

# Synthesis and reactivity of *P*-ferrocenylalkylidenephosphanes and related iminophosphanes and diphosphenes

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Received 26 March 1996; accepted 6 May 1996

## Abstract

*P*-Ferrocenyl-substituted alkylidenephosphanes have been prepared and characterized spectroscopically. Their ready conversion to the corresponding acylphosphanes and 1,2-diacylidiphosphanes, as well as a new type of phosphirene synthesis are presented. The X-ray structure of the tetraferrocenyl-substituted diacyldiphosphane has been investigated. Furthermore, *P*-ferrocenyl iminophosphanes and their complexation behaviour are described. Diferrocenyldiphosphene, which is known to be unstable, has been stabilized by complexation; this has been confirmed by NMR-spectroscopy and X-ray structure analysis.

**Keywords:** Alkylidenephosphane; Diphosphene; Iminophosphane; Ferrocene; Diphosphane; Acylphosphane

## 1. Introduction

The nature of the interaction between an electrophilic center and a ferrocenyl substituent is of particular interest, since the examples of such compounds reported so far show interesting physical and chemical properties [1,2]. In contrast to the stabilization of an electrophilic carbon center by the ferrocenyl moiety, which has been investigated extensively [3], considerably less information concerning ferrocenyl derivatives with an electrophilic phosphorus center is available. Cowley and coworkers reported the synthesis of some ferrocenyl-substituted phosphanylium ions [1] and, very recently, we described a ferrocenyl-diphosphene and its unusual dimerization behaviour [2].

In this paper we report the synthesis and reactivity of the first *P*-ferrocenyl-substituted alkylidenephosphanes. Further investigations were centered on the stabilization of the analogous iminophosphanes and diphosphenes by transition metal complexation.

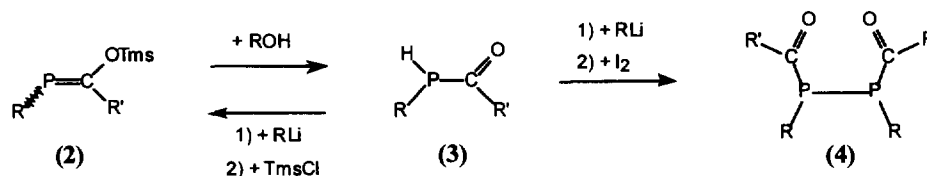
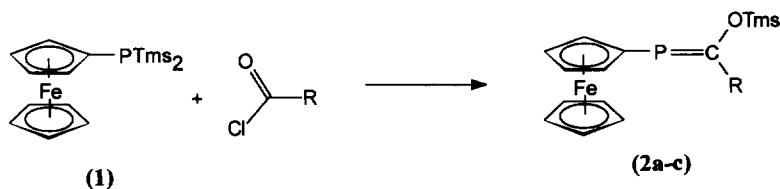
## 2. Results and discussion

Utilizing the convenient route to phosphalkenes by Becker [4], the *P*-ferrocenyl derivatives (**2a–c**) were obtained by treatment of the ferrocenylbis(trimethylsilyl)phosphane (**1**) with acylchlorides in toluene solution (Scheme 1). (The synthetic scope of the reaction of (**1**) with acid chlorides seems to be merely limited by the carbonyl activity of the latter, as in the case of carbonylchloride, where no reaction occurs over a period of 3 weeks at ambient temperature.) In the same manner, compounds which exhibit a ferrocenyl group merely at the carbon atom (**2d–f**) were also synthesized. *C*-ferrocenyl-substituted alkylidenephosphanes were previously reported by Roesky and coworkers [5] and Schrock and coworkers [6].

The compounds (**2a–f**) were isolated by removing the solvent and the formed chlorosilane under vacuum as viscous oils, of which (**2a**) was further purified by distillation in vacuum.

While stable in the absence of air and moisture, the alkylidenephosphanes (**2a–f**) easily react with alcohols, forming the acylphosphanes (**3a–f**) via proton shift from the oxygen to the phosphorus atom. Metallation of

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(3) with *n*-butyllithium and subsequent treatment with trimethylchlorosilane affords the initial acylidene phosphanes (2). Oxidation of the lithiated acyl phosphanes (3a–d) by metallation and subsequent addition of iodine furnishes the ferrocenyl-substituted diacyclodiphosphanes (4a–d) (Scheme 2).

Identification of compounds (2,3,4) is based on mass- and NMR-spectroscopic investigations. A selection of characteristic <sup>31</sup>P NMR data is listed in Table 1.

As apparent from Table 1, the chemical shifts lie in the high field region of acylidene phosphanes, which is expected as a consequence of the donating properties of the siloxy substituent [7]. The <sup>31</sup>P NMR data of the acyl phosphanes and diphosphanes show no peculiarities.

Considering the complexation potential of the ferrocenyl-substituted diphosphanes (4) towards metal cations, the structure of the 1,2-diferrocenoyl-1,2-diferrocenyl-diphosphane (4c) is of particular interest. (An investigation of the electrochemical properties depending on the presence of metal cations is currently in progress.)

Crystals of (4c) suitable for an X-ray structure deter-

mination were grown slowly over a period of 2 weeks at ambient temperature, and the molecular structure was verified to be 1,2-diferrocenoyl-1,2-diferrocenyl-diphosphane (4c). The X-ray structure analysis of (4c) is illustrated in Fig. 1, and the pertinent metrical parameters are listed in the Table 2. The molecule exhibits C<sub>2</sub> symmetry and the two chiral phosphorus atoms adopt the same absolute configuration. The substituents at the diphosphane unit exhibit a nearly staggered conformation ( $\angle C(1)P(1)P(1a)C(1a) = 63.7(1)^\circ$ ) which minimizes the mutual steric interactions. The P–C(Fc) bond distance (181.8(3) pm) is slightly shortened with respect to a normal single bond, which might be interpreted as dative interaction. In accord with the concept of negative hyperconjugation [8] the P–C(21) (186.9(3) pm) and the P–P (223.7(2) pm) bond lengths are slightly longer than in (<sup>t</sup>BuCO)PhPP(<sup>t</sup>BuCO)Ph [9]. Both Cp-rings adopt an eclipsed orientation. The average Fe–C distances between the metal and the substituted cyclopentadienyls are markedly shorter than those between Fe and the C<sub>5</sub>H<sub>5</sub> moieties. This feature can be rationalized as a consequence of the dative interaction of the Cp-rings with the phosphorus atoms, which re-

Table 1  
<sup>31</sup>P NMR values for (2), (3) and (4)

Compound	R, R'	(2)	(3)		(4)
		( <sup>31</sup> P)	( <sup>31</sup> P)	<sup>1</sup> J <sub>PH</sub>	( <sup>31</sup> P)
a	Fc, <sup>t</sup> Bu	119.2	–57.9	230.2	7.3
b	Fc, Ph		–45.6	235.6	13.3
	(Z)-Isomer	137.7			
	(E)-Isomer	138.5			
c	Fc, Fc		–48.9	230.5	17.0
	(Z)-Isomer	121.0			
	(E)-Isomer	122.1			
d	Ph, Fc		–33.7	224.8	7.7
	(Z)-Isomer	134.0			
	(E)-Isomer	140.9			
e	Mes <sup>+</sup> , Fc	145.5	–43.1	234.5	
f	N <sup>1</sup> Pr <sub>2</sub> , Fc	196.4	3.1	230.5	

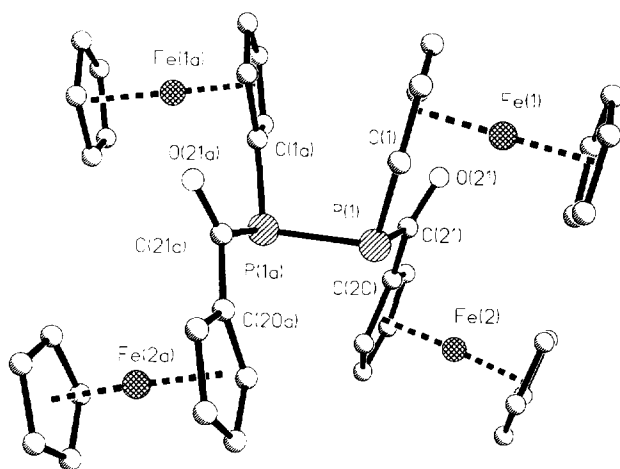


Fig. 1. Crystal structure of (4c).

Table 2  
Selected bond lengths (pm) and angles (deg) for (4c)

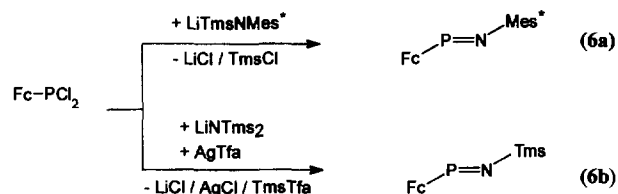
P(1)–P(1a)	223.7(2)	PCp–Fe	164.6(2)
P(1)–C(1)	181.8(3)	Cp–Fe	165.2(2)
P(1)–C(21)	186.9(3)	COCP–Fe	163.2(2)
C(20)–C(21)	147.3(4)	Cp–Fe	164.2(2)
C(21)–O(21)	120.5(4)	C(1)P(1)P(1a)C(1a)	63.7(1)
Fc–P–P	104.5(1)	P–CO–Fc	114.5(2)
Fc–P–CO	104.3(2)	P–C=O	122.8(2)
P–P–CO	95.5(1)	Fc–C=O	122.7(3)
Σ(P)	304.3	Σ(C21)	360.0

sults also in an electron transfer from the iron atoms towards these Cp-rings [10].

Addition of the carbenoid  $\text{Tms}_2\text{CClLi}$  to (2a) does not produce the expected phosphirane (5a) but rather the ferrocenylphosphirene (5b) (Scheme 3). Owing to the  $\pi$ -donation effect of the siloxy group in the methylenephosphane, a bis(methylene)phosphorane intermediate (5a') seems to be less stable, but undergoes subsequent ring closure to (5a). Subsequent elimination of siloxane from this intermediate then affords the 1*H*-phosphirene (5b) as the final product. The constitution of (5b) was confirmed by its characteristic NMR data ( $d(^{31}\text{P})$  –204.5;  $d(^{13}\text{C})$  157.9, 116.4;  $^1J_{\text{CP}} = 61.4$ , 48.4 Hz). It should be mentioned that the transformation of phosphiranes to phosphirenes via an elimination reaction has been observed previously [11].

### 3. Ferrocenyl-substituted iminophosphane and -diphosphene complexes

Following common procedures, the iminophosphanes (6a) and (6b) were generated by reaction of etheric solutions of the ferrocenyl dichlorophosphane with

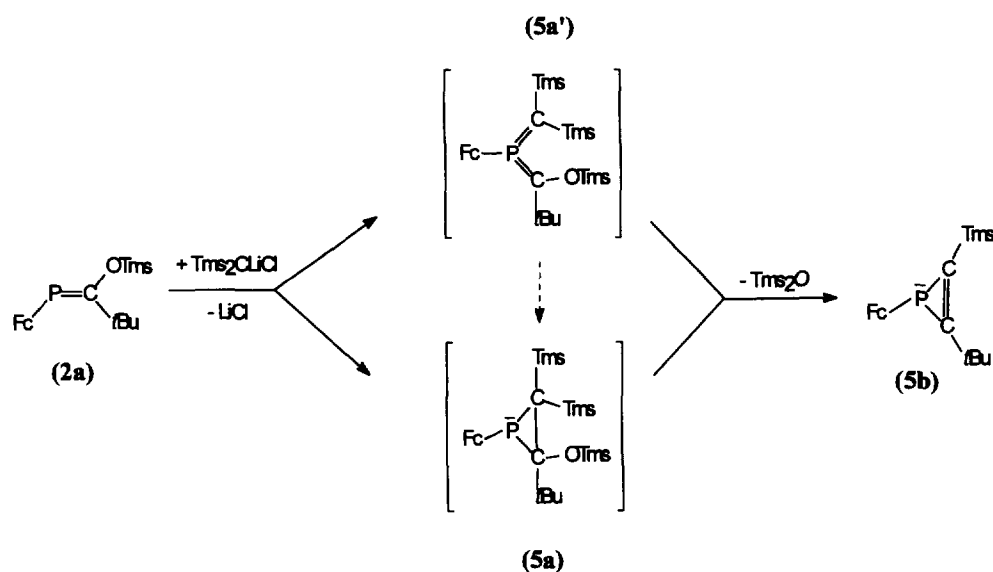


Scheme 4. Formation of  $\text{Fc-P=N-Mes}^+$  (6a) and  $\text{Fc-P=N-Tms}$  (6b).

trimethylsilylamides at  $-78^\circ\text{C}$  (Scheme 4). The selective formation of the products was confirmed by the  $^{31}\text{P}$  NMR spectra which showed downfield shifts ( $d$  400.5 (6a); 466.0 (6b)), which lie in the characteristic range of *P*-aryl-substituted derivatives [12]. Attempts to isolate these compounds (by filtration of lithium amide and evaporation of the solvent) resulted in decomposition, to further not well-characterized products. The lower stability may be attributed to an enhanced polarity of the  $\text{P=N}$  bond in (6a) compared with  $\text{Ph-P=N-Mes}^+$  [13], in which the steric demand of the *P*-substituent is comparable with (6a).

Even if free (6a) was too unstable to be isolated, it could be trapped by reaction with  $\text{C}_2\text{H}_4\text{Pt}(\text{PPh}_3)_2$ , to give the thermally stable  $\sigma$ -complex (7), which could be isolated as a dark red-brown microcrystalline solid. The presence of a single iminophosphane ligand is readily deduced from the  $\text{AX}_2$  pattern in the  $^{31}\text{P}$  NMR spectrum. The large values of  $^2J_{\text{PP}}$  (185.5 Hz) and  $^1J_{\text{PPt}}$  (5763 Hz) and a rather small coordination shift ( $\Delta\delta = 72.6$  ppm) reveal an 'end-on' coordination of the iminophosphane fragment to the transition metal [14].

The  $\eta^1$ -coordination mode of the iminophosphane ligand in the complex (7) differs from the  $\eta^2$ -coordination of the diphosphene in the related complex,  $[(\text{Ph}_3\text{P})_2\text{PtFc-P=P-Mes}^+]$  [2].



Scheme 3. Formation of (5).

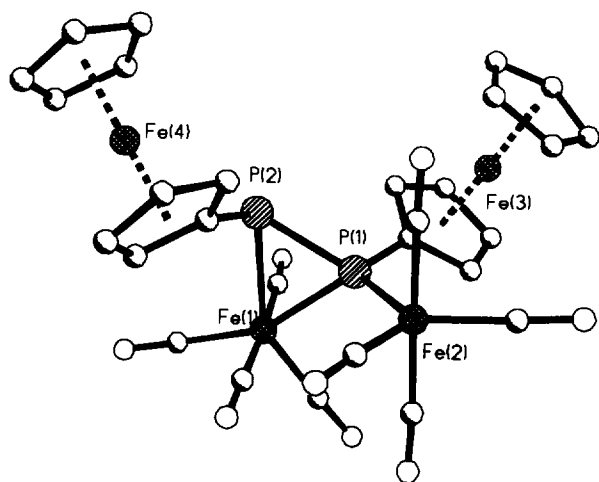


Fig. 2. Crystal structure of (8).

A compound showing a ferrocenyl-substituted diphosphine ligand which displays both  $\eta^1$ - and  $\eta^2$ -coordination to the metal was verified by treatment of  $\text{FcPCl}_2$  with Collman's reagent, which furnishes the  $\eta^1$ ,  $\eta^2$ -ligated diphosphine complex (8). Preliminary identification of (8) was based on NMR spectroscopic observations, the shielded resonances of two phosphorus atoms ( $\delta$  30.3,  $-36.1$ ;  $^1J_{\text{PP}} = 424.5$  Hz) clearly indicating the side-on coordination of the unsymmetrical  $\text{P}_2$ -unit.

The constitution of (8) was further confirmed by a X-ray crystal structure analysis, for which suitable (red colored) crystals had been obtained via crystallization from a toluene solution at  $-30^\circ\text{C}$ . The molecular structure, shown in Fig. 2, confirmed the presence of an  $\eta^1$ - and  $\eta^2$ - $\text{Fe}(\text{CO})_4$ , at a *trans*-diphosphene. The P–P bond length (214.2(2) pm, Table 3) is comparable with those found in the analogous diphenyl complex [15]. The terminally bonded iron tetracarbonyl moiety exhibits a distorted trigonal bipyramidal arrangement with the phosphorus atom in equatorial position. This is in contrast to the analogous diphenyldiphosphene complex ( $\eta^1, \eta^2$ - $(\text{PhP})_2(\text{Fe}(\text{CO})_4)_2$ ), in which this phosphorus atom is coordinated as an axial ligand. Further bond lengths and angles show no particularities.

Table 3  
Selected bond lengths (pm) and angles (deg) for (8)

P(1)–P(2)	214.2(2)	PCp–Fe(3)	163.7(2)
P(1)–C(11)	180.5(6)	Fe(3)–Cp	165.0(2)
P(2)–C(31)	182.0(6)		
P(1)–Fe(2)	225.9(2)	PCp–Fe(4)	163.6(2)
P(1)–Fe(1)	238.4(2)	Fe(4)–Cp	165.4(2)
P(2)–Fe(1)	241.1(3)		
P(1)–P(2)–C(31)	104.8(2)	Fe(2)–P(1)–P(2)	129.3(1)
C(11)–P(1)–P(2)	105.4(2)	P(1)–P(2)–Fe(1)	62.8(1)
P(1)–Fe(1)–P(2)	53.1(1)		

## 4. Experimental

### 4.1. General

All experiments were carried out under a dry argon atmosphere using common Schlenk techniques. Solvents were dried and freshly distilled from Na–K alloy before use. NMR spectra were recorded on a Bruker AMX 300:  $^{31}\text{P}$  NMR spectra at 121.5 MHz using 85%  $\text{H}_3\text{PO}_4$  as external standard;  $^1\text{H}$  NMR spectra at 300 MHz, and  $^{13}\text{C}$  NMR spectra at 75.5 MHz, with tetramethylsilane as external standard;  $^{195}\text{Pt}$  NMR spectra at 64.2 MHz with reference to aqueous  $\text{PtCl}_6^{2-}$ .

### 4.2. X-ray crystallographic studies of 4c and 8

The structures were solved by direct methods (SHELXTL-PLUS). The non-hydrogen atoms were refined anisotropically on  $F^2$  (SHELXL-93). H atoms were refined isotropically using a riding model. An absorption correction on the basis of  $\psi$ -scans were applied (4c:  $T_{\text{max./min.}} = 0.880/0.795$ ; 8:  $T_{\text{max./min.}} = 0.984/0.838$ ). Further details are given in Table 4. Atomic coordinates and equivalent isotropic displacement parameters are given in Tables 5 and 6 respectively [16].

### 4.3. Ferrocenylbistrimethylsilylphosphane (1)

A solution of 1.31 g (6 mmol)  $\text{FcPH}_2$  in 40 ml DME was cooled to  $0^\circ\text{C}$  and treated with 8.25 ml (13.2 mmol)

Table 4  
Crystallographic data and summary of data collection and refinement

	4c	8
Formula	$\text{C}_{42}\text{H}_{36}\text{Fe}_4\text{O}_2\text{P}_2 \cdot 2$ toluene	$\text{C}_{28}\text{H}_{18}\text{Fe}_4\text{O}_8\text{P}_2$
Formula weight	1042.3	767.8
Crystal system	monoclinic	monoclinic
Space group	$C2/c$ (no.15)	$P2_1/c$ (no.14)
<i>a</i> (Å)	19.782(8)	15.499(12)
<i>b</i> (Å)	8.886(3)	11.275(10)
<i>c</i> (Å)	26.255(12)	17.123(10)
$\beta$ (deg)	90.12(3)	101.31(5)
<i>V</i> (Å <sup>3</sup> )	4615(3)	2934(4)
<i>Z</i>	4	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.50	1.74
$\mu$	1.35	2.10
Diffractionmeter	Nicolet R3m	Nicolet R3m
Radiation	Mo K $\alpha$	Mo K $\alpha$
$\lambda$ (Å)	0.71073	0.71073
<i>T</i> (K)	293	293
Max $2\theta$ (deg)	50	45
No. of data	9162	4034
No. of unique data	4069	3867
Parameters	289	379
<i>R</i> ( <i>F</i> ) for $I > 2\sigma(I)$	0.040	0.042
<i>wR</i> 2( $F^2$ ) for all data	0.113	0.093

of a solution of *n*-butyllithium in hexane. While stirring for 2 h, the reaction mixture was warmed to ambient temperature. The resulting deep red solution was treated with an excess of freshly distilled, argon-flushed TmsCl (1.5 ml) at 0 °C. After stirring for further 2 h and warming to room temperature, the volatiles were removed in vacuum and the residue extracted twice with 15 ml of toluene. After separation of the solids and removal of the solvent, (1) is obtained as a viscous orange oil (2.13 g, 98%). <sup>31</sup>P NMR (toluene): -167.0 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): Cp', 5H, 4.19 (s); H<sub>α/β</sub>, 4H, 4.16 (m); Tms, 18 H, 0.38 (d, <sup>3</sup>J<sub>HP</sub> = 4.4 Hz). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): C<sub>ipso</sub> 76.23 (d, <sup>1</sup>J<sub>CP</sub> = 14.1 Hz); C<sub>α</sub> 73.72 (d, <sup>2</sup>J<sub>CP</sub> = 8.8 Hz); Cp, 70.27 (s); C<sub>β</sub> 69.59 (d, <sup>3</sup>J<sub>CP</sub> = 2.7 Hz); Tms 2.35 (d, <sup>2</sup>J<sub>CP</sub> = 12.2 Hz). Mass spectrum (70 eV): 362.0751 (found), 362.0738 (calc.), M<sup>+</sup> (40%); 290, FcPHTms<sup>+</sup> (55%); 218, FcPH<sub>2</sub><sup>+</sup> (21%); 121, CpFe<sup>+</sup> (35%); 73, Tms<sup>+</sup> (100%).

#### 4.4. Methylene phosphanes (2)

2 mmol of the carboxylic acid chloride were dissolved in 15 ml of toluene. This solution was treated

Table 5  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters for (4c)

	x	y	z	U <sub>eq</sub>
Fe(1)	5423(1)	2959(1)	3818(1)	53(1)
C(1)	5320(2)	3758(4)	3097(1)	52(1)
C(2)	6012(2)	3572(4)	3224(1)	64(1)
C(3)	6118(2)	2047(5)	3337(1)	72(1)
C(4)	5507(2)	1289(4)	3289(1)	66(1)
C(5)	5005(2)	2321(4)	3138(1)	58(1)
C(6)	5034(2)	4491(5)	4316(1)	81(1)
C(7)	4680(2)	3130(6)	4350(2)	89(1)
C(8)	5142(3)	1997(5)	4491(1)	89(1)
C(9)	5779(3)	2670(5)	4543(1)	86(1)
C(10)	5716(2)	4220(5)	4430(1)	79(1)
Fe(2)	3367(1)	8425(1)	3347(1)	54(1)
C(11)	3609(3)	7839(6)	4067(2)	92(1)
C(12)	3934(2)	9179(7)	3934(2)	103(2)
C(13)	3440(3)	10233(5)	3815(2)	97(1)
C(14)	2818(2)	9567(5)	3870(2)	83(1)
C(15)	2910(2)	8092(5)	4031(1)	80(1)
C(16)	2979(2)	6929(4)	2842(1)	62(1)
C(17)	2803(2)	8395(5)	2697(1)	73(1)
C(18)	3396(2)	9244(5)	2627(1)	73(1)
C(19)	3953(2)	8290(4)	2717(1)	66(1)
C(20)	3695(2)	6830(4)	2854(1)	56(1)
P(1)	5008(1)	5615(1)	2926(1)	50(1)
C(21)	4071(2)	5468(4)	3002(1)	54(1)
O(21)	3797(1)	4354(3)	3164(1)	76(1)
C(1T)	7400(3)	-1185(5)	4005(2)	100(2)
C(2T)	6905(5)	-1820(7)	3677(2)	147(3)
C(3T)	6247(5)	-2074(6)	3889(3)	134(3)
C(4T)	6135(4)	-1690(6)	4366(3)	127(2)
C(5T)	6603(3)	-1116(6)	4664(2)	102(2)
C(6T)	7231(2)	-888(5)	4488(2)	83(1)
C(7T)	7742(3)	-251(7)	4838(2)	148(3)

Table 6  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters for (8)

	x	y	z	U <sub>eq</sub>
Fe(1)	8878(1)	334(1)	7466(1)	56(1)
Fe(2)	7896(1)	702(1)	5080(1)	53(1)
Fe(3)	7299(1)	-3124(1)	5545(1)	51(1)
Fe(4)	5816(1)	2254(1)	7427(1)	47(1)
P(1)	7952(1)	-256(1)	6247(1)	43(1)
P(2)	7297(1)	154(2)	7205(1)	49(1)
C(1)	7764(4)	2243(7)	5081(4)	74(2)
C(2)	6721(5)	477(6)	4867(4)	58(2)
C(3)	9073(5)	922(6)	5274(4)	65(2)
C(4)	7943(5)	-135(7)	4197(5)	74(2)
C(5)	8872(4)	-1079(7)	7953(4)	73(2)
C(6)	9107(5)	1010(7)	8442(5)	81(2)
C(7)	9900(5)	-71(7)	7159(4)	70(2)
C(8)	8878(4)	1797(7)	7024(4)	64(2)
O(1)	7702(4)	3273(5)	5059(4)	127(2)
O(2)	5984(3)	334(5)	4704(3)	80(2)
O(3)	9804(3)	1134(5)	5407(3)	94(2)
O(4)	7937(4)	-630(6)	3618(3)	112(2)
O(5)	8893(4)	-1934(6)	8311(3)	110(2)
O(6)	9241(4)	1438(6)	9054(4)	131(3)
O(7)	10515(3)	-366(5)	6969(3)	101(2)
O(8)	8927(3)	2720(5)	6776(3)	89(2)
C(11)	8023(3)	-1854(5)	6232(3)	41(1)
C(12)	8557(4)	-2491(5)	5781(4)	54(2)
C(13)	8546(4)	-3695(6)	5972(5)	74(2)
C(14)	8017(5)	-3826(6)	6550(4)	70(2)
C(15)	7690(4)	-2708(6)	6709(4)	61(2)
C(21)	6631(8)	-2677(11)	4451(5)	123(5)
C(22)	6873(6)	-3909(9)	4478(5)	95(3)
C(23)	6475(5)	-4444(6)	5043(5)	77(2)
C(24)	5999(5)	-3615(8)	5361(5)	90(3)
C(25)	6098(6)	-2567(8)	5009(7)	113(4)
C(31)	6871(4)	1648(5)	6993(4)	50(2)
C(32)	6152(4)	1968(6)	6353(4)	63(2)
C(33)	5949(5)	3185(6)	6450(5)	71(2)
C(34)	6527(4)	3630(6)	7107(5)	69(2)
C(35)	7098(4)	2694(6)	7457(4)	63(2)
C(41)	4532(4)	2465(6)	7546(4)	59(2)
C(42)	5102(4)	2849(6)	8226(4)	60(2)
C(43)	5644(4)	1913(7)	8555(4)	69(2)
C(44)	5404(5)	920(6)	8060(5)	71(2)
C(45)	4717(4)	1257(6)	7439(4)	61(2)

with 2 mmol of pure bis(trimethylsilyl)phosphane (1) at ambient temperature. After stirring for 24 h, the volatiles were removed and spectroscopically pure (2) remained in almost quantitative yield.

#### 4.5. 1-Ferrocenyl-2-trimethylsiloxy-2-*t*-butylphosphathene (2a)

<sup>31</sup>P NMR: 119.2 (s); <sup>1</sup>H NMR: H<sub>α</sub> 4.96 (m, 2H); H<sub>β</sub> 4.35 (m, 2H); Cp 4.19 (s, 5H); <sup>1</sup>Bu 1.38 (s, 9H); Tms 0.10 (s, 9H). <sup>13</sup>C NMR: P=C-O 216.5 (d, <sup>1</sup>J<sub>CP</sub> = 74.4 Hz); C<sub>β</sub> 74.7 (d, <sup>3</sup>J<sub>CP</sub> = 5.7 Hz); C<sub>ipso</sub> 73.8 (d, <sup>1</sup>J<sub>CP</sub> = 18.3 Hz); Cp 70.9 (d, <sup>3</sup>J<sub>CP</sub> = 1.9 Hz); C<sub>α</sub> 70.7 (d, <sup>2</sup>J<sub>CP</sub> = 1.2 Hz); 43.2 (d, <sup>2</sup>J<sub>CP</sub> = 24.4 Hz); C(CH<sub>3</sub>)<sub>3</sub> 30.0

(d,  $^3J_{CP} = 14.9$  Hz); Si(CH<sub>3</sub>)<sub>3</sub> 1.6 (s); C(CH<sub>3</sub>)<sub>3</sub>. Mass spectrum (70 eV, EI): 374.0922 (found), 374.0918 (calc.) M<sup>+</sup> (85%); 289, M<sup>+</sup> – BuCO (100%); 216, FcPH<sup>+</sup> (58%); 73, Tms<sup>+</sup> (43%).

#### 4.6. 1-Ferrocenyl-2-trimethylsiloxy-2-phenylphosphathene (2b)

<sup>31</sup>P NMR: 137.7 (s) Z-isomer, 138.5 (s) E-isomer; (Z/E) = 20/1. <sup>1</sup>H NMR: Ph 8.00–8.04 (m) 5H; H<sub>β</sub> 4.67 (m) 2H; H<sub>α</sub> 4.31 (m) 2H; Cp' 4.10 (s) 5H; Tms 0.09 (s) 9H. <sup>13</sup>C NMR: P=C–O 196.9 (d,  $^1J_{CP} = 53.0$  Hz); C<sub>ipso</sub>(Ph) 140.8 (d,  $^2J_{CP} = 37.0$  Hz); C<sub>4</sub> 133.8 (d,  $^5J_{CP} = 1.5$  Hz); C<sub>3/3'</sub> 128.0 (d,  $^4J_{CP} = 6.5$  Hz); C<sub>2/2'</sub> 125.4 (d,  $^3J_{CP} = 19.1$  Hz); C<sub>ipso</sub>(Fc) 76.4 (d,  $^1J_{CP} = 39.3$  Hz); C<sub>α</sub> 74.1 (d,  $^2J_{CP} = 9.6$  Hz); C<sub>β</sub> 71.2 (d,  $^3J_{CP} = 2.5$  Hz); Cp' 70.2 (d,  $^3J_{CP} = 1.3$  Hz); Si(CH<sub>3</sub>)<sub>3</sub> 1.0 (s). Mass spectrum (70 eV, EI): 394.0605 (found), 394.0605 (calc.) M<sup>+</sup> (15%); 217, FcPH<sup>+</sup> (100%); 121, CpFe<sup>+</sup> (45%); 105, PhCO<sup>+</sup> (46%); 73, Tms<sup>+</sup> (48%).

#### 4.7. 1,2-Diferrocenyl-2-trimethylsiloxyphosphathene (2c)

<sup>31</sup>P NMR: 121.1 (s) Z-isomer, 122.1 (s) E-isomer, (Z/E) = 12/1. <sup>1</sup>H NMR: H<sub>α</sub> 4.90/4.59 (m, 2 × 2H); H<sub>β</sub> 4.22 (m, 2 × 2H); Cp' 4.12/4.15 (s, 2 × 5H); Tms 0.18 (s, 9H). <sup>13</sup>C NMR: P=C–O 209.6 (d,  $^1J_{CP} = 31.3$  Hz); C<sub>ipso</sub> 84.9 (d,  $^1J_{CP} = 44.6$  Hz)/77.3 (d,  $^1J_{CP} = 31.3$  Hz); C<sub>α/β</sub> 75.8–71.3 (d); Cp' 71.1 (s)/70.0 (s); Si(CH<sub>3</sub>)<sub>3</sub> 1.77 (s). Mass spectrum: 502.0285 (found), 502.0268 (calc.) M<sup>+</sup> (2%); 430, M<sup>+</sup> – SiC<sub>3</sub>H<sub>8</sub> (12%); 213, FcCO<sup>+</sup> (100%).

#### 4.8. 1-Phenyl-2-trimethylsiloxy-2-ferrocenylphosphathene (2d)

<sup>31</sup>P NMR: 134.0 (s) Z-isomer, 140.9 (s) E-isomer, (Z/E) = 5/1. <sup>1</sup>H NMR: Ph 7.14–7.81 (m); H<sub>β</sub> 4.93 (m); Cp' 4.24 (s); H<sub>α</sub> 4.13 (m); Tms 0.04 (s). <sup>13</sup>C NMR: P=C–O 202.9 (d,  $^1J_{CP} = 58.3$  Hz); C<sub>ipso</sub>(Ph) 140.5 (d,  $^1J_{CP} = 38.5$  Hz); C<sub>2/2'</sub> 135.3 (d,  $^2J_{CP} = 10.7$  Hz); C<sub>3/3'</sub> 135.0 (d,  $^3J_{CP} = 11.8$  Hz); C<sub>4</sub> 129.1 (d,  $^4J_{CP} = 4.2$  Hz); C<sub>ipso</sub>(Fc) 88.0 (d,  $^2J_{CP} = 37$  Hz); Cp' 71.46 (s); C<sub>α</sub> 70.5 (d,  $^3J_{CP} = 1.9$  Hz); C<sub>β</sub> 70.4 (s); Si(CH<sub>3</sub>)<sub>3</sub> 0.63 (s). Mass spectrum (70 eV, EI): 394, M<sup>+</sup> (100%); 213, FcCO<sup>+</sup> (55%); 73, Tms<sup>+</sup> (89%).

#### 4.9. 1-Tri(*t*-butyl)phenyl-2-trimethylsiloxy-2-ferrocenylphosphathene (2e)

<sup>31</sup>P NMR: 145.5 (s); <sup>1</sup>H NMR: H<sub>meta</sub> 7.47 2H; Cp' 4.11 5H; H<sub>α</sub> 3.97 2H; H<sub>β</sub> 3.44 2H; <sup>t</sup>Bu<sub>ortho</sub> 1.62 18H; <sup>t</sup>Bu<sub>para</sub> 1.47 9H; Tms 0.63 9H. <sup>13</sup>C NMR: P=C–O 195.89 (d,  $^1J_{CP} = 45$  Hz); C<sub>2/2'</sub> 156.14 (d,  $^2J_{CP} = 2.2$  Hz); C<sub>4</sub> 150.7 (s); C<sub>ipso</sub>(Mes<sup>+</sup>) 133.95 (d,  $^1J_{CP} =$

53.8 Hz); C<sub>3/3'</sub> 129.14 (d,  $^3J_{CP} = 59.9$  Hz); C<sub>ipso</sub>(Fc) 87.07 (d,  $^1J_{CP} = 12.6$  Hz); Cp' 69.50 (s); C<sub>α</sub> 68.75 (s); C<sub>β</sub> 68.22 (d,  $^3J_{CP} = 2.3$  Hz); C(CH<sub>3</sub>)<sub>3ortho</sub> 38.63 (s); C(CH<sub>3</sub>)<sub>3ortho</sub> 33.38 (d,  $^4J_{CP} = 7.3$  Hz); C(CH<sub>3</sub>)<sub>3para</sub> 35.49 (s); C(CH<sub>3</sub>)<sub>3para</sub> 32.03 (s); Si(CH<sub>3</sub>)<sub>3</sub> 1.59 (d,  $^4J_{CP} = 6.9$  Hz). Mass spectrum (70 eV, EI): 562, M<sup>+</sup> (70%); 213, FcCO<sup>+</sup> (96.7%); 73, Tms<sup>+</sup> (100%); 57, <sup>t</sup>Bu<sup>+</sup> (92%).

#### 4.10. Diacyldiphosphanes (4)

2 mmol of the corresponding methylenephosphane (2) dissolved in 5 ml toluene were treated with 0.05 ml degassed and argon-flushed ethanol at room temperature. This mixture was stirred for 2 h and the volatiles removed in vacuum. The residual (3) was redissolved in 10 ml of DME and cooled to –78 °C. On adding 1.38 ml (2.2 mmol) of *n*-butyllithium in hexane solution, the mixture turned dark red. After stirring for 1 h at this temperature, a solution of 0.28 g (1.1 mmol) iodine dissolved in 5 ml DME was added slowly. Warming to ambient temperature, and removal of the solvents yielded, after extraction of the residue with toluene and subsequent separation of the solids, a toluene solution of (4), from which the products separated slowly on addition of an equal amount of pentane.

#### 4.11. 1,2-Dipivaloyl-1,2-diferrocenyldiphosphane (4a)

<sup>31</sup>P NMR: 7.3 (s). <sup>1</sup>H NMR: 4.2 (m). <sup>13</sup>C NMR: 74.6–68.7 (m). Mass spectra (70 eV, EI): 602 M<sup>+</sup> (2%); 517, M<sup>+</sup> – <sup>t</sup>BuCO (1.5%); 301, M<sup>+</sup>/2 (54.8%); 217, FcPH<sup>+</sup> (100%); 57, <sup>t</sup>Bu (82.1%).

#### 4.12. 1,2-Diferrocenyl-1,2-diferrocenyldiphosphane (4c)

<sup>31</sup>P NMR: 17.0 (s). Mass spectrum (FAB): 858, M<sup>+</sup> (1%); 429, M<sup>+</sup>/2 (10%); 401, M<sup>+</sup>/2 – CO (28%); 213, FcCO<sup>+</sup> (15%); 136, (100%). <sup>1</sup>H NMR: H<sub>α/β</sub> 4.28 (m) 8H; Cp' 4.08 (s) 10H; <sup>t</sup>Bu 1.22 (s) 18H. <sup>13</sup>C NMR: C<sub>q</sub> 224.0 (d,  $^1J_{CP} = 46.2$  Hz); C<sub>α</sub> 75.8 (d,  $^2J_{CP} = 16.9$  Hz); C<sub>β</sub> 71.5 ( $^3J_{CP} = 4.9$  Hz); Cp' 70.1 (s); <sup>t</sup>Bu<sub>q</sub> 50.0 ( $^1J_{CP} = 31.6$  Hz); <sup>t</sup>Bu 27.1 ( $^2J_{CP} = 4.9$  Hz).

#### 4.13. 1-Ferrocenyl-2-trimethylsilyl-3-*t*-butyl phosphirene (5b)

<sup>31</sup>P NMR: 204.5 (s). <sup>1</sup>H NMR: H<sub>β</sub> 4.93 (m); H<sub>α</sub> 4.13 (m); Cp' 4.10 (s); <sup>t</sup>Bu 1.16 (s); Tms 0.04 (s). <sup>13</sup>C NMR: C<sub>qa</sub> 157.93 (d,  $^1J_{CP} = 61.4$  Hz); C<sub>qb</sub> 116.40 (d,  $^1J_{CP} = 48.4$  Hz); C<sub>ipso</sub>(Fc) 86.05 (d,  $^1J_{CP} = 75.9$  Hz); C<sub>α</sub> 77.08 (d,  $^2J_{CP} = 30.9$  Hz); C<sub>β</sub> 71.85 (d,  $^3J_{CP} = 15.2$  Hz); Cp' 69.83 (s); <sup>t</sup>Bu<sub>q</sub> 34.65 (d,  $^2J_{CP} = 8.0$  Hz); <sup>t</sup>Bu 30.04 (s); Si(CH<sub>3</sub>)<sub>3</sub> 0.63 (s). Mass spectrum (70 eV, EI): 370.0990 (found), 370.1011 (calc.), M<sup>+</sup> (6.6%); 216, FcPH<sup>+</sup> (100%); 73, Tms<sup>+</sup> (33%).

#### 4.14. $\mu_2$ -( $\eta^1\eta^2$ )Diferrocenyldiphosphenebis[tetra-carbonyliron] (8)

0.64 g (3 mmol)  $\text{Na}_2\text{Fe}(\text{CO})_4$ , suspended in 30 ml toluene were treated at  $-78^\circ\text{C}$  with 0.86 g (3 mmol)  $\text{FcPCL}_2$  dissolved in 10 ml of toluene. After warming slowly to room temperatures the solids were removed by filtration. Crystallisation at  $-30^\circ\text{C}$  afforded (8) as dark red crystals, which were recrystallized from toluene (yield: 0.4 g (0.5 mmol, 34.7%).  $^{31}\text{P}$  NMR:  $\text{P}_A$ , 30.3 (d,  $^1J_{\text{PP}} = 424.5$  Hz);  $\text{P}_X$ ,  $-36.1$  (d,  $^1J_{\text{PP}} = 424.5$  Hz).  $^1\text{H}$  NMR:  $\text{H}_\alpha^b$  4.53 (m);  $\text{Cp}^a$  4.38 (s);  $\text{H}_\beta^b$  4.36 (m);  $\text{Cp}^b$  4.29 (s);  $\text{H}_\alpha^a$  4.24 (m);  $\text{H}_\beta^a$  4.14 (m). Mass spectrum (FAB): 768,  $\text{M}^+$  (5%); 740,  $\text{M}^+ - \text{CO}$  (17%); 712,  $\text{M}^+ - 2\text{CO}$  (12%); 384,  $\text{M}^+ / 2$  (55%); 356,  $\text{M}^+ / 2 - \text{CO}$  (32%); 216,  $\text{FcP}^+$  (100%).

#### 4.15. Bis(triphenylphosphino)- $\eta^1$ -P-ferrocenyl(tri-tertbutylphenyl)iminophosphinoplatinum(0) (7)

To a mixture of 0.32 g (1.1 mmol)  $\text{FcPCL}_2$  and 0.82 g (1.1 mmol)  $(\text{Ph}_3\text{P})\text{PtC}_2\text{H}_4$  in 10 ml THF, cooled to  $-78^\circ\text{C}$ , a solution of 1.1 mmol  $\text{Mes}^*\text{NTmsLi}$  (prepared by addition of 0.76 ml (1.2 mmol)  $^n\text{BuLi}$  to 0.37 g (1.1 mmol)  $\text{Mes}^*\text{NHTms}$  in ether at room temperatures) in ether was added. While stirring, the mixture was warmed to ambient temperature, the volatiles were removed in vacuum and the remaining residue was extracted with  $2 \times 7$  ml of toluene to remove the formed  $\text{LiCl}$  by filtration. Evaporation of the solvent yielded 0.76 g (0.64 mmol, 58.2%) of (7) as a dark red solid.  $\delta$  ( $^{31}\text{P}$ ): 327.9; (t)  $^2J_{\text{PP}} = 185.5$   $^1J_{\text{P,Pt}} = 5763$  Hz; 46.4; (d)  $^2J_{\text{PP}} = 185.5$  Hz  $^1J_{\text{P,Pt}} = 3933$  Hz.  $\delta$  ( $^{195}\text{Pt}$ ):  $-4549$  ppm. Mass spectrum (FAB): 1195,  $\text{M}^+ + \text{H}$  (43%); 932,  $\text{M}^+ - \text{PPh}_3$  (25%); 719,  $\text{Pt}(\text{PPh}_3)_2^+$  (40%); 264 (100%).

#### Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for continued financial support. K.A. thanks the Finnish Academy for financial support.

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