Reaction of $[PPh_4][HFe(CO)_4]$ with Dichlorophosphines: A New Entry to Classical and Nonclassical Functionalized Phosphorus Complexes

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The reactivity of dichlorophosphines $RPCl_2$ (R = Ph, Me, *t*-Bu, N(*i*-Pr)$_2$) toward the anionic iron hydrido carbonyl metalate $[PPh_4][HFe(CO)_4]$ (1) is investigated. Reactions strongly depend on the nature of the phosphorus substituent and experimental conditions. In all cases stable secondary halophosphine complexes $RP(H)ClFe(CO)_4$ (**2a–d**) are obtained. Moreover treatment of phenyldichlorophosphine with **1** leads to the formation of a 1,2-dihalodiphosphane complex, $(CO)_4FeP_2Cl_2Ph_2$ (**3a**), a side-on end-on diphosphene complex, $[[Fe(CO)_4][\mu\text{-}Fe(CO)_4](PPh)_2]$ (**5a**), and a trimetallic anionic diphosphane species, $[PPh_4][((CO)_4Fe)_3P_2Ph_2H]$ (**6a**). Besides the formation of the diphosphane complex $(CO)_4FeP_2Cl_2Me_2$ (**3b**) and of the anionic diphosphane $[PPh_4][((CO)_4Fe)_3P_2Me_2H]$ (**6b**), the reaction of methyldichlorophosphine with **1** affords an anionic phosphido complex, $[Ph_4P][((CO)_4Fe)_2PHMe]$ (**9b**), and the dihalogeno triphosphorus iron four-membered ring, $Fe(CO)_3(PMeCl)_2PMeFe(CO)_4$ (13). On the other hand, addition of *tert*-butyl-dichlorophosphine to 2 equiv of **1** gives only the anionic phosphido complex $[Ph_4P][((CO)_4Fe)_2PH\text{-}t\text{-}Bu]$, (**9c**). The behavior of (diisopropylamino)dichlorophosphine toward **1** is entirely different. The transient generation of phosphinidene complexes $X{-}P{=}Fe(CO)_4$ (**14d–f**) (X = N(*i*-Pr)$_2$, Cl, H) is postulated in order to explain the formation of spectroscopically characterized anionic phosphido complexes $[Ph_4P][((CO)_4Fe)_2PHX]$ (**9d–f**). Addition of methanol to the mixture **9d–f** allows the synthesis of another new anionic phosphido species, $[Ph_4P][((CO)_4Fe)_2PHOMe]$ (**9g**). The structure of **9g** has been determined by X-ray diffraction.

Introduction

The behavior of dichlorophosphines toward carbonyl metalate mono- or dianions is a field of considerable current interest. Among the most exciting recent results, it was found that the reaction of dichlorophosphines with $Na_2M_2(CO)_{10}$ (M = Cr, Mo, or W) or $Na_2Fe(CO)_4$ led either to various phosphinidene, $[(CO)_5M]_2PR$, or diphosphene complexes, $[(CO)_5M]_nRP{=}PR$ (n = 1 or 2) with different modes of ligation.[1,2] Of interest also is a more special procedure involving cleavage of the P–N bond in (dimethylamino)dichlorophosphine, Me_2NPCl_2, by neutral iron hydrides $(\eta^5\text{-}C_5R'_5)(CO)_2FeH$ or $(\eta^5\text{-}C_5R'_5)(CO)Fe(Me_3P)H$ which allows the formation of diverse metallophosphines of high Lewis basicity.[3]

The focus of the present work is to explore the reactivity of dichlorophosphines toward an anionic iron hydrido carbonyl metalate, $[HFe(CO)_4]^-$. Such a study is of potential interest for several reasons. First, various possible reactions can take place, viz., complexation of the phosphorus lone pair, HCl elimination, hydride transfer, phosphorus nitrogen bond cleavage, etc. Secondly, drastic changes in the reactivity of dichlorophosphines are expected due to the nature of the phosphorus substituent. Third, versatile new synthons in organic or organometallic chemistry could be prepared. Finally, a new field of investigation for the synthesis of unknown mono- or polymetallic complexes of phosphorus derivatives could be initiated.

In a previous communication,[4] we have reported a simple quantitative preparation of stable halophosphine complexes $(CO)_4FeP(H)(Cl)(R)$ (**2**) and an original mode of formation of a side-on end-on nonhindered diphosphene complex, $\{[Fe(CO)_4][\mu\text{-}Fe(CO)_4](PPh)_2\}$ (**5a**). We also described the synthesis of original trimetallic anionic diphosphane species $[Ph_4P][(Fe(CO)_4)_3P_2Ph_2H]$ (**6a**) and $[Et_4N][(Fe(CO_4))_2(W(CO)_5)P_2Ph_2H]$ (8).

Herein we describe full details of this work as well as the following: (i) the preparation of new stable synthons, the 1,2-dihalodiphosphane complexes $(CO)_4FeP_2Cl_2Ph_2$ (**3a**) and $(CO)_4FeP_2Cl_2Me_2$ (**3b**); (ii) the formation of the first three anionic phosphido complexes, $[Ph_4P][((CO)_4Fe)_2PHMe)]$ (**9b**), $[Ph_4P][((CO)_4Fe)_2PH\text{-}t\text{-}Bu]$ (**9c**), and $[Ph_4P][((CO)_4Fe)_2PHOMe]$ (**9g**) (we have determined the structure of **9g** by single-crystal X-ray diffraction); (iii) the synthesis of a novel functionalized phosphorus iron

(1) (a) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7751. (b) Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7750. (c) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Organometallics* **1984**, *3*, 1044. (d) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085. (e) Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460. (f) Norm, J.; Zsolnai, L.; Hunter, G. *Angew. Chem.* **1983**, *95*, 1018; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 977. (g) Lang, K.; Orama, O.; Huttner, G. *J. Organomet. Chem.* **1985**, *291*, 293 and references therein.

(2) Phosphinidene and diphosphene complexes were also obtained by other various methods. See, for example: Jones, R. A.; Seeberger, M. H.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 6424 and references therein.

(3) (a) Malisch, W.; Maisch, R.; Colqhoun, J.; McFarlane, W. *J. Organomet. Chem.* 1981, *C1*, 220. (b) Angerer, W.; Sheldrick, W. S.; Malisch, W. *Chem. Ber.* **1985**, *118*, 1261. (c) Malisch, W.; Jörg, K.; Gross, E.; Schmeusser, M., Meyer, A. *Phosphorus Sulfur* **1986**, *26*(1), 25.

(4) Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Attali, S.; Sanchez, M. *Organometallics* **1986**, *5*, 1914.

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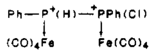
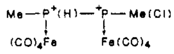
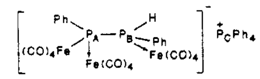
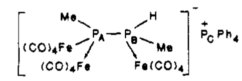
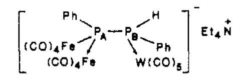
Table I. ^{1}H and ^{31}P NMR Data[a,b] for Complexes 2a–d, 3a,b, 4a,b, 5a,b, 6a,b, and 8

compds	signal	^{1}H NMR δ	^{31}P NMR δ	coupling const (J), Hz
PhP(H)ClFe(CO)$_4$ (**2a**)	Ph	6.63 (m)	154.7	$^1J_{PH}$ = 391
		7.07 (m)		
	H	7.00 (d)		
MeP(H)ClFe(CO)$_4$ (**2b**)	Me	2.28 (dd)	114.2	$^1J_{PH}$ = 295
	H	7.43 (dq)		$^2J_{PH}$ = 8.8
t-BuCP(H)ClFe(CO)$_4$ (**2c**)	t-Bu	0.92 (d)	156.3	$^1J_{PH}$ = 368
	H	6.12 (d)		$^3J_{PH}$ = 20
[(CH$_3$)$_2$CH]$_2$NP(H)ClFe(CO)$_4$ (**2d**)	CH$_3$	0.90 (d)	112.9	$^1J_{PH}$ = 448
	CH	3.50 (m)		$^3J_{PH}$ = 14.8
	P–H	7.97 (d)		
PhP(Cl)PPh(Cl)Fe(CO)$_4$				
3a			169.25, 78.50 (50%)	$^1J_{PP}$ = 309.87
3a′	Ph	6.60 (m) and 7.10 (m)	168.70, 85.89 (50%)	$^1J_{PP}$ = 295.78
MeP*(Cl)*PMe(Cl)Fe(CO)$_4$				
3b			167.3 (d), 91.2 (d) (40%)	$^1J_{PP}$ = 282
3b′	Me	1.60 (m)	166.3 (d), 80.3 (d) (60%)	$^1J_{PP}$ = 295.5
				
4a			164.8 (d)	$^1J_{PP}$ = 171
			66.1 (dd)	$^1J_{PH}$ = 346
4a′			161.4 (d)	$^1J_{PP}$ = 191
			67.1 (dd)	$^1J_{PH}$ = 345
				
4b			156.13 (d), 37.12 (dd) (45%)	$^1J_{PP}$ = 165.4, $^1J_{PH}$ = 353
4b′			153.7 (d), 43.78 (dd) (55%)	$^1J_{PP}$ = 173.55, $^1J_{PH}$ = 351.7
 **5a**	Ph	5.83 (m)	P_A 52.1 (d)	$^1J_{PP}$ = 415
		6.09 (m)	P_B −34.5 (d)	
 **6a**	H	4.38 (d)	P_A 91.15 (d)	$^1J_{P_AP_B}$ = 234.8
	Ph	5.94 (m)	P_B 42.71 (dd)	$^1J_{P_BH}$ = 342
		6.34 (m)	P_C 22.01	
 **6b**			P_A 52.9 (d)	$^1J_{PP}$ = 197.2
			P_B 28.3 (dd)	$^1J_{P_BH}$ = 326.2
			P_C 22.01	
 **8**	H	6.75 (dd)	P_A 74.85 (d)	$^1J_{P_AP_B}$ = 220
	Ph	7.35 (m)	P_B −6.64 (dd)	$^1J_{PW}$ = 208.5
		7.66 (m)		$^1J_{P_BH}$ = 324.4
				$^2J_{HW}$ = 22.7
				$^2J_{P_AH}$ = 7.92

[a] Spectra were recorded on a solution of the compound in CH_2Cl_2 or CD_2Cl_2. [b] Abbreviations: d, doublet; m, unresolved multiplet; dd, doublet of doublet; dq, doublet of quartet.

four-membered ring, **13** (the possible intermediacy of terminal phosphinidene complexes XP=Fe(CO)$_4$ (**14d**, X = N(i-Pr)$_2$; **14e**, X = Cl; **14f**, X = H) is discussed).

Results and Discussion

We have already reported[4] that secondary halophosphine complexes RP(H)(Cl)Fe(CO)$_4$ (**2a–d**) are quantitatively formed when the hydride [Ph$_4$P][HFe(CO)$_4$] (**1**) and a dichlorophosphine, RPCl$_2$—each in dichloromethane solution—are simultaneously mixed, dropwise, at room temperature (reaction 1).

$$\mathrm{RPCl_2} + \underset{\mathbf{1}}{[\mathrm{Ph_4P}][\mathrm{HFe(CO)_4}]} \rightarrow \underset{\mathbf{2a\text{–}d}}{\mathrm{RP(H)(Cl)Fe(CO)_4}} + \mathrm{Ph_4PCl} \quad (1)$$

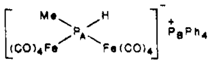
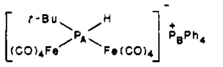
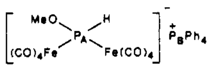
a, R = Ph; **b**, R = Me; **c**, R = t-Bu; **d**, R = N(i-Pr)$_2$

This reaction provides a convenient, one-step preparation under mild conditions of halophosphines stabilized by complexation. A few examples of these species were already reported,[5-7] but all involved a low yield and multistep synthesis. We have also observed that the reaction of **1** with RPCl$_2$ strongly depends on the ratio of both reagents, order of addition, and nature of the phosphorus substituents.

Reaction of PhPCl$_2$ with 1. When a dichloromethane solution of the hydride **1** was slowly added to a solution of phenyldichlorophosphine (stoichiometry 1:1) in dichloromethane, at room temperature, a side-on end-on diphosphene complex **5a** was obtained (reaction 2). The mechanism of formation of **5a** is given in Scheme I and corroborated by the isolation of the intermediates **3a**. Thus, addition of PhPCl$_2$ in dichloromethane to a solution of **2a** in the same solvent at room temperature leads to the formation of the diphosphane **3a** (two diastereoisomers,

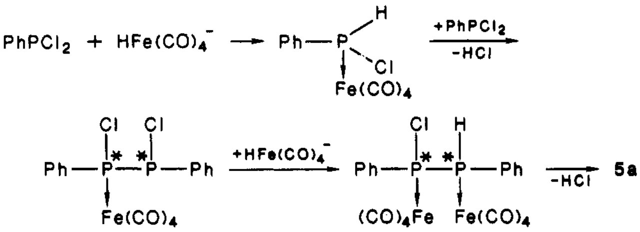
(5) (a) Vahrenkamp, H. *Philos. Trans. R. Soc. Ser. A London*, **1982**, *308*, 17. (b) Müller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2322.
(6) (a) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488. (b) Marinetti, A.; Mathey, F. *Phosphorus Sulfur* **1984**, *19*, 311.
(7) King, R. B.; Fu, W. K. *J. Organomet. Chem.* **1984**, *C33*, 272.

Table II. ^1H and ^{31}P NMR Data[a,b] for Anionic Complexes 9b, 9c, and 9g

compds	^1H NMR signal	^1H NMR δ	^{31}P NMR δ	^{31}P NMR coupling const, Hz
 9b	Me	1.9 (m)	P_A −29.6	$^1J_{PH}$ = 297.9
	H	4.22 (m)	P_B 22.01	$^2J_{PH}$ = 9.1
	Ph	6.68 (m)		
 9c	*t*-Bu	1.12 (dd)	P_A 34.5	$^1J_{PH}$ = 283
	H	4.56 (dd)	P_B 22.01	$^3J_{PH}$ = 14.8
	Ph	6.01 (m)		$^4J_{HH}$ = 5.8
 9g	MeO	3.44 (d)		
	Ph	6.22 (m)	P_A 202	$^1J_{PH}$ = 299.5
	H	7.83 (d)	P_B 22.01	$^3J_{PH}$ = 13.8

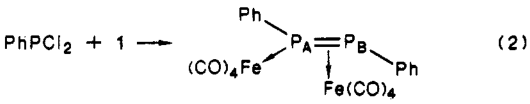
[a] Spectra were recorded on a solution of the compound in CH_2Cl_2 or CD_2Cl_2. [b] d, doublet; m, multiplet; dd, doublet of doublet.

Scheme I



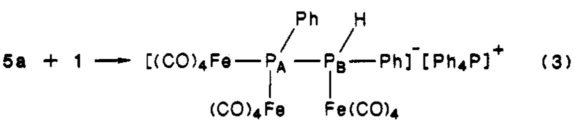
3a 4a

see Table I). Reaction of $PhPCl_2$ with $^1/_2$ equiv of 1 was also found to give **3a**. Moreover, treatment of **3a** with 1 equiv of 1 afforded the unstable diphosphane **4a** which has been only characterized in solution by ^{31}P NMR (see Table I). Finally, intramolecular elimination of hydrogen chloride from **4a** gave rise to the diphosphene complex **5a**. This four-step mechanism is in agreement with the 1:1 stoichiometry involved in the direct synthesis of **5a** (reaction 2).



5a

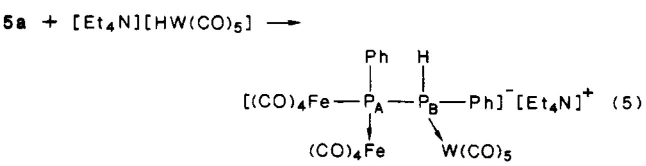
Further addition of 1 equiv of 1 to **5a** results in the formation of the trimetallic anionic diphosphane species $[Ph_4P][(Fe(CO)_4)_3P_2Ph_2H]$ (**6a**) (reaction 3). We have found that **6a** is more conveniently prepared in high yield according to reaction 4.



6a

$$2PhPCl_2 + 3\ 1 \rightarrow \mathbf{6a} \qquad (4)$$

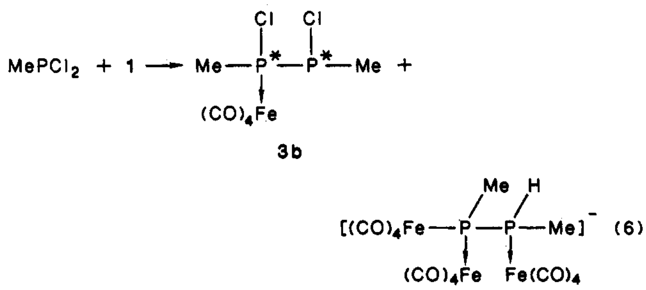
The formation of **6a** could be explained by an oxidative addition of $HFe(CO)_4^-$ on the P_B phosphorus atom of **5a**. If our assumption is correct, **5a** must react with another metallic hydride such as $[HW(CO)_5]^-$ (7). Actually, the new trimetallic anionic diphosphane 8 is quantitatively formed (reaction 5). ^{31}P and ^1H NMR spectra of 8 clearly show that the phosphorus atom P_B is effectively bonded to a proton and to $W(CO)_5$ (see Table I).



8

An interesting peculiarity of the subsequent transformations **4a** → **5a** → **6a** is the change in the mode of coordination of phosphorus ligands: η_1, η_1 for **4a**, η_1, η_2 for **5a**, and finally η_1, η_1, η_1 for **6a**.

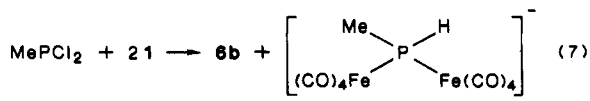
Reaction of $MePCl_2$ with 1. A significant change already occurs when 1 is stoichiometrically added to methyl dichlorophosphine: only the diphosphane species **3b** (two diastereoisomers) and the new trimetallic anionic diphosphane **6b** are obtained (1:1 ratio) (reaction 6).



3b 6b

The overall reaction would be expected to adhere to a mechanism similar to the one described for the synthesis of **3a** and **6a** (Scheme II). Indeed **3b** is available from treatment of **2b** with $MePCl_2$ or addition of 0.5 mol of 1 to 1 mol of $MePCl_2$ (Table I). On the other hand, the formation of **6b** requires the **3b** → **4b** → **5b** → **6b** successive transformations. Examination of the solution ^{31}P NMR spectrum—when addition of 1 to methyldichlorophosphine is performed at 0 °C—reveals the presence of two AB systems which are consistent with the transient formation of **4b** (two diastereoisomers, Table I). Nevertheless no traces of diphosphene complex **5b** were detected probably because of the high reactivity of this compound which could be trapped by 1 as soon as it is generated.

The different behavior of methyldichlorophosphine toward 1—in comparison with phenyldichlorophosphine—is again illustrated when 1 equiv of $MePCl_2$ is added to 2 equiv of 1 in dichloromethane: besides the expected formation of the trimetallic anionic diphosphane complex **6b**, the new anionic phosphido complex **9b** is also generated (reaction 7) (see Table II).

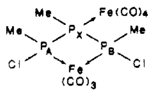


9b

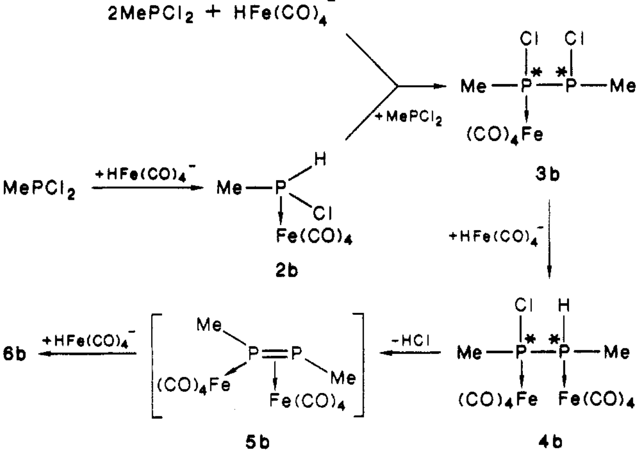
The formation of **9b** is of particular interest since it is the first anionic phosphido complex with a phosphorus–hydrogen bond. Neutral species such as **10**[8] or **11**[9] for

(8) Grobe, J.; Haubold, R. *Z. Anorg. Allg. Chem.* **1985**, *526*, 145.
(9) King, R. B.; Fu, W. K.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 3095.

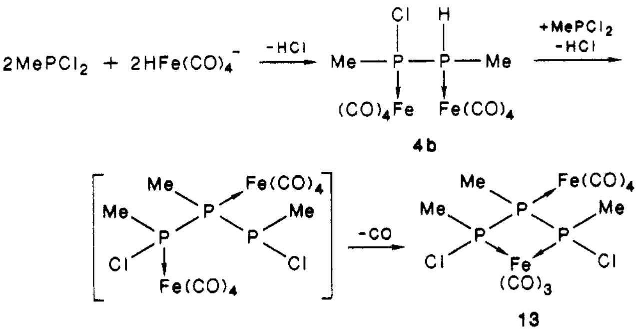
Table III. ^{1}H and ^{31}P NMR Data[a,b] for Compound 13

compd	^{1}H NMR signal	^{1}H NMR δ		^{31}P NMR δ	^{31}P NMR coupling const, Hz
 13	Me	2.07 (m)	isomer *d*	P_A 162.67	$^1J_{P_AP_X}$ = 348
				P_B 162.58	$^1J_{P_BP_X}$ = 351
				P_X 11.06	$^2J_{P_AP_B}$ = 60.3
		2.70 (m)	meso 1 (or 2)	P_A 161.50	$^1J_{P_AP_X}$ = 349
				P_X 11.90	
			meso 2 (or 1)	P_A 158.56	$^1J_{P_AP_X}$ = 325.5
				P_X 19.74	

Scheme II



Scheme III



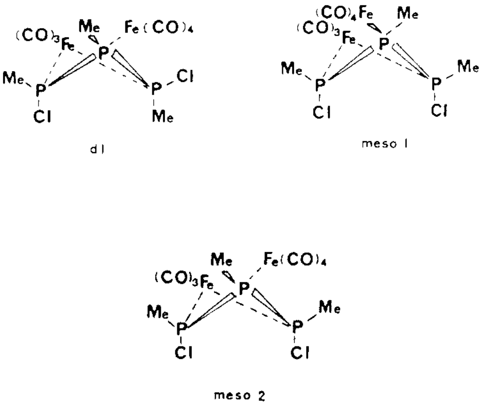
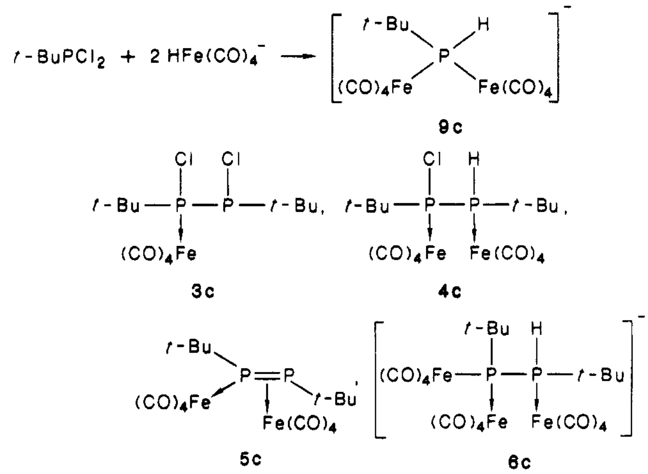
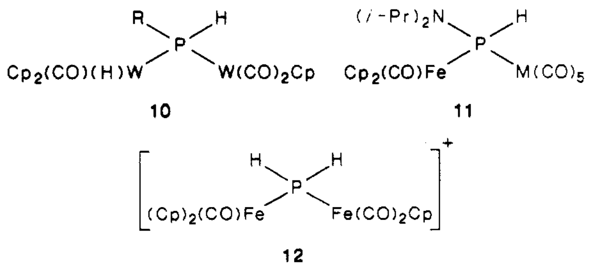


Figure 1. Isomers *dl* and meso (1 and 2) of **13**.

Scheme IV



example, have already been reported as well as a cationic species like the diferrophosphonium ion **12**.[10]



Also noteworthy is the fact that 3 mol of $MePCl_2$ reacts with 2 mol of the hydride **1** leading to the iron phosphorus four-membered ring **13** in 30% yield. **13** presumably results from an intermolecular dehydrochlorination between **4b**—preliminary formed—and $MePCl_2$, followed by CO elimination and cyclization (Scheme III).

Three isomers (Figure 1) are expected due to the presence of one *pseudochiral* (–P–*P*–P) and two identical chiral centers (–*P*–P–*P*–). Indeed the $^{31}P\{^1H\}$ NMR spectroscopy of **13** reveals the presence of one ABX (isomer *dl*) and two AA′X (meso 1 and meso 2) spin systems. Computer simulation by routine methods afforded parameters listed in Table III.

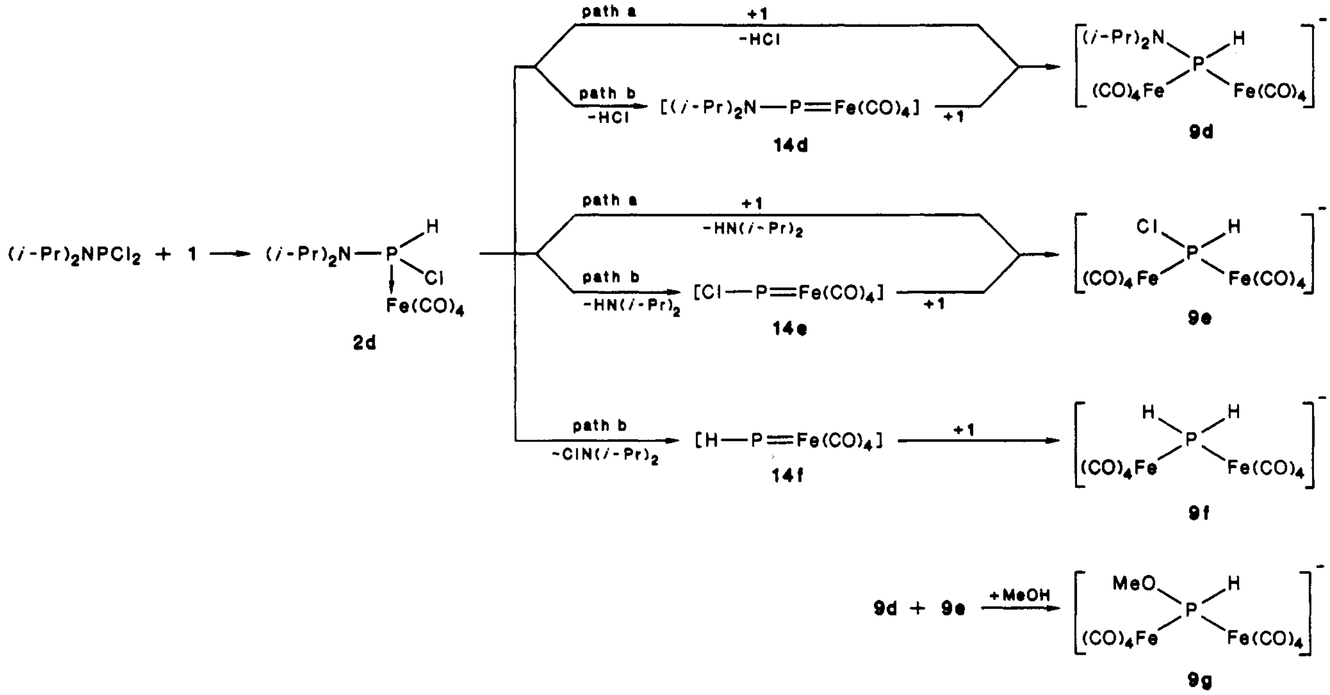
This reaction provides an easy way of obtaining a novel iron–phosphorus four-membered ring in which the three phosphorus atoms are tetracoordinated. Additional interest is due to the presence of two functional phosphorus atoms in the molecule that could allow the synthesis of various other new iron triphosphetane cycles.

Reaction of *t*-BuPCl$_2$ with 1. Addition of **1** to *tert*-butyldichlorophosphine results only in the formation of **2c** (Table I) while treatment of the same phosphine with 2 mol of **I** leads to the other new anionic phosphido complex **9c** (Scheme IV). Steric effects due to the *tert*-butyl group thus cause important differences and explain the synthesis of **9c** (Table III). This means that formation of complex **3c** or **4c** is hindered and therefore derivative **5c** or **6c** cannot be obtained.

Reaction of (*i*-Pr)$_2$NPCl$_2$ with 1. The secondary halo (diisopropylamino)phosphine complex **2d** is the only available product when a 1:1 ratio of (diisopropyl-

(10) (a) Schäfer, H. *Angew. Chem.* **1981**, *93*, 595. (b) *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 608.

Scheme V



amino)dichlorophosphine and hydride 1 are reacted at room temperature in dichloromethane.

Entirely different results were obtained when 2 mol of 1 were added to 1 mol of (diisopropylamino)dichlorophosphine (Scheme V). The ^{31}P NMR coupled spectra of the solution show signals corresponding to the three anionic species **9d**(δ 56.9 (d of t,$^1J_{PH}$ = 315.2 Hz, $^3J_{PH}$ = 13.6 Hz)), **9e** (δ 179.1 (d,$^1J_{PH}$ = 303.9 Hz)), and **9f**(δ -90 ppm(t,$^1J_{PH}$ = 297.5 Hz)). The same results are obtained from the reaction of 1 equiv of **1** with 1 equiv of **2d**. Attempts to isolate these compounds failed. Nevertheless, addition of methanol to this mixture afforded only a new anionic phosphido complex, **9g** (Table II), arising from the methanolysis of the P–N bond of **9d** and of the P–Cl bond of **9e**. Two pathways can be proposed for the formation of anionic species **9d,e**, each involving the halophosphine complex **2d** which presents three good leaving groups (H, Cl, N(i-Pr)$_2$). Elimination of hydrogen chloride and diisopropylamine—between **2d** and **1**—can be either intermolecular (pathway a) or intramolecular with the transient generation of phosphinidene complexes X—P=Fe(CO)$_4$ (X = N(i-Pr)$_2$ or Cl) which react further with **1** (pathway b). However, only the mechanism involving an intramolecular elimination of chlorodiisopropylamine could explain the production of **9f**. Therefore, we prefer to postulate that the anionic phosphido complexes **9d–f** might come from the trapping of the phosphinidene complexes **14d–f** with **1**, respectively. It is of interest to note that **9f** is also detected when **1** is treated with the (tetramethylpiperidino)dichlorophosphine. Moreover such an assumption is in agreement with recent experiments reported by Mathey, who trapped the (diethylamino)phosphinidene complex Et_2N—P=W(CO)$_5$ in a reaction involving an elimination of bromodiethylamine.[11]

It seems quite likely that the formation of the anionic species **9b** or **9c** from the reaction of $MePCl_2$ or t-$BuPCl_2$ with **1** proceeds via the same mechanism. Obviously, only an intra- or intermolecular dehydrochlorination can take place here. Indeed, addition of 1 equiv of **1** to **2c**, for example, leads to the expected complex **9c**.

(11) Mercier, F.; Mathey, F. *Tetrahedron Lett.* **1986**, *27*, 1323.

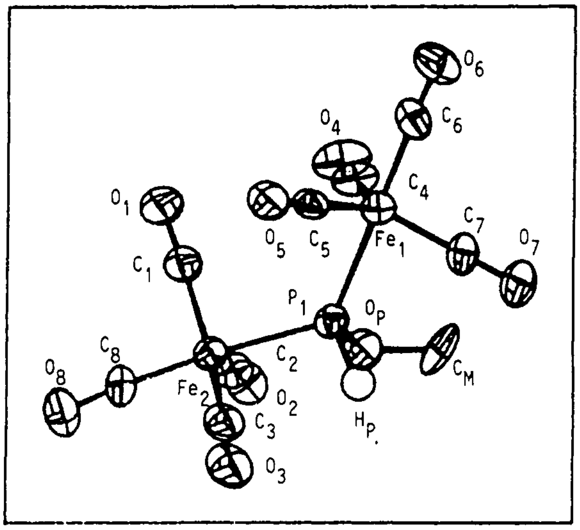


Figure 2. ORTEP drawing of **9g** showing the atomic numbering scheme.

X-ray Structural Analysis of 9g. To ascertain further the structure of complexes of type **9**, an X-ray structure analysis of **9g** has been undertaken. **9g** has been retained as it gave the best crystals for an X-ray analysis.

An ORTEP plot of the anionic part of **9g** with numbering scheme is shown in Figure 2, and selected bond lengths and angles are gathered in Table IV. The structure found is in perfect agreement with our formulation: **9g** consists of an anionic part $[Fe_2(CO)_8P(OMe)H]^-$ associated with the $[PPh_4]^+$ cation. In the anionic part, two Fe(CO)$_4$ units are bridged by a P(OMe)H phosphido bridge and the two iron units are at a nonbonded distance. Moreover, it has to be pointed out that the Fe(1)–P(1)–Fe(2) angle is very large compared to the values found for other phosphido-bridged dinuclear compounds with or without a metal–metal bond.[12,13] This illustrates further the great flexibility of the phosphido bridges.

(12) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.
(13) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for 9g with Esd's in Parentheses

Bond Distances			
Fe(1)-P(1)	2.263 (3)	Fe(2)-P(1)	2.260 (3)
Fe(1)-C(4)	1.75 (1)	Fe(2)-C(8)	1.73 (1)
Fe(1)-C(5)	1.76 (1)	Fe(2)-C(1)	1.76 (1)
Fe(1)-C(6)	1.80 (1)	Fe(2)-C(2)	1.755 (9)
Fe(1)-C(7)	1.76 (1)	Fe(2)-C(3)	1.74 (1)
P(1)-H(P)	1.386 ( )	P(1)-O(P)	1.593 (6)
Fe(1)···Fe(2)	3.995 (2)	O(P)-C(M)	1.411 (2)
Bond Angles			
C(4)-Fe(1)-C(5)	119.3 (5)	C(1)-Fe(2)-C(2)	122.0 (5)
C(4)-Fe(1)-C(7)	119.8 (5)	C(1)-Fe(2)-C(3)	119.3 (5)
C(5)-Fe(1)-C(7)	120.3 (5)	C(2)-Fe(2)-C(3)	118.3 (5)
C(6)-Fe(1)-P(1)	178.9 (5)	C(8)-Fe(2)-P(1)	173.1 (4)
C(6)-Fe(1)-C(7)	94.0 (5)	C(1)-Fe(2)-C(8)	90.2 (5)
C(6)-Fe(1)-C(4)	90.4 (5)	C(2)-Fe(2)-C(8)	91.5 (5)
C(6)-Fe(1)-C(5)	93.5 (5)	C(3)-Fe(2)-C(8)	94.8 (5)
C(4)-Fe(1)-P(1)	88.8 (3)	C(1)-Fe(2)-P(1)	83.7 (4)
C(5)-Fe(1)-P(1)	86.4 (3)	C(2)-Fe(2)-P(1)	89.0 (4)
C(7)-Fe(1)-P(1)	87.0 (4)	C(3)-Fe(2)-P(1)	90.9 (4)
Fe(1)-P(1)-Fe(2)	124.1 (1)		
Fe(1)-P(1)-O(P)	112.9 (3)		
Fe(2)-P(1)-O(P)	109.1 (3)		

Table V. Infrared Spectra in the ν_{CO} Stretching Region (cm^{-1}) of the Isolated Complexes

2a	2073 m, 1993 m, 1965 s, 1954 s[a]
2b	2063 m, 1986 m, 1952 s, 1946 s[a]
2c	2065 m, 1997 m, 1968 s, 1955 s[a]
2d	2068 m, 2000 m, 1968 s, 1958 s[a]
3a	2070 w, 2061 s, 1997 s, 1972 vs, 1959 m, 1952 s[a,c]
3b	2059 sh, 2052 s, 1980 sh, 1955 s (br)[a]
5a	2109 m, 2054 sh, 2051 s, 2046 s, 2024 m, 1981 m, 1969 m, 1961 m, 1959 sh, 1941 m[a]
6a	2050 w, 2035 m, 2021 s, 1940 s (br)[b]
6b	2043 w, 2032 m, 2019 s, 1923 s (br)[b]
8	2071 w, 2039 m, 2021 s, 1939 s, 1919 sh[b]
9b	2034 m, 2012 s, 1919 s (br)[b]
9c	1985 s, 1960 s, 1910 (br)[b]
9g	2040 w, 2015 s, 1925 s (br)
13	2072 sh, 2068 sh, 2062 s, 1998 m, 1972 sh, 1962 s[a]

[a] Hexane solution. [b] Dichloromethane solution. [c] Two diastereoisomers.

The geometry about each iron atom is a nearly perfect trigonal-bipyramidal geometry, the only major deviation coming from the C(8)–Fe(2) and Fe(2)–P(1) bonds which are not strictly linear.

Examination of the Fe–P and Fe–C bond distances shows no significant differences between the two $Fe(CO)_4P$ units, suggesting that the negative charge is fully delocalized on the anion.

Experimental Section

All experiments were performed in an atmosphere of dry argon. Dry and oxygen-free solvents were used at all times. Melting points are uncorrected. ^1H NMR spectra were recorded on a Brucker WM 250 or a Bruker AC80 spectrometer. ^1H chemical shifts are reported in parts per million relative to Me_4Si as internal reference. ^{31}P NMR spectra were obtained on a Bruker WM250 or a Bruker AC80. Downfield shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Beckman IR 10 or Perkin-Elmer 225 spectrometer, using polystyrene for calibration (see Table V). Mass spectra were obtained on a Varian MAT 311A. $[Ph_4P][HFe(CO)_4]$ and $[NEt_4][HW(CO)_5]$ were synthetized by published procedures.[14,15]

(14) Mitsudo, T.; Watanabe, Y.; Nakanishi, H.; Morishima, I.; Inubushi, T.; Takegami, Y. J. Chem. Soc., Dalton Trans. **1978**, 1298.

Table VI. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement

formula	$C_{33}H_{24}O_9P_2Fe_2$
M_r	739.18
a, Å	19.176 (2)
b, Å	16.564 (2)
c, Å	21.962 (2)
α, deg	90.0
β, deg	105.08 (1)
γ, deg	90.0
Z	8
V, $Å^3$	6735.33
d(calcd), g/cm^3	1.456
space group	$C2/c$
cryst dimens, mm	0.2 × 0.2 × 0.25
radiatn	Mo Kα
abs coeff μ, cm^{-1}	9.86
unique data	6773
data used in refinement	$1949 F_o > 2.5(F_o)$

General Procedure for the Preparation of Complexes 2a–d. Dichlorophosphine $RPCl_2$ (1 mmol) in 10 mL of dichloromethane and 1 mmol of **1** in 10 mL of dichloromethane were simultaneously added to 20 mL of dichloromethane at room temperature. After the solution was stirred under an argon atmosphere for 1 h, the solvent was removed under reduced pressure and the resulting mixture was treated with three 20 mL-portions of pentane. Upon evaporation of the pentane, the complexes of halophosphines **2a–d** were obtained as oils.

Mass spectra (m/z): **2a**, 312 with successive loss of 4 CO; **2b**, 250 with successive loss of 4 CO; **2c**, 292 with successive loss of 4 CO; **2d**, 335 with the successive loss of 4 CO.

Anal. Calcd for $C_{10}H_6ClFeO_4P$ (**2a**): C, 38.44; H, 1.93; Cl, 11.35; P, 9.91. Found: C, 38.05; H, 1.91; Cl, 11.26; P, 9.78.

Anal. Calcd for $C_5H_4ClFeO_4P$ (**2b**): C, 23.99; H, 1.61; Cl, 14.16; P, 12.37. Found: C, 23.66; H, 1.64; Cl, 14.02; P, 12.21.

Anal. Calcd for $C_8H_{10}ClFeO_4P$ (**2c**): C, 32.86; H, 3.45; Cl, 12.12; P, 10.59. Found: C, 32.65; H, 3.36; Cl, 12.03; P, 10.45.

Anal. Calcd for $C_{10}H_{15}ClFeNO_4P$ (**2d**): C, 35.80; H, 4.50; Cl, 10.56; P, 9.23. Found: C, 35.61; H, 4.47; Cl, 10.42; P, 9.02.

Synthesis of 5a. To 1 mmol of $PhPCl_2$ in 20 mL of CH_2Cl_2 was added dropwise 1 mmol of **1** in 10 mL of CH_2Cl_2 at room temperature. The solution was stirred for 1 h and then evaporated to dryness. Extraction of the residue with 3 × 20 mL of pentane and evaporation of the solution gave **5a** which was recrystallized at –20 °C in a 1:1 mixture of CH_2Cl_2 and hexane as orange crystals (60% yield).

Anal. Calcd for $C_{20.5}H_{11}ClFe_2P_2O_8$ (**5a**·$^1/_2CH_2Cl_2$): C, 41.41; H, 1.85; Fe, 18.85; P, 10.43; Cl, 5.97. Found: C, 41.44; H, 1.81; Fe, 19.05; P, 10.94; Cl, 5.91.

Synthesis of 3a and 3b. To 1 mmol of $RPCl_2$ (R = Ph, Me) in 20 mL of CH_2Cl_2 was added dropwise 0.5 mmol of **1** in 10 mL of CH_2Cl_2 at room temperature. The solution was then stirred for 1 h. Evaporation to dryness and extraction of the residue with pentane gave, after concentration of the extracts and cooling to –20 °C, **3a** as yellow crystals (80% yield; mass spectrum, m/z 455 (Cl 35)) and **3b** as pale yellow crystals (30% yield; mass spectrum, m/z 330 (Cl35)).

Anal. Calcd for $C_{16}H_{10}Cl_2FeP_2O_4$ (**3a**): C, 36.92; H, 2.19. Found: C, 36.68; H, 2.30. Calcd for $C_6H_6Cl_2FeP_2O_4$ (**3b**): C, 21.75; H, 1.81. Found: C, 21.52; H, 1.68.

Synthesis of 6a, 6b, and 9b. To 2 mmol of **1** dissolved in 20 mL of CH_2Cl_2 was added dropwise 1 mmol of $RPCl_2$ (R = Ph, Me) in 10 mL of CH_2Cl_2. The solution was stirred for 1 h and then evaporated to dryness. Extraction of the residue with diethyl ether gave a solution of **6a** or **6b** + **9b**. Evaporation of the ether and crystallization in methanol at –20 °C gave **6a** and **6b** as yellow crystals. In the case of complex **6b**, concentration of the mother solution in half and cooling to –20 °C afforded **9b** as pale yellow crystals, in 20% yield.

Anal. Calcd for $C_{48}H_{31}Fe_3P_3O_{12}$ (**6a**): C, 54.34; H, 2.92; Fe, 15.85; P, 8.77; Cl, 0. Found: C, 54.25; H, 2.78; Fe, 15.51; P, 8.76; Cl, 0.30. Anal. Calcd for $C_{38}H_{27}Fe_3P_3O_{12}$ (**6b**): C, 48.71; H, 2.88.

(15) Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. Organometallics **1982**, 5, 679.

Table VII. Atomic Coordinates with Esd's in Parentheses

	x	y	z	B_{eq}, Å^2
Fe(1)	3291 (1)	408 (1)	3975 (1)	6.93
Fe(2)	3534 (1)	−1316 (1)	2776 (1)	6.81
P(1)	3276 (1)	−35 (2)	2998 (1)	6.72
OP	2588 (3)	269 (4)	2472 (3)	8.98
CM	2380 (5)	1090 (6)	2422 (5)	9.80
C(1)	4436 (5)	−991 (6)	3047 (4)	8.05
C(2)	3030 (5)	−1167 (7)	1993 (4)	9.39
C(3)	3091 (5)	−1693 (6)	3316 (5)	9.85
C(4)	3994 (5)	−269 (6)	4285 (4)	7.73
C(5)	2392 (5)	71 (7)	3815 (4)	8.82
C(6)	3307 (6)	742 (6)	4759 (5)	9.36
C(7)	3488 (5)	1370 (6)	3724 (5)	7.82
C(8)	3826 (6)	−2249 (6)	2592 (5)	8.73
O(1)	5028 (3)	−797 (4)	3220 (3)	10.78
O(2)	2683 (4)	−1108 (5)	1483 (3)	12.74
O(3)	2796 (5)	−1984 (5)	3664 (4)	16.56
O(4)	4467 (4)	−699 (4)	4500 (3)	10.08
O(5)	1804 (3)	−133 (5)	3707 (3)	12.16
O(6)	3338 (5)	971 (5)	5250 (3)	13.88
O(7)	3624 (4)	2002 (4)	3566 (3)	9.93
O(8)	4044 (4)	−2859 (4)	2441 (4)	12.87
P(2)	324 (1)	1688 (1)	−609 (1)	5.70
C1A	464 (4)	2579 (6)	−1014 (5)	5.43
C2A	356 (4)	3329 (8)	−803 (4)	5.77
C3A	481 (5)	4009 (6)	−1125 (5)	6.79
C4A	715 (4)	3935 (7)	−1656 (5)	6.38
C5A	832 (5)	3184 (8)	−1878 (4)	7.59
C6A	723 (5)	2506 (6)	−1559 (5)	7.58
C1B	1153 (4)	1339 (5)	−111 (4)	5.55
C2B	1147 (5)	799 (6)	362 (5)	6.88
C3B	1773 (7)	478 (6)	731 (4)	7.60
C4B	2417 (6)	711 (6)	643 (5)	7.44
C5B	2442 (5)	1241 (7)	166 (5)	7.86
C6B	1813 (6)	1556 (5)	−214 (4)	6.58
C1C	−287 (5)	1869 (5)	−121 (4)	5.62
C2C	−978 (5)	1580 (5)	−297 (4)	7.36
C3C	−1430 (5)	1718 (7)	80 (6)	8.92
C4C	−1187 (7)	2131 (7)	629 (6)	9.59
C5C	−507 (7)	2427 (6)	817 (4)	9.08
C6C	−42 (5)	2289 (6)	449 (5)	7.34
C1D	−47 (5)	943 (6)	−1192 (4)	5.58
C2D	198 (4)	160 (7)	−1162 (4)	6.18
C3D	−128 (6)	−380 (6)	−1627 (6)	7.39
C4D	−675 (6)	−153 (7)	−2110 (5)	7.84
C5D	−942 (5)	628 (8)	−2150 (4)	7.12
C6D	−620 (5)	1185 (5)	−1690 (5)	6.98
HP	3760 (0)	320 (0)	2710 (0)	7.00
H1CM	1920 (0)	1330 (0)	2080 (0)	7.00
H2CM	2430 (0)	1410 (0)	2160 (0)	7.00
H3CM	2850 (0)	1460 (0)	2290 (0)	7.00
HC1A	150 (0)	3360 (0)	−349 (0)	7.00
HC3A	420 (0)	4580 (0)	−899 (0)	7.00
HC4A	810 (0)	4480 (0)	−1919 (0)	7.00
HC5A	1080 (0)	3090 (0)	−2589 (0)	7.00
HC6A	790 (0)	1870 (0)	−1719 (0)	7.00
HC2B	630 (0)	600 (0)	430 (0)	7.00
HC3B	1780 (0)	140 (0)	1130 (0)	7.00
HC4B	2940 (0)	430 (0)	950 (0)	7.00
HC5B	2970 (0)	1410 (0)	90 (0)	7.00
HC6B	1820 (0)	2020 (0)	−589 (0)	7.00
HC2C	−1169 (0)	1280 (0)	−759 (0)	7.00
HC3C	−1989 (0)	1370 (0)	−39 (0)	7.00
HC4C	−1579 (0)	2270 (0)	900 (0)	7.00
HC5C	−329 (0)	2790 (0)	1270 (0)	7.00
HC6C	480 (0)	2520 (0)	580 (0)	7.00
HC2D	600 (0)	−19 (0)	−769 (0)	7.00
HC3D	60 (0)	−1029 (0)	−1599 (0)	7.00
HC4D	−969 (0)	−569 (0)	−2509 (0)	7.00
HC5D	−1419 (0)	840 (0)	−2569 (0)	7.00
HC6D	−789 (0)	1820 (0)	−1729 (0)	7.00

Found: C, 48.56; H, 2.63. Anal. Calcd for $C_{33}H_{24}Fe_3P_2O_8$ (**9b**): C, 50.89; H, 3.08. Found: C, 50.72; H, 3.23.

Synthesis of 8. To 0.5 mmol of **5** in solution in CH_2Cl_2 was added 0.5 mmol of [NEt$_4$][HW(CO)$_5$]. The solution was stirred for 10 min and then evaporated to dryness. Crystallization in a minimum amount of CH_3OH gave **8** as yellow crystals in nearly quantitative yield.

Anal. Calcd for $C_{33}H_{31}Fe_2NP_2O_{13}W$: C, 39.32; H, 3.07; N, 1.39; P, 6.15; Fe, 11.12; W, 18.27. Found: C, 39.15; H, 2.98; N, 1.28; P, 6.18; Fe, 10.96; W, 18.21.

Synthesis of 13. To 1.5 mmol of $MePCl_2$ in dichloromethane (20 mL) was added 1 mmol of **1** in 10 mL of CH_2Cl_2. The solution was stirred at room temperature for half an hour and then evaporated to dryness. Extraction of the residue with pentane, concentration of the extract, and cooling to −20 °C gave **13** as pale yellow crystals (50% yield).

Anal. Calcd for $C_{10}H_9Cl_2Fe_2P_3O_7$: C, 23.21; H, 1.74. Found: C, 23.08; H, 1.82. Mass spectrum: m/z 517 (Cl 35).

Synthesis of 9c. To 2 mmol of **1** dissolved in 20 mL of CH_2Cl_2 was added dropwise 1 mmol of t-BuPCl$_2$ in 10 mL of CH_2Cl_2. The solution was stirred for 2 h and then evaporated to dryness. Extraction of the residue with diethyl ether gave **9c** as an oil (60%) contaminated by 5% of another anionic phosphorus complex not identified. Further purification of **9c** failed.

Synthesis of 9g. To 2 mmol of **1** dissolved in 20 mL of CH_2Cl_2 was added dropwise 1 mmol of (i-Pr)$_2$NPCl$_2$ in 10 mL of CH_2Cl_2. The solution was stirred for 2 h and then evaporated to dryness. Extraction of the residue with diethyl ether gave a mixture of compounds **9d**, **9e**, and **9f**. Treatment of this solution with 2 mL of methanol followed by evaporation of the solvent gave **9g** as a powder which was recrystallized from methanol as yellow crystals. The yields were variable ranging from 30 to 60%.

Anal. Calcd for $C_{29}H_{24}Fe_2O_8P_2$: C, 53.66; H, 3.25; P, 8.40; Fe, 15.77. Found: C, 53.31; H, 3.12; P, 8.55; Fe, 15.82.

X-ray Studies. Parallelepipedic crystals were obtained from methanol solution. Preliminary unit cell dimensions and monoclinic symmetry ($C2/c$) were determined by Weissenberg and precession photographs.

Cell parameters were refined by a least-squares fitting of the angular position of 25 reflections and are recorded with other crystal data in Table VI.

The intensities of 6773 reflections ($2° < \theta < 20°$) were collected on an automatic Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation. The intensity of three standard reflections was checked periodically, and no decrease was observed during data collection. The data were corrected for Lorentz and polarization factors and for anomalous dispersion of the iron and phosphorus atoms but not for absorption.

The structure was solved by multisolution techniques using SHELX package, allowing the location of iron and phosphorus atoms. Fourier synthesis leads to the position of the non-hydrogen atoms. The structure was refined by using the XFLSN program with anisotropic Fe, P, C, and O atoms.[16]

Refinement with 1949 reflections ($F_o > 2.56(F_o)$) reached the $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$ and $R = \sum|F_o - F_c|/\sum|F_o|$ values of 6.5% and 6.1%, respectively. At this stage of refinement, a Fourier difference map showed significant electronic density at the presumed hydrogen positions. They were introduced isotropically (B = 7 Å^2) in the refinement. Finally the R_w and R factors reached the values of 0.033 and 0.042. Final atomic parameters and thermal parameters are reported in Table VII.

Registry No. **1**, 103616-27-9; **2a**, 103501-06-0; **2b**, 103501-08-2; **2c**, 103501-07-1; **2d**, 103501-05-9; **3a**, 108121-84-2; **3b**, 108121-85-3; **5a**, 103501-09-3; **6a**, 103501-12-8; **6b**, 108121-87-5; **8**, 103533-07-9; **9b**, 108121-89-7; **9c**, 108121-97-7; **9d**, 108121-93-3; **9e**, 108121-94-4; **9f**, 108121-95-5; **9g**, 108121-91-1; **13**, 108121-92-2; [NEt$_4$][HW(CO)$_5$], 80907-47-7; dichlorophenylphosphine, 644-97-3; dichloromethylphosphine, 676-83-5; dichloro-*tert*-butylphosphine, 25979-07-1; (N,N-diisopropylamino)dichlorophosphine, 921-26-6.

Supplementary Material Available: A listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

(16) *International Tables for X-Ray Crystallography*; Kynoch: Birminghan, England, 1974; Vol. IV, pp 99–107.