.3(0.3)	
P2-C7-C8	115.1(0.3)	113.2(0.3)	114.5(0.3)	
P2-C10-C9	112.8(0.3)	115.3(0.3)	111.2(0.3)	113.9(1)
C1-C2-C3	111.0(0.5)	111.7(0.5)	113.3(0.5)	
C2-C3-C4	110.8(0.5)	112.8(0.5)	110.8(0.5)	
C7-C8-C9	111.0(0.5)	112.3(0.5)	111.7(0.5)	
C8-C9-C10	112.2(0.5)	111.2(0.5)	113.8(0.5)	111.9(1)
C1-C2-C5	125.7(0.5)	122.9(0.5)	124.2(0.5)	
C3-C2-C5	123.0(0.5)	125.2(0.5)	122.4(0.5)	
C2-C3-C6	125.0(0.5)	124.3(0.5)	125.9(0.5)	
C4-C3-C6	124.1(0.5)	122.8(0.5)	123.1(0.5)	
C7-C8-C11	124.6(0.5)	123.4(0.5)	123.3(0.5)	
C9-C8-C11	124.2(0.5)	124.1(0.5)	124.9(0.5)	
C8-C9-C12	124.0(0.5)	123.6(0.5)	123.6(0.5)	
C10-C9-C12	123.6(0.5)	124.9(0.5)	122.5(0.5)	124.0(1)

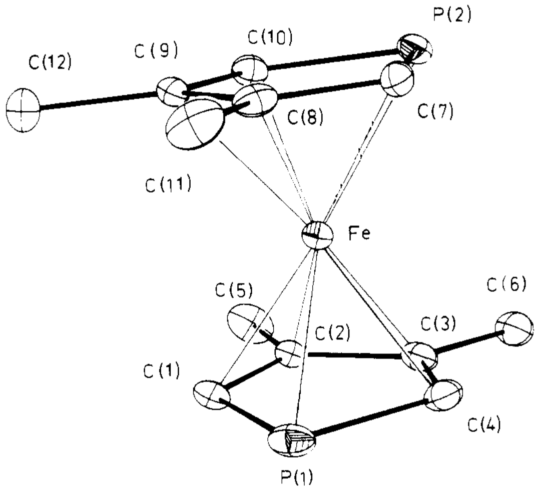


Figure 1.

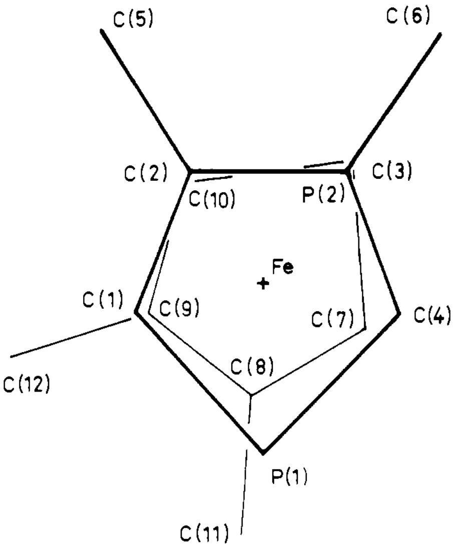


Figure 2.

plexes or with free phospholes. The possible meaning of these features has been discussed elsewhere.[3,5] Some more specific spectroscopic features were also observed on functional derivatives. When one of the phosphol-1-yl group bears a function on C(2), quite logically the two methyl groups of this cycle become distinct on the ^{1}H NMR spectrum but, more unexpectedly, an inequivalence is also observed for the two methyls of the other phosphol-1-yl cycle: $\Delta(\delta Me)$ is as high as 0.07 ppm

Table VII, Least-Squares Planes[a]

	Mean Plane through C1, C2, C3, C4 and	P1, C1, C4	
molecule I:	$-0.7891X + 0.1406Y - 0.5980Z + 16.8215 = 0$; Fe 1.6425(7) P1 −0.011(1)	$-0.7962X + 0.1382Y - 0.5891Z + 16.8530 = 0$ Fe 1.6393(7)	(Pl 1, Pl 2)
molecule II:	$-0.7867X + 0.0609Y - 0.61437Z + 10.6096 = 0$; FeP 1.6344(7) P1P −0.084(1)	$-0.8214X + 0.0874Y - 0.5636Z + 10.1891 = 0$ FeP 1.6146(7)	(Pl 3, Pl 4)
molecule III;	$-0.7998X - 0.1112Y - 0.5899Z + 5.1733 = 0$; FeS 1.6448(7) P1S −0.014(1)	$-0.8067X - 0.1101Y - 0.5807Z + 5.1098 = 0$ FeS 1.6419(7)	(Pl 5, Pl 6)
	Mean Plane through C7, C8, C9, C10 and	P2, C7, C10	
molecule I:	$-0.7814X + 0.1003Y - 0.6160Z + 14.0120 = 0$; Fe −1.6291(7) P2 0.027(1)	$-0.8171X + 0.0799Y - 0.5709Z + 14.2836 = 0$ Fe −1.6108(7)	(Pl 7, Pl 8)
molecule II:	$-0.8129X - 0.0036Y - 0.5823Z + 7.9103 = 0$; FeP −1.6396(7) P2P 0.013(1)	$-0.8196X - 0.0016Y - 0.5730Z + 7.8698 = 0$ FeP −1.6364(7)	(Pl 9, Pl 10)
molecule III:	$-0.7755X - 0.1561Y - 0.6117Z + 2.4631 = 0$; FeS −1.6277(7) P2S 0.077(1)	$-0.8066X - 0.1768Y - 0.5640Z + 2.4298 = 0$ FeS − 1.6104(7)	(Pl 11, Pl 12)

Dihedral Angles between Planes (deg)

PL1-PL2	0.67	PL11-PL12	3.48	PL1-PL5	14.48
PL3-PL4	3.84	PL1-PL7	2.57	PL3-PL5	10.00
PL5-PL6	0.66	PL3-PL9	4.39	PL7-PL9	6.52
PL7-PL8	3.50	PL5-PL11	3.18	PL7-PL11	14.73
PL9-PL10	0.67	PL1-PL3	4.66	PL9-PL11	9.16

[a] The equation of each plane is expressed with coordinates X, Y, Z referred to an orthogonal system (A, B, C) oriented with respect to the crystallographic axis such that A and B are parallel to a and b and C is parallel to c^*.

for **7**. On the contrary, in $CDCl_3$ the two CH groups of the nonfunctional cycle remain indistinguishable in the general case except for the alcohols **12a** and **13** (this fact does not mean that they are equivalent; indeed, when using CCl_4 as a solvent instead of $CDCl_3$, the C*H*P of **7** appear as three doublets).

The origin of this inequivalence remains obscure at the present time. The two methyl and CH groups of the nonfunctional phosphol-1-yl are diastereotopic but such large inequivalences are perhaps in fact indicative of restricted rotations of the phosphol-1-yl cycles around their common axis. A variable-temperature NMR study of these molecules will be undertaken in order to clarify this question. From another standpoint it is also puzzling to note that the two phosphorus atoms of monofunctional compounds are quite normally largely distinct in NMR except in the case of the two diastereoisomeric secondary alcohols **12a** and **12b**. Finally the appearance of a P···OH coupling in **13** is characteristic of a strong steric hindrance slowing down the OH exchange. Such couplings are rare but have been already described in the literature; see, for example, ref 19 and 20.

Crystal Structure of $[PC_4H_2(CH_3)_2]_2Fe$ (2). The crystal structure of $[PC_4H_2(CH_3)_2]_2Fe$ consists of discrete molecules in which an iron atom is sandwiched between two π-bonded phosphol-1-yl groups. There are three such molecules in the asymmetric unit. All $PC_4H_2(CH_3)_2$ rings are roughly parallel to the $(1\,0\,\bar{1})$ plane of the unit cell and the individual molecules are linked only by van der Waals type interactions; Table V gives the shortest intermolecular distances.

Figure 1 shows molecule I together with the labeling scheme for the atoms; labeling schemes for molecules II and III are the same as for I followed by P (prime) and S (second) for each atom. The nonhydrogen atoms are represented by their ellipsoids of thermal motion scaled to enclose 50% of the electron density.[30]

Table VI gives bond lengths (Å) and angles (deg) for each molecule and the average values. Figure 2 shows the projection of molecule I on the plane defined by atoms P1, C1, and C4. Table VII gives the least-squares planes of interest.

The values of Tables VI and VII show that the overall geometry of all three molecules is similar. The two phosphol-1-yl rings of each molecule are not strictly planar but slightly bent around the axis defined by respectively C1 and C4 and C7 and C10. The carbon moieties of the two rings are both planar within experimental error, but the phosphorus atoms lie out of these carbon mean planes by 0.011 (1) to 0.084 (1) Å on the opposite side to iron, with a average value of 0.04 (1) Å, close to those found in phosphaferrocene[4] and phosphacymantrene.[3] The dihedral angles between the mean planes C1 to C4 and C1-P1-C4 are 0.67, 0.66, and 0.67° and those between mean planes C7 to C10 and C7-P2-C10 are 3.84, 3.50, and 3.48°, indicating that for each molecule one phospholyl ring is more bent than the other.

The carbon-carbon bond lengths in the phosphol-1-yl rings are equivalent and their mean value is 1.410 (2) Å, and the corresponding C-C-C angles have a mean value of 111.9 (1)°; these data are close to those found in other π-bonded five-membered carbon rings.

Phosphorus-carbon bond distances are equivalent with a mean value of 1.767 (1.7) Å and a C-P-C angle of 88.22 (8)° in mean; these values agree also with those found in phosphaferrocene (1.763 Å and 88.40°) and are close to those found in 2,6-dimethyl-4-phenylphosphorin (1.74 Å),[31] 1-benzylphosphole (1.783 Å),[32] and aluminum tris(dibenzoylphosphide) (1.772 Å).[33]

As shown in Figure 2 the two phosphol-1-yl rings of one molecule superpose roughly when projected on each other. The phosphorus atom of one ring superposes with a β carbon atom of the other. The C1 to C4 and C7 to C10 mean planes are not parallel; the dihedral angles lie between 2.57 and 4.39°.

The phosphol-1-yl rings of the three molecules are only roughly parallel as indicated by the dihedral angles of the mean planes in Table VII. No systematic correlation could be found between the dihedral angles of these planes.

Experimental Section

Most of the ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded either on a Bruker WH 90 spectrometer by Miss Anne Breque or on a JEOL PS 100 FT spectrometer by Mrs. Raymonde Mankowski-Favelier. Chromatographic purifications were performed on silica gel 70-230 mesh (Merck). All the reactions were run under argon. The starting phospholes were prepared according to ref 16 and 34.

2,2′,5,5′-Tetraphenyl-1,1′-diphosphaferrocene (1). A mixture of 1,2,5-triphenylphosphole (3.1 g, 0.01 mol) and lithium in thin pieces (0.28 g, 0.04 g-atom) in THF (100 cm^3) is stirred at room temperature for 5 h. The solution becomes dark red. After filtration (moisture is strictly excluded), anhydrous $FeCl_2$ (2.54 g, 0.02 mol) is added to the filtrate. The reaction medium is then stirred again at room temperature for 12 h and finally refluxed for 1 h. After evaporation to dryness, the residue is extracted with benzene. The benzene extract is chromatographed with hexane-benzene (80:20), mp 230 °C, yield 1.37 g (53%). Anal. Calcd for $C_{32}H_{24}FeP_2$: C, 73.02; H, 4.60; Fe, 10.61; P, 11.77. Found: C, 73.27; H, 4.39; Fe, 10.53; P, 11.29. δ^{31}P (**1**) −63.6 ppm. For ^{1}H NMR data see ref 8.

1,1′-Diphosphaferrocene (3) and 3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene (2). A THF naphthalene-sodium solution is prepared with 0.75 g of Na (0.032 g-atom) and 4.5 g of naphthalene (0.035 mol) in 100 cm^3 of THF. 1-Phenylphosphole (2.7 g, 0.016 mol) is added to this solution. The mixture is stirred at room temperature for 4 h. The solution turns from deep blue to dark red. Anhydrous $MgBr_2$ (3.0 g, 0.016 mol) is then added. A discoloration is observed. After additional stirring for 2 h, 1.2 g (0.01 mol) of anhydrous $FeCl_2$ is added. The reaction medium is stirred again at room temperature for 16 h and then refluxed for 1 h. After evaporation to dryness, the residue is extracted with benzene. The benzene extract is dried and then reextracted with hexane. At −30 °C the main part of the naphthalene crystallizes out of the hexane solution. After filtration and evaporation of the filtrate, the residual naphthalene is eliminated by sublimation at 30-40 °C under 0.01 Torr. The remaining orange solid is practically pure, yield 0.64 g (~30%). Further purification of **3** can be achieved by chromatography with hexane-benzene (80:20). Similarly from 3 g (0.016 mol) of 1-phenyl-3,4-dimethylphosphole, 1.4 g of **2** (~60%) is obtained, mp 140 °C (methanol). Anal. Calcd for $C_{12}H_{16}FeP_2$: C, 51.83; H, 5.80; Fe, 20.09; P, 22.28. Found: C, 51.66; H, 5.83; Fe, 20.67; P, 22.18. For ^{13}C NMR data see ref 8.

2-Formyl-3,4-dimethyl-1-phosphaferrocene (5). A mixture of 3,4-dimethylphosphaferrocene (**4**,[5] 1.1 g, 0.005 mol), freshly distilled $POCl_3$ (0.8 cm^3), and *N*-methyl-*N*-phenylformamide (1 g) in dichloromethane (15 cm^3) is heated at 50 °C with stirring for 4 h. After hydrolysis and neutralization with CO_3Na_2, the CH_2Cl_2 layer is dried over sodium sulfate and evaporated. The residue is chromatographed with benzene, mp 76 °C, yield 0.56 g (43%). Anal. Calcd for $C_{12}H_{13}FeOP$: C, 55.42; H, 5.04. Found: C, 55.26; H, 4.92. ^{1}H NMR: δ 2.18 (s, Me), 2.41 (s, Me), 4.20 (d, J_{H-P} = 36 Hz, CHP), 4.20 (s, C_5H_5), 9.81 (d, J_{H-P} = 4.4 Hz, CHO). ^{31}P NMR: δ −62.0 ppm. ^{13}C NMR: δ 14.3 (s, Me), 16.4 (s, Me), 73.0 (s, C_5H_5), 83.0 (d, J_{C-P} = 59.6 Hz, Cα), 88.2 (d, J_{C-P} = 57.3 Hz, Cα), 94.5 (d, J_{C-P} = 4.5 Hz, Cβ), 101.1 (d, J_{C-P} = 8.1 Hz, Cβ), 196.5 (d, J_{C-P} = 28 Hz, CHO). IR (KBr): ν_{CO} 1641 cm^{-1}. Mass spectrum (70 eV, 70 °C): *m/e* 260 (*I* = 100%, M), 232 (*I* = 38%, M − CO).

2-Hydroxymethyl-3,4-dimethyl-1-phosphaferrocene (6). A mixture of aldehyde **5** (0.52 g, 2 × 10^{-3} mol) and $LiAlH_4$ (0.2 g) in ether (25 cm^3) is stirred at room temperature for 3 h. After destruction of the excess of $LiAlH_4$ with ethyl acetate, the mixture is hydrolyzed and neutralized with HCl (1 N). The organic solvents are removed and the water layer is extracted with dichloromethane. The organic phase is dried over sodium sulfate and evaporated. The residue is chromatographed with benzene-ethyl acetate (90:10). An orange oil is thus obtained, yield 0.28 g (53%). Anal. Calcd for $C_{12}H_{15}FeOP$: C, 54.99; H, 5.77. Found: C, 54.75; H, 5.80. ^{1}H NMR: δ 2.17 (s, Me), 3.75 (d, J_{H-P} = 36 Hz, CHP), 4.10 (s, C_5H_5); the CH_2OH signal is masked by the C_5H_5 peak. δ^{31}P: −79.6. ^{13}C NMR: δ 13.4 (s, Me), 16.8 (s, Me), 61.2 (d, J_{C-P} = 12.9 Hz, CH_2OH), 71.7 (s, C_5H_5), 76.5 (d, J_{C-P} = 58 Hz, CαH), 93.6 (d, J_{C-P} = 4.5 Hz, Cβ), 96.7 (d, J_{C-P} = 6.7 Hz, Cβ). IR ν_{OH} 3250 (very broad).

2-Acetyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (7). To a solution of preformed $CH_3COCl-AlCl_3$ complex in 30 cm^3 of CH_2Cl_2 prepared with 0.7 g of $AlCl_3$ (0.0052 mol) and 0.45 g of CH_3COCl (0.0057 mol) is added dropwise at room temperature 1.39 g of diphosphaferrocene **2** (0.005 mol) in 10 cm^3 of CH_2Cl_2. The mixture is stirred and heated at 50 °C for 3 h and then poured on ice. The organic layer is washed with water until neutrality, dried over sodium sulfate, and evaporated. The residue is chromatographed with benzene, mp ~71 °C; yield 1.2 g (74%). Anal. Calcd for $C_{14}H_{18}FeOP_2$: C, 52.53; H, 5.67. Found: C, 52.60; H, 5.55. IR (KBr): ν(CO) 1650 cm^{-1}.

2-Benzoyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (8). To a solution of preformed $C_6H_5COCl-AlCl_3$ complex in 5 cm^3 of CH_2Cl_2 prepared with 0.13 g of $AlCl_3$ (10^{-3} mol) and 0.12 cm^3 of C_6H_5COCl (10^{-3} mol) is added 0.28 g of diphosphaferrocene **2** (10^{-3} mol) in 15 cm^3 of CH_2Cl_2. The mixture is stirred at room temperature for 4 h and then treated as above for **7**, mp ~70 °C, yield 0.16 g (42%). Anal. Calcd for $C_{19}H_{20}FeOP_2$: C, 59.68; H, 5.23. Found: C, 59.88; H, 5.42. IR ($CDCl_3$): ν(CO) 1620 cm^{-1}. Mass spectrum (70 eV, 100 °C): *m/e* 382 (*I* = 100%, M), 277 (*I* = 30%, M − COC_6H_5).

2,2′-Diacetyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocenes (9a and 9b). The acetylation reaction is performed in the same way as for **7** starting with 0.83 g of $AlCl_3$ (0.0062 mol), 0.51 g of CH_3COCl (0.0065 mol), and 0.69 g of diphosphaferrocene **2** (0.0025 mol). The organic residue is chromatographed with benzene-ethyl acetate (95:5), total yield of **9a** + **9b** 0.58 g (64%). Anal. Calcd for $C_{16}H_{20}FeO_2P_2$: C, 53.06; H, 5.57; Fe, 15.42. Found: C, 52.98; H, 5.59; Fe, 15.83. IR (KBr): ν(CO) 1655 cm^{-1}. **9a** and **9b** are separated as indicated in the Discussion: **9a**, mp 128 °C (CS_2); **9b**, mp 134 °C (CS_2).

2-Formyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (10). A mixture of 0.67 cm^3 of $POCl_3$ (0.0075 mol) and 1.02 g of *N*-methyl-*N*-phenylformamide (0.0075 mol) is stirred for 10 min (both reagents were freshly distilled). Then 0.69 g of diphosphaferrocene **2** (0.0025 mol) in 5 cm^3 of CH_2Cl_2 is added. The reaction medium is stirred at room temperature for 1 h and then at 50 °C for 2 h. After the usual workup the organic product is chromatographed with benzene, mp 162 °C, yield 0.45 g (58%). Anal. Calcd for $C_{13}H_{16}FeOP_2$: C, 51.01; H, 5.27; Fe, 18.25. Found: C, 50.84; H, 5.18; Fe, 18.35. IR (KBr): ν(CO) 1658 cm^{-1}.

2-Hydroxymethyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (11). To 0.45 g (1.47 × 10^{-3} mol) of aldehyde **10** in 5 cm^3 of ether is added dropwise 3.7 × 10^{-4} mol of $LiAlH_4$ in THF (filtrated and titrated solution). After 1 h of stirring at room temperature, the reaction mixture is treated by ethyl acetate and then water is added. The ethereal phase is washed by water until neutrality and dried over sodium sulfate. After evaporation the organic residue is chromatographed with benzene-ethyl acetate (95:5), mp 127 °C, yield 0.24 g (53%). Anal. Calcd for $C_{13}H_{18}FeOP_2$: C, 50.68; H, 5.89. Found: C, 50.64; H, 5.70. IR (KBr): ν(OH) 3200 cm^{-1}. Mass spectrum (70 eV, 120 °C): *m/e* 308 (*I* = 100%, M), 290 (*I* = 23%, M − H_2O).

2-α-Hydroxyethyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocenes (12a and 12b). To 1.21 g (3.8 × 10^{-3} mol) of acetyldiphosphaferrocene **7** in 50 cm^3 of methanol is added at room temperature sodium borohydride in small batches until the complete disappearance of **7** (checked by TLC). After evaporation, the residue is taken up with a mixture of CH_2Cl_2 and water. The organic phase is washed until neutrality, dried over sodium sulfate, and evaporated. The crude mixture of **12a** and **12b** is chromatographed with benzene-ethyl acetate (95:5). **12a** (first eluted): mp 100-105 °C (methanol); yield 0.65 g (52%). IR (KBr): ν(OH) 3485 cm^{-1} (shoulder at 3370 cm^{-1}). **12b**: mp 70-72 °C (methanol); yield 0.35 g (29%). IR (KBr): ν(OH) 3250 cm^{-1}.

2-α-Hydroxyisopropyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (13). To 0.33 g (10^{-3} mol) of acetyldiphosphaferrocene **7** in 15 cm^3 of ether is added at room temperature 1.2 × 10^{-3} mol of CH_3MgI in ethereal solution. The mixture is refluxed for 1.5 h. After hydrolysis the ethereal phase is dried over sodium sulfate and evaporated. The crude product is recrystallized in hexane at −20 °C and then chromatographed with benzene-ethyl acetate (90:10), mp ~98 °C, yield 0.09 g (15%). Anal. Calcd for $C_{15}H_{22}FeOP_2$: C, 53.57; H, 6.54.

Found: C, 53.57; H, 6.52. Mass spectrum (70 eV, 120 °C): *m/e* 336 (I = 32%, M), 318 (I = 100%, M − H_2O).

2-Ethyl-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (14). To 7.1 g of $AlCl_3$ (0.053 mol) in 50 cm^3 of ether is cautiously added in small batches 0.5 g (0.013 mol) of $LiAlH_4$ suspended in 20 cm^3 of ether. The mixture is stirred for 30 min at 0 °C. Then 0.69 g (3×10^{-3} mol) of acetyldiphosphaferrocene **7** in 10 cm^3 of ether is added dropwise while maintaining the temperature below 5 °C. After 1 h of stirring, 4 cm^3 of formic acid and, then, 20 cm^3 of water are cautiously added at 0 °C. After 0.5 h the ethereal layer is decanted, washed until neutrality, dried over sodium sulfate, and evaporated. The residue is chromatographed with hexane; 0.2 g of an orange oil is thus obtained (33%). Anal. Calcd for $C_{14}H_{20}FeP_2$: C, 54.93; H, 6.59. Found: C, 54.72; H, 6.58.

X-ray Data Collection and Processing. Suitable single crystals were obtained by vacuum sublimation of crude product at room temperature. A systematic search in reciprocal space using a Philips PW1100 automatic diffractometer[21] and precession camera photographs shows that crystals of $(PC_4H_2(CH_3)_2)_2Fe$ belong to the monoclinic system and that space group is $P2_1/c$. The unit-cell dimensions and their standard deviations were refined at room temperature (20 ± 2 °C) with Mo Kα radiation (λ = 0.709 30 Å) using the method outlined by Busing and Levy for a four-circle diffractometer.[22] The experimental density was measured by flotation in a aqueous KI solution. Final results are $P_2C_{12}H_{16}Fe$, mol wt 278, a = 22.612 (13) Å, b = 12.373 (12) Å, c = 13.725 (8) Å, β = 99.07 (4)°, V = 3791 Å^3, d_{obsd} = 1.44 ± 0.02 g cm^{-3}, Z = 12, d_{calcd} = 1.46 g cm^{-3}, $P2_1/c$ ($C5_{2h}$), μ = 14.37 cm^{-1}.

A parallelepiped crystal of dimensions 0.25 × 0.25 × 0.09 mm was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head.[23] All quantitative data were obtained from a Picker four-circle diffractometer controlled by a PDP8/I computer using graphite-monochromated Mo Kα radiation. The monochromator was set at an angle of 11.68°. The refined parameters listed above and the orientation matrix were obtained using standard Picker routines. Intensity data were collected using the $\theta/2\theta$ scan technique with a scan rate of 2°/min and a scan width of 1.6° + (Mo Kα_1,α_2 splitting).

Each reflection was scanned only if its top intensity was greater than three times the corresponding background intensity. Stationary background counts (20 s) were recorded at each end of the scan. Attenuation filters were inserted whenever the scan count exceeded 7000 counts/s. The intensities of three standard reflections were monitored throughout the data collection at intervals of 300 measurements; their intensities did not vary by more than 2% during the entire data collection period. In order to detect spurious electronic default on the paper tape punching unit and improve measurements of weak reflections due to poor diffraction quality, all hkl, $hk\bar{l}$ and their equivalent $\bar{h}k\bar{l}$, and $\bar{h}kl$ reflections within $\theta < 30°$ were recorded. The variance estimated from counting statistics of an integrated intensity I was $\sigma^2(I) = \sigma_{\mathrm{count}}{}^2 + (pI)^2$. Equivalent reflections were averaged using the program DSORTH;[24] out of 9077 measurements, 17 had very bad agreement and were revealed to have erroneous character punched on paper tape. In case of doubt in correction of errors they were eliminated. Finally 1100 reflections were measured once and 3827 had more than one contributors to averages; factors $R = \Sigma[I_o - \bar{I}]/\Sigma I_o$ and $R_w = \Sigma[wI - w\bar{I}]/\Sigma wI$ with $w = 1/\sigma^2(I)$ were 0.042 and 0.056. After averaging of equivalents, an independent set of 3774 reflections with $I > 4\sigma(I)$ was corrected for Lorentz and polarization factors. No absorption corrections were applied in view of the small crystal dimensions (A^* between 1.52 and 1.40).

The structure was solved using direct methods. The most probable set of MULTAN[25] was the correct one and the Fourier computed with these phases permitted the location of all nonhydrogen atoms.

For all structure-factor calculations, the atomic scattering factors used were those tabulated by Moore[26] using Pepinsky's[27] modification. The effects of anomalous dispersion were included for iron and phosphorus atoms; the values of $\Delta f'$ and $\Delta f''$ are those given in ref 28. Atomic coordinates and individual anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least squares using the program SFLS-5.[29] In all least-squares computations, the function minimized was $\Sigma w([F_o] - [F_c])^2$ where $[F_o]$ and $[F_c]$ are the observed and calculated structure factor amplitudes. The weight w was taken as $1/\sigma^2(F_o)$ with a p value of 0.08. Refinement converged to $R_1 = \Sigma[[F_o] - [F_c]|/\Sigma[F_o]$ and $R_2 = (\Sigma w[[F_o] - [F_c]]^2/\Sigma w[F_o]^2)^{1/2}$ of 0.046 and 0.064. The standard deviation of unit weight observation was 1.42.

A difference map computed at the end of isotropic refinement revealed electron density concentrations close to the calculated positions for hydrogen atoms (C–H = 1 Å). These were included in all subsequent calculations with isotropic temperature factors of 6 Å^2, but not refined. The final difference map shows no maxima greater than 0.40 e Å^{-3}.

Supplementary Material Available: Atomic coordinates and the thermal parameters with their standard deviations (Tables II and III), observed and calculated structure factors (Table IV) (F_o and F_c × 10), and intermolecular contacts less than 3 Å (Table V) (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Equipe IRCHA-CNRS; (b) Institut le Bel.
(2) F. Mathey, *Tetrahedron Lett.*, 4155 (1976).
(3) F. Mathey, A. Mitschler, and R. Weiss, *J. Am. Chem. Soc.*, **100**, 5748 (1978).
(4) F. Mathey, A. Mitschler, and R. Weiss, *J. Am. Chem. Soc.*, **99**, 3537 (1977).
(5) F. Mathey, *J. Organomet. Chem.*, **139**, 77 (1977).
(6) It has been shown recently that arsenin could be acetylated mainly on C(4) by $CH_3COCl + AlCl_3$: A. J. Ashe III, Woon-Tung Chan, and T. W. Smith, *Tetrahedron Lett.*, 2537 (1978). However, the same type of experiment fails when arsenin is replaced by phosphorin, probably because P is much more nucleophilic than As: T. W. Smith, Ph.D. Dissertation, University of Michigan, 1977. Thus, up to now, phosphametallocenes remain the only known phosphorus heterocycles with a classical "aromatic" chemistry.
(7) A. Brèque, F. Mathey, and C. Santini, *J. Organomet. Chem.*, **165**, 129 (1979).
(8) G. de Lauzon, F. Mathey, and M. Simalty, *J. Organomet. Chem.*, **156**, C33 (1978).
(9) E. H. Braye, I. Caplier, and R. Saussez, *Tetrahedron*, **27**, 5523 (1971).
(10) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6205 (1971).
(11) L. D. Freedman, B. R. Ezzell, R. N. Jenkins, and R. M. Harris, *Phosphorus*, **4**, 199 (1974).
(12) F. Mathey and C. Santini, unpublished results.
(13) (a) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957); (b) G. D. Broadhead, J. M. Osgerby, and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).
(14) The same type of chirality was observed in 2-methylazaferrocene which was resolved into its optical antipodes: K. Bauer, H. Falk, and K. Schlögl, *Angew. Chem., Int. Ed. Engl.*, **8** 135 (1969).
(15) (a) M. D. Rausch and D. J. Ciappenelli, *J. Organomet. Chem.*, **10**, 127 (1967); (b) G. Märkl, F. Lieb, and A. Merz, *Angew. Chem., Int. Ed. Engl.*, **6**, 87 (1967).
(16) F. Mathey and R. Mankowski-Favelier, *Bull. Soc. Chim. Fr.*, 4433 (1970); *Org. Magn. Reson.*, **4**, 171 (1972); L. D. Quin, S. G. Borleske, and J. F. Engel, *J. Org. Chem.*, **38**, 1858 (1973).
(17) L. D. Quin, S. G. Borleske, and R. C. Stocks, *Phosphorus*, **5**, 161 (1973).
(18) T. Bundgaard and H. J. Jakobsen, *Tetrahedron Lett*, 3353 (1972).
(19) C. F. Griffin and S. K. Kundu, *J. Org. Chem.*, **34**, 1532 (1969).
(20) F. Mathey, *Tetrahedron*, **29**, 707 (1973).
(21) "Computer Controlled Single Crystal X-ray Diffractometer PW1100/16. Users Manual," N. V. Philips Gloeilampenfabrieken, Eindhoven, The Netherlands, 1974, Section 4.
(22) W. R. Busing, "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 319.
(23) Currently used following an original design of W. Petter, E. T. H., Zürich, private communication.
(24) DSORTH: B. Rees, private communication.[1b]
(25) G. Germain, P. Main, and M. H. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970); *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(26) F. M. Moore, *Acta Crystallogr.*, **16**, 1169 (1963).
(27) V. Vand, P. F. Eiland, and R. Pepinsky, *Acta Crystallogr.*, **10**, 303 (1957).
(28) "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.
(29) C. T. Prewitt, Report ORNL-TM305, "A Fortran IV Full-Matrix Crystallographic Least-Squares Program", Oak Ridge, Tenn., 1966.
(30) Drawings are done using program ORTEP II: C. K. Johnson, Report ORNL 3794, Oak Ridge, Tenn., 1965.
(31) J. C. J. Bart and J. J. Daly, *Angew. Chem., Int. Ed. Engl.*, 7, 811 (1968).
(32) Ph. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, *J. Am. Chem. Soc.*, **92**, 5779 (1970).
(33) G. Becker and H. P. Beck, *Z. Anorg. Allg. Chem.*, **430**, 91 (1977).
(34) I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J. Chem. Soc.*, 2184 (1965).