Preparation of *P,N*-Heterodifunctional Ferrocene-Coordinating Ligands by Selective Functionalization of Polyphosphanes by the Staudinger Reaction – Crystal and Molecular Structure of a New Cyclometallaphosphoraniminophosphane of Palladium(II)

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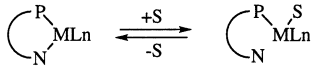
Staudinger reactions of the β-ferrocenylvinyl azide **1** with several diphosphanes in a 1:1 molar ratio afford the monoiminophosphorane derivatives **2**–**4**, whereas with a 2:1 stoichiometry these reactions afford the bis(iminophosphoranes) **5**–**7**. Similar results are obtained for the reactions of **1** with tris(diphenylphosphanylmethyl)ethane (*triphos*) and tris[2-(diphenylphosphanyl)ethyl]phosphane (*tetraphos*). Reaction of these *P,N*-difunctional ferrocene ligands with dichlorobis(benzonitrile)palladium(II) leads to the Pd^{II}-metallacycle derivatives **13** and **14**. The molecular structures of **5d** and **13** have been established by X-ray crystallography.

Ferrocene derivatives containing phosphane groups have proved to be very useful in coordination chemistry[1] and have found application in enantioselective transition-metal-catalyzed reactions[2]. In contrast to the large number of ferrocene-derived phosphanes and their complexes in which the phosphorus atom is directly bonded to a cyclopentadienyl ring, ligands with a tether connecting the two functionalities are less common[3], although chiral analogues have been attracting interest owing to their catalytic activity[4].

There is also a general interest in transition-metal complexes with heterodifunctional ligands because of their potential as catalysts[5] and their proven usefulness in the preparation of heterobimetallic species[6]. Heterodifunctional ligands provide versatile binding sites for metals, and thus effective catalysts may be generated from complexes of bifunctional chelate ligands in which one arm of the chelate is more loosely bound than the other, so that an equilibrium opening a coordinate site and thus providing access to a reactive intermediate can be established.



Since M−N π bonds are known to be more labile than M−P π bonds in some complexes[7], the use of bidentate ligands containing one phosphorus and one nitrogen donor can be expected to improve the catalytic activity. In this context, the preparations and catalytic activities of a number of rhodium, iridium, palladium and platinum *P,N* complexes, which contain a soft phosphorus(III) center at one end and a hard nitrogen center (amino, amido, imine or pyridine ring) at the other, have been reported[8].

Following our work on the preparation of new ferrocene derivatives by means of aza Wittig reactions[9], we now wish to report on the efficient synthesis of *P,N*-heterodifunctional ferrocene-based ligands. Our approach is based on the Staudinger imination[10] of trivalent phosphorus compounds with azides to produce an iminophosphorane function after nitrogen evolution. This method, which allows the partial oxidation of diphosphanes using the β-ferrocenylvinyl azide **1**, is applicable to diphosphanes of various alkene chain lengths, and even to tri- and tetraphosphanes.

Results and Discussion

Reaction of the starting β-ferrocenylvinyl azide **1**[9] with the appropriate diphosphane (1:1 molar ratio) in dry dichloromethane for 15 h at room temperature provides the corresponding monoiminophosphorane **2**, along with trace amounts of the bis(iminophosphorane) **5**. Compounds **2** could be isolated in yields ranging from 33 to 66% after purification by column chromatography and recrystallization. Similarly, reactions of **1** with (*E*)-1,2-bis(diphenylphosphanyl)ethene and 1,1′-bis(diphenylphosphanyl)ferrocene afford the monoiminophosphoranes **3** (46%) and **4** (21%), respectively. However, when reactions of azide **1** with diphosphanes (2:1 molar ratio) were carried out in diethyl ether at −15°C, the major product is the corresponding bis(iminophosphorane) **5** (45−89%), together with a small amount of the monoiminophosphorane **2**. Under these conditions, reaction with 1,1′-bis(diphenylphosphanyl)ferrocene provides the bis(iminophosphorane) **6**, while

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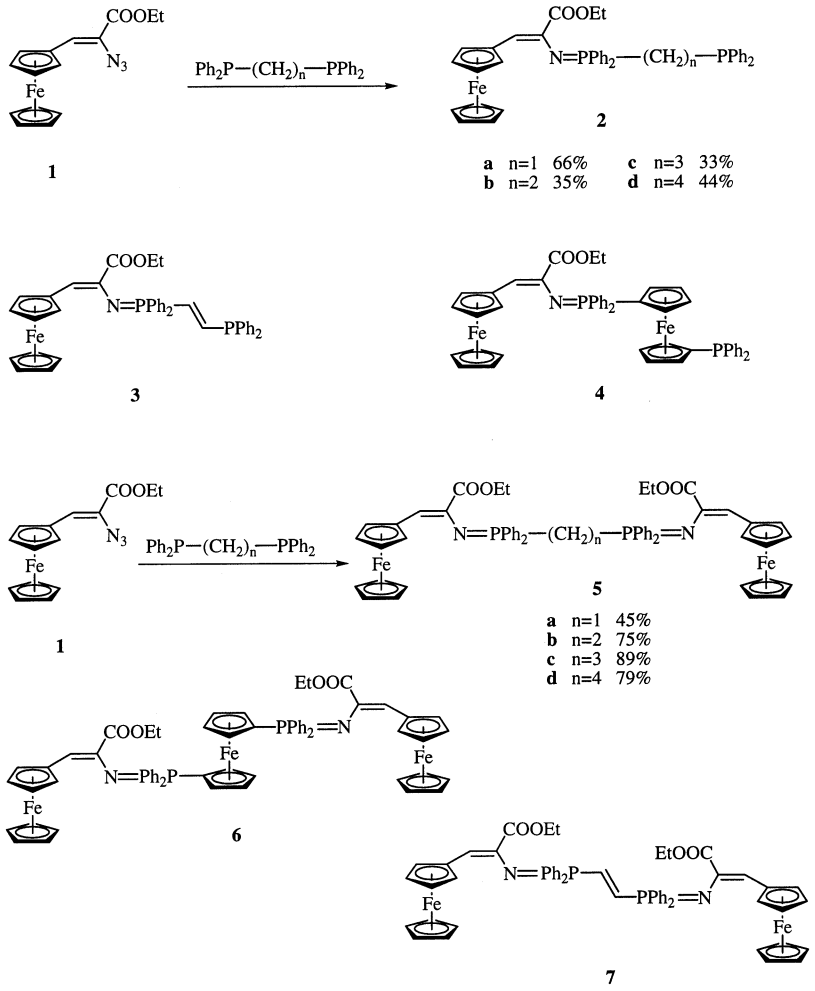
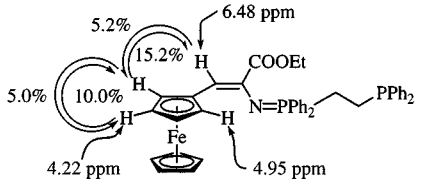
that with (*E*)-1,2-bis(diphenylphosphanyl)ethene afforded **7**, albeit in very low yield (9%) (Scheme 1).

Scheme 1



The ^{1}H-NMR spectra of compounds **2** and **5** show characteristic features: the ferrocenyl hydrogen atoms give a singlet at $\delta = 4.01-4.12$ for the unsubstituted cyclopentadienyl ring, and two pseudo triplets at $\delta = 4.17-4.59$ and $\delta = 4.90-5.06$, corresponding to an AA′MM′ pattern for the monosubstituted ring, while the vinylic proton signal appears as a doublet at $\delta = 6.14-6.53$ due to P^V coupling. The ^{13}C{^{1}H}-NMR spectra also exhibit the typical signals for monosubstituted ferrocenes. NOE experiments performed on compound **2b** allowed us to assign the α- and β-protons of the substituted cyclopentadienyl ring (Figure 1).

Figure 1. Selected NOE correlations for compound **2b**



Some salient ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR data for compounds **2** and **5** are compiled in Table 1. The ^{13}C-NMR spectrum of monoiminophosphorane **3** can be described as an AMX system, the ethylenic carbon atom $C-P^{III}$ signal appears at $\delta = 148.41$ as a doublet ($^1J_{P\text{-}C} = 23.4$ Hz), while the ethylenic $C-P^V$ signal appears at $\delta = 134.73$ as a doublet of doublet ($^1J_{P\text{-}C} = 87.2$ Hz, $^2J_{P\text{-}C} = 10.5$ Hz). In the bis(iminophosphorane) **7**, the two ferrocene subunits are equivalent; the C=O carbon atom signals appear as an apparent triplet and the ethylenic carbon atom signals $C-P^V$ appear at $\delta = 141.16$ as five-line multiplets. The ^{31}P{^{1}H}-NMR spectrum of **3** features two doublets centered at $\delta = 1.04$ and $\delta = -7.25$, attributable to the pentavalent and trivalent phosphorus atoms, respectively, whereas the spectrum of bis(iminophosphorane) **7** shows only one singlet at $\delta = 0.63$. In the ^{1}H- and ^{13}C-NMR spectra of compounds **4** and **6**, the characteristic signals of mono- and disubstituted ferrocenes are observed. In the ^{13}C-NMR spectrum of compound **4**, the disubstituted ferrocene ring signals appear as a set of six pairs of doublets, whereas in compound **6** it gives rise to a set of three pairs of doublets, besides only one set of signals for the two monosubstituted ferrocenes, indicating that they are equivalent. The ^{31}P-NMR spectrum of compound **4** shows two singlets at $\delta = 4.40$ and $\delta = -19.04$, assigned to the pentavalent and trivalent phosphorus atoms respectively, while that of compound **6** shows

Table 1. $^{13}C\{^1H\}$-NMR[a] and $^{31}P\{^1H\}$-NMR[b] data of the diphosphane framework in compounds **2** and **5**[c]

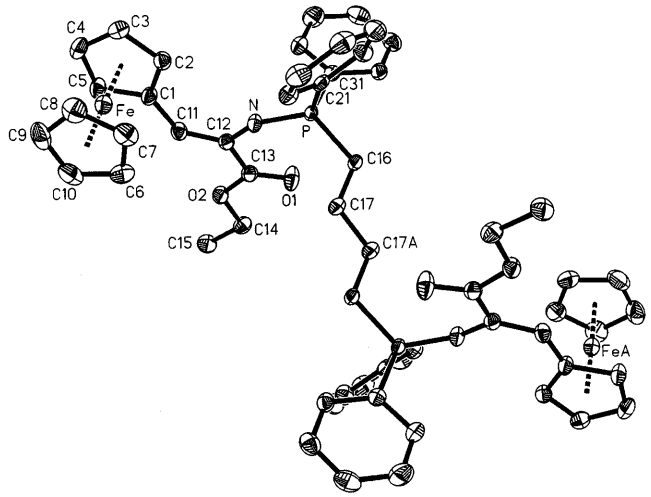
2 **5**

	C-1	C-2	C-3	C-4	P^V	P^{III}
2a	31.68 (dd, $^1J_{P(V)}$ = 59.5, $^1J_{P(III)}$ = 30.5)				3.36 (d, $^2J_{PP}$ = 53.8)	−29.49
2b	26.88 (dd, $^1J_{P(V)}$ = 66.2, $^2J_{P(III)}$ = 16.9)	19.37 (dd, ^1J = 13.9, ^2J = 4.0)			8.15 (d, $^3J_{PP}$ = 48.8)	−12.93
2c	31.39 (dd, $^1J_{P(V)}$ = 65.1, $^3J_{P(III)}$ = 12.5)	18.52 (dd, $^2J_{P(V)}$ = 17.0, $^2J_{P(III)}$ = 2.5)	29.37 (dd, $^1J_{P(III)}$ = 26.5, $^3J_{P(V)}$ = 14.5)		6.91	−18.87
2d	30.10 (d, $^1J_{P(V)}$ = 66.6)	23.06 (dd, $^2J_{P(V)}$ = 15.5, $^3J_{P(III)}$ = 3.5)	27.54 (dd, $^2J_{P(III)}$ = $^3J_{P(V)}$ = 14.5)	27.71 (d, $^1J_{P(III)}$ = 11.4)	7.32	−16.61
5a	31.43 (quint, $^1J+^1J$ = 108.0)				−2.64	
5b	23.13 (quint, $^1J+^2J$ = 130.2)				8.60	
5c	30.27 (dd, ^1J = 64.0, ^3J = 10.9)	15.22 (m)			6.73	
5d	30.07 (d, ^1J = 66.4)	23.05 (dd, ^2J = 16.0, ^3J = 3.1)			7.36	

[a] Chemical shift δ(^{13}C) relative to TMS; coupling constants in Hz. − [b] Chemical shift δ(^{31}P) relative to external 85% H_3PO_4; coupling constants in Hz. − [c] Solvent $CHCl_3$.

only one singlet at δ = 5.34. The constitution of compound **5d** was further corroborated by a single-crystal X-ray diffraction study. The molecular structure shows an inversion centre in the C17−C17a bond mid point. The P−N bond lenght [1.566(2) Å] is within the expected values. An ORTEP drawing of **5d** is shown in Figure 2; selected bond lengths and angles are given in the caption.

Figure 2. ORTEP plot of compound **5d**[a]



[a] 50% probability ellipsoids; selected bond lengths [Å] and angles [°]: P−N 1.566(2), N−C(12) 1.384(3), C(1)−C(11) 1.453(3), C(11)−C(12) 1.350(3); C(12)−N−P 131.6(2), C(12)−C(11)−C(1) 127.5(2), C(11)−C(12)−N 122.8(2).

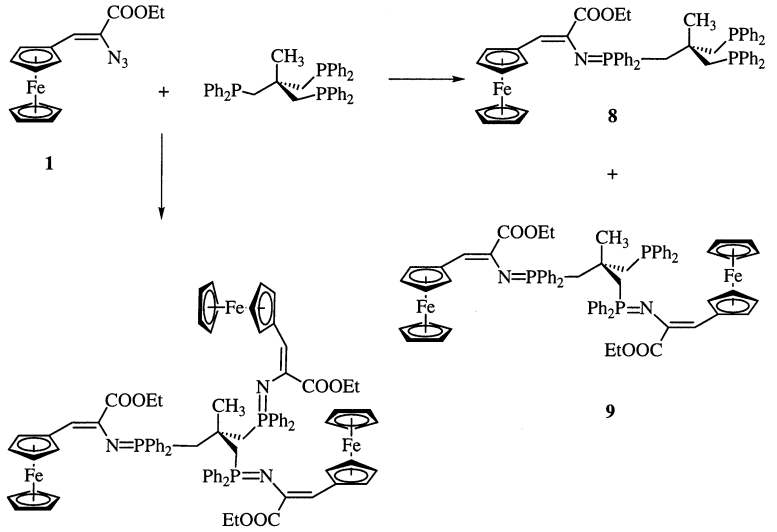
Reaction of the β-ferrocenylvinyl azide **1** with tris(diphenylphosphanylmethyl)ethane (*triphos*) (1:1 molar ratio) in dry dichloromethane at room temperature afforded a mixture of the monoiminophosphorane **8** (21%) and the bis(iminophosphorane) **9** (7%), which were readily separated by column chromatography. However, when the reaction was carried out in diethyl ether at −15°C in a 3:1 molar ratio, the corresponding tris(iminophosphorane) **10** was obtained in good yield as the sole reaction product (77%) (Scheme 2).

The ^1H-NMR spectrum of the bis(iminophosphorane) **9** shows two sets of signals for the two ferrocene subunits, indicating that they are non-equivalent. ^1H-, ^{13}C- and ^{31}P-NMR data of the *triphos* framework in compounds **8**, **9** and **10** are compiled in Table 2.

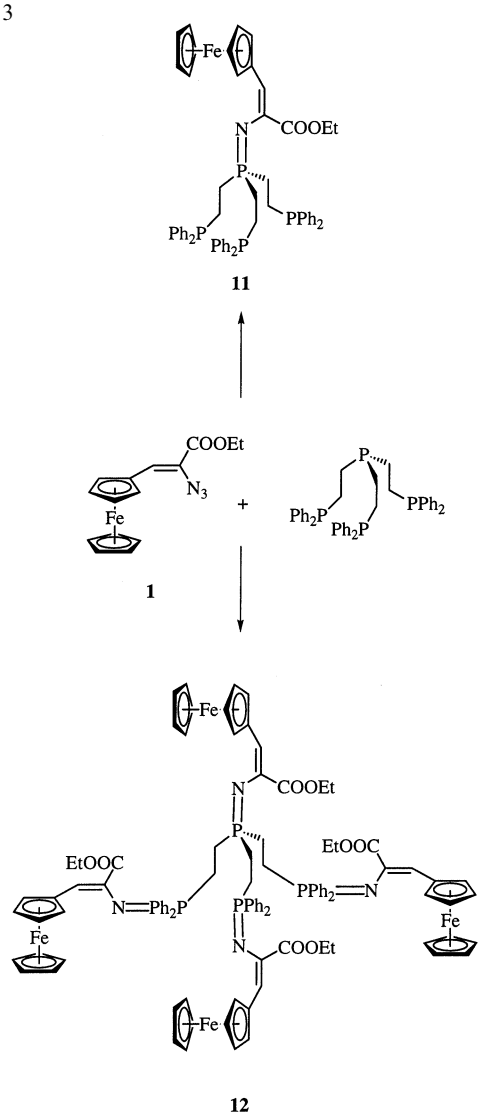
Reaction of azide **1** with tris[2-(diphenylphosphanyl)-ethyl]phosphane (*tetraphos*) in a 1:1 molar ratio in dichloromethane at room temperature afforded the monoiminophosphorane **11** in 31% yield. However, when the reaction was carried out in a 4:1 molar ratio in diethyl ether at −15°C, the main product was found to be the tetra(iminophosphorane) **12** (28%) (Scheme 3). The ^1H- and ^{13}C-NMR spectra of compound **12**, which bears four ferrocene subunits, showed the non-equivalence of one ferrocene group.

At this point, it seemed interesting to assess the complexation behavior of these heterodifunctional ferrocene derivatives **2** and **8** with palladium(II) (Scheme 4), as these compounds possess a complex-forming diphenylphosphanyl group and an iminophosphorane function, which has also demonstrated its versatility in forming M−N σ bonds to transition metals[11].

Scheme 2



Scheme 3



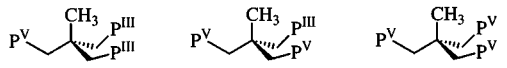
The ferrocene derivative **2a** was found to react cleanly with dichlorobis(benzonitrile)palladium(II) in toluene at −15°C affording the new *P,N*-chelate **13**, the structure of which has been determined by X-ray analysis (Figure 3). The ^{31}P-NMR spectrum of **13** features two doublets, with the iminophosphorane unit resonating at lower field (δ = 44.23) than the diphenylphosphanyl center (δ = 14.16).

Complex **13** represents the first example of a ferrocene derivative containing an iminophosphorane phosphane ligand. The palladium atom has a distorted square-planar coordination geometry. The large Pd−Cl1 bond length (2.3719 Å) compared to Pd−Cl2 (2.3133 Å) is consistent with the larger *trans* influence of P compared to N. The P−N bond length (1.628 Å) indicates that this bond is slightly elongated due to the coordination, since free iminophosphoranes show shorter P−N bond lengths (1.567 Å). The P^V atom geometry corresponds to a distorted tetrahedron, with the N−P−C angle [102.3(1)°] being the smallest. The distortion is probably due to the chelate ring stress.

The complexation behavior of **8** with Pd^{II} under the same reaction conditions was found to be different from that of **2a** and the *P,P*-chelate **14** was formed (Scheme 4). The ^{31}P-NMR spectrum showed this clearly, featuring only two singlets at δ = 0.1, characteristic of a non-coordinated iminophosphorane function, and at δ = 15.60, attributable to the coordinated diphenylphosphane groups.

The difference of 26.6 ppm between the chemical shifts of the P^{III} and P^V centers in **8** is reduced to 15.7 ppm in **14**. The ^{13}C-NMR spectrum of **14** shows two sets of signals for the aromatic rings of the diphenylphosphanyl groups and phosphorus-coupled resonances split into "a non 1:2:1 triplet". Such a triplet could be observed due to a ^{13}C nucleus and two ^{31}P nuclei forming an AXX′ spin system, as characteristic splitting clearly indicates that the two chemically equivalent phosphorus atoms are bound to palladium in a *cis* manner[12]. The differing complexation behavior of

Table 2. NMR data of the triphos framework in compounds **8**, **9** and **10**[c]

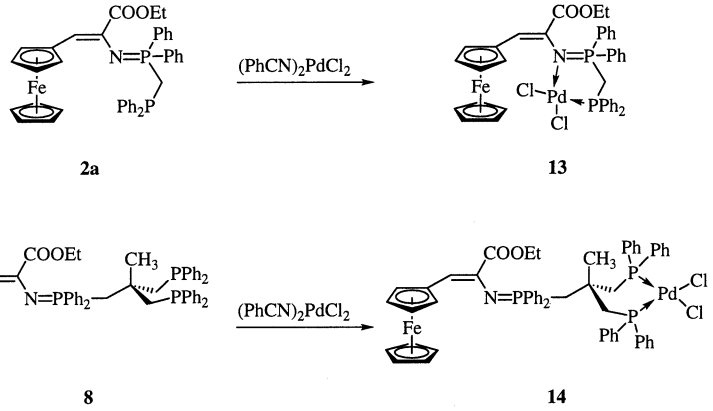


8 **9** **10**

	^{1}H NMR[a] CH_3	CH_2P^V	CH_2P^{III}	^{13}C NMR[a] CH_3	CH_2P^V	^{31}P NMR[b] CH_2P^{III}	CCH_2		
8	0.88−0.85 (m)	3.00 (d, $^2J_{P(V)}$ = 11.4)	2.62 (d, ^2J_H = 15.0), 2.42 (d, ^2J_H = 15.0)	28.08 (m)	40.90 (dt, $^1J_{P(V)}$ = 58.2, $^3J_{P(III)}$ = 8.2)	42.83 (dt, $^1J_{P(III)}$ = 9.0, $3J_{P(V)}$ = 9.0)	39.50 (dt, $^2J_{P(III)}$ = 13.8, $^2J_{P(V)}$ = 3.5)	0.20 (s)	−26.86 (s)
9	0.86 (m)	3.38 (dd, ^2J_H = 12.0, $^2JH_{P(V)}$ = 11.8), 3.19 (dd, ^2J_H = 12.0, $^2J_{HP(V)}$ = 11.8)	2.58 (d, $^2J_{P(III)}$ = 1.0)	26.76 (m)	41.00 (m)	42.77 (m)	40.10 (dt, $^2J_{P(III)}$ = 14.2, $^2J_{P(V)}$ = 3.8)	0.92 (s)	−26.97 (s)
10	0.70 (m)	3.20 (m)			40.16 (m)			1.89 (s)	

[a] Chemical shift δ(^{1}H and ^{13}C) relative to TMS; coupling constants in Hz. − [b] Chemical shift δ(^{31}P) relative to external 85% H_3PO_4. − [c] Solvent $CHCl_3$.

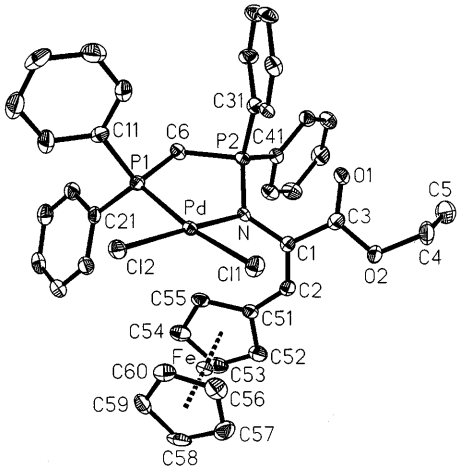
Scheme 4



2a **13**

8 **14**

Figure 3. ORTEP plot of compound **13**[a]



[a] 50% probability ellipsoids; selected bond lengths [Å] and angles [°]: Pd−N 2.062(3), Pd−P(1) 2.2259(11), Pd−Cl(2) 2.3133(9), Pd−Cl(1) 2.3719(11), P(2)−N 1.628(2); N−Pd−P(1) 87.35(8), P(1)−Pd−Cl(2) 88.71(4), N−Pd−Cl(1) 91.75(9), Cl(2)−Pd−Cl(1) 93.10(3), C(6)−P(1)−Pd 105.60(12), N−P(2)−C(6) 102.32(14), P(2)−N−Pd 112.5(2), P(2)−C(6)−P(1) 108.8(2).

2a and **8** may be due to their structural features, since the second diphenylphosphanyl group of **8** has stronger coordination ability toward Pd^{II} that the iminophosphorane group of **2a**.

A final word about the conformation of the ligand **8** and of its complex **14** is relevant. In triphos[13] the signal of the CH_3C protons exhibits a chemical shift of δ = 0.95, while in transition-metal complexes[14] these protons give rise to a signal in the range δ = 1.12−2.09. In the ^{13}C-NMR spectra, the signal of the CH_3C carbon atom appears at δ = 29.5 in the free ligand, while in complexes it appears at δ = 36−40. In all these cases, the triphos fragment adopts a "CH_3-*out*" conformation. The ^{1}H-NMR spectra of compounds **8** and **14** show the signal of the CH_3C protons at δ = 0.85 and δ = 0.14, respectively, while in the ^{13}C-NMR spectra the signal of this methyl carbon atom appears at δ = 28.08 and δ = 28.15, respectively. In view of the fact that in cyclic compounds with bridgehead 1,1,1-trisubstituted ethane fragments, the signal of the "CH_3C-*in*" group is shifted upfield relative to that of the "CH_3-*out*" group[15], the conformation of the triphos fragment in compounds **8** and **14** seems likely to be another than the "CH_3-*out*" one.

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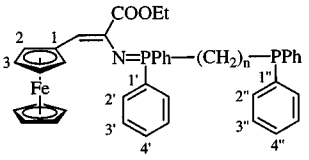
Experimental Section

All experiments were carried out with the exclusion of air and moisture under nitrogen. Solvents were purified and dried according to standard methods. Compound **1** was prepared according to a literature procedure[9]. − NMR: Bruker AC200 or Varian Unity 300. − MS: Fisons Autospec 5000 VG. − IR: Nicolet Impact 400. − Elemental analyses: Perkin-Elmer 240c. − Melting points were determined with a Kofler hot-plate and are uncorrected.

Preparation of Monoiminophosphoranes **2** *and* **4**. − *General Procedure:* To a solution of the β-ferrocenylvinyl azide **1** (0.50 g, 1.53 mmol) in 10 ml of dry CH_2Cl_2, an equimolar amount of the appropriate diphosphane in 10 ml of dry CH_2Cl_2 was added at room temperature. The reaction mixture was stirred for 15 h. The solvent was then removed in vacuo and the remaining residue was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent.



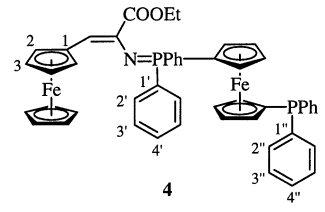
2

2a: 66%, red prisms, m.p. 143−144°C, R_f = 0.375. − IR (Nujol): ν = 1693, 1590, 1415, 1220, 1109, 806 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.87−7.70 (m, 4 H), 7.42−7.12 (m, 16 H), 6.37 (d, 1 H, ^4J_P = 8.2 Hz, CH=C), 4.96 (pseudo-t, 2 H, *J* = 1.8 Hz, 2-H/5-H), 4.21 (pseudo-t, 2 H, *J* = 1.8 Hz, 3-H/4-H), 4.12 (s, 5 H, Cp), 3.82 (q, 2 H, ^3J = 7.1 Hz, CH_2CH$_3$), 3.55 (dd, 2 H, *J* = 12.1, 1.0 Hz, CH_2P), 1.09 (t, 3 H, ^3J = 7.1 Hz, CH_2CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.95 (d, ^3J = 8.0 Hz, CO), 138.33 (dd, ^1J = 15.5 Hz, ^3J = 7.5 Hz, C-1′′), 134.90 (dd, ^1J = 104.1 Hz, ^3J = 1.0 Hz, C-1′), 134.06 (d, ^2J = 7.5 Hz, CH=*C*), 132.92 (d, ^2J = 20.0 Hz, C-2′′), 131.15 (dd, ^2J = 9.0 Hz, ^4J = 1.5 Hz, C-2′), 130.42 (d, ^4J = 2.4 Hz, C-4′), 128.40 (C-4′′), 128.20 (d, ^3J = 6.4 Hz, C-3′′), 128.07 (d, ^3J = 12.0 Hz, C-3′), 115.65 (d, ^3J = 22.0 Hz, *C*H=C), 83.25 (C-1), 69.69 (C-2/C-5), 68.95 (Cp), 68.14 (C-3/C-4), 60.53 (*C*H_2CH$_3$), 31.68 (dd, $^1J_{P(V)}$ = 59.5 Hz, $^1J_{P(III)}$ = 30.5 Hz, CH_2P), 14.14 (CH_2*C*H$_3$). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 3.36 (d, P^V), −29.49 (d, P^{III}), $^2J_{PP}$ = 53.8 Hz. − MS (EI, 70 eV); *m/z* (%): 681 (98) [M^+], 616 (81), 431 (35), 121 (100). − $C_{40}H_{37}FeNO_2P_2$ (681.54): calcd. C 70.49, H 5.47, N 2.06; found C 70.58, H 5.63, N 1.99.

2b: 35%, red prisms, m.p. 62−64°C, R_f = 0.393. − IR (Nujol): ν = 1695, 1590, 1416, 1210, 1109, 806 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.78−7.67 (m, 4 H, 2′′-H), 7.45−7.39 (m, 6 H, 4′-H, 3′-H), 7.27−7.24 (m, 10 H, 3′-H, 3′′-H, 4′′-H), 6.48 (d, 1 H, ^4J = 7.3 Hz, CH=C), 4.95 (pseudo-t, 2 H, *J* = 1.7 Hz, 2-H/5-H), 4.22 (pseudo-t, 2 H, *J* = 1.7 Hz, 3-H/4-H), 4.07 (s, 5 H, Cp), 3.90 (q, 2 H, ^3J = 7.1 Hz, CH_2CH$_3$), 2.75−2.58 (m, 2 H, CH_2-P^V), 2.27−2.12 (m, 2 H, CH_2P^{III}), 1.07 (t, 3 H, ^3J = 7.1 Hz, CH_2CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.91 (d, ^3J = 6.9 Hz, CO), 137.62 (d, ^1J = 13.5 Hz, C-1′′), 134.05 (d, ^2J = 7.0 Hz, CH=*C*), 133.48 (d, ^1J = 98.9 Hz, C-1′), 132.59 (d, ^2J = 18.4 Hz, C-2′′), 131.17 (d, ^2J = 8.8 Hz, C-2′), 130.68 (d, ^4J = 2.7 Hz, C-4′), 128.65 (C-4′), 128.44 (d, ^3J = 6.5 Hz, C-3′′), 128.28 (d, ^3J = 10.7 Hz, C-3′), 116.24 (d, ^3J = 20.6 Hz, *C*H=C), 82.99 (C-1), 69.66 (C-2/C-5), 68.90 (Cp), 68.28 (C-3/C-4), 60.56 (*C*H_2CH$_3$), 26.88 (dd, $^1J_{P(V)}$ = 66.2 Hz, $^2J_{P(III)}$ = 16.9 Hz), 19.37 (dd, ^1J = 13.9 Hz, ^2J = 4.0 Hz), 14.13 (CH_2*C*H$_3$). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 8.15 (d, P^V), −12.93 (d, P^{III}), $^3J_{PP}$ = 48.8 Hz. − MS (EI, 70 eV); *m/z* (%): 695 (100) [M^+], 183 (55), 121 (34). − $C_{41}H_{39}FeNO_2P_2$ (695.56): calcd. C 70.80, H 5.65, N 2.01; found C 70.55, H 5.80, N 2.12.

2c: 33%, red prisms, m.p. 49−51°C, R_f = 0.428. − IR (Nujol): ν = 1693, 1585, 1415, 1211, 1110, 806 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.82−7.70 (m, 4 H), 7.44−7.20 (m, 16 H), 6.44 (d, 1 H, ^4J = 7.5 Hz, CH=C), 4.91 (br. s, 2 H, 2-H/5-H), 4.18 (br. s, 2 H, 3-H/4-H), 4.05 (s, 5 H, Cp), 3.94 (q, 2 H, ^3J = 7.2 Hz, CH_2CH$_3$), 2.62−2.45 (m, 2 H, CH_2P^V), 2.10−1.95 (m, 2 H, CH_2P^{III}), 1.58−1.42 (m, 2 H, C$H_2CH_2P^{III}$), 1.09 (t, 3 H, ^3J = 7.2 Hz, CH_2CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 168.04 (d, ^3J = 7.0 Hz, CO), 138.32 (d, ^1J = 12.5 Hz, C-1′′), 134.12 (d, ^2J = 6.4 Hz, CH=*C*), 134.13 (d, ^1J = 98.6 Hz, C-1′), 132.58 (d, ^2J = 18.5 Hz, C-2′′), 131.06 (d, ^2J = 9.0 Hz, C-2′), 130.50 (d, ^4J = 2.5 Hz, C-4′), 128.37 (C-4′), 128.28 (d, ^3J = 7.0 Hz, C-3′′), 128.18 (d, ^3J = 11.4 Hz, C-3′), 115.97 (d, ^3J = 21.0 Hz, *C*H=C), 83.07 (C-1), 69.60 (C-2/C-5), 68.88 (Cp), 68.18 (C-3/C-4), 60.50 (*C*H_2CH$_3$), 31.39 (dd, $^1J_{P(V)}$ = 65.1 Hz, $^3J_{P(III)}$ = 12.5 Hz, CH_2-P^V), 29.37 (dd, $^1J_{P(III)}$ = 26.5 Hz, $^3J_{P(V)}$ = 14.5 Hz, CH_2P^{III}), 18.52 (dd, $^2J_{P(V)}$ = 17.0 Hz, $^2J_{P(III)}$ = 2.5 Hz, *C*$H_2CH_2P^{III}$), 14.13 (CH_2*C*H$_3$). − ^{31}P NMR ($CDCl_3$): δ = 6.91 (s, P^V), −18.87 (s, P^{III}). − MS (EI, 70 eV); *m/z* (%): 709 (100) [M^+], 183 (25), 121 (31). − $C_{42}H_{41}FeNO_2P_2$ (709.59): calcd. C 71.09, H 5.82, N 1.97; found C 71.00, H 5.89, N 1.85.

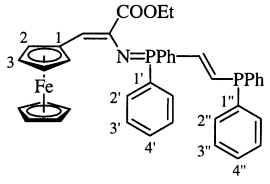
2d: 44%, orange prisms, m.p. 88−90°C, R_f = 0.40. − IR (Nujol): ν = 1695, 1595, 1415, 1216, 1114, 806 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.80−7.65 (m, 4 H), 7.47−7.28 (m, 16 H), 6.41 (d, 1 H, ^4J = 7.2 Hz, CH=C), 4.91 (s, 2 H, 2-H/5-H), 4.20 (s, 2 H, 3-H/4-H), 4.08 (s, 5 H, Cp), 3.91 (q, 1.7 H, ^3J = 7.2 Hz, CH_2CH$_3$), 3.43 (q, 0.3 H, ^3J = 6.9 Hz, CH_2CH$_3$), 2.53 (br. s, 2 H, CH_2P^V), 2.02 (br. s, 2 H, CH_2P^{III}), 1.57 (br. s, 4 H, C$H_2CH_2CH_2P^{III}$), 1.20 (t, 0.4 H, ^3J = 6.9 Hz, CH_2CH_3), 1.07 (t, 2.6 H, ^3J = 7.2 Hz, CH_2CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 168.01 (d, ^3J = 6.5 Hz, CO), 138.74 (d, ^1J = 13.5 Hz, C-1′′), 134.30 (d, ^2J = 6.9 Hz, CH=*C*), 133.96 (d, ^1J = 98.6 Hz, C-1′), 132.64 (d, ^2J = 18.5 Hz, C-2′′), 131.07 (d, ^2J = 9.0 Hz, C-2′), 130.55 (d, ^4J = 2.4 Hz, C-4′), 128.42 (C-4′), 128.32 (d, ^3J = 6.0 Hz, C-3′′), 128.21 (d, ^3J = 11.0 Hz, C-3′), 115.79 (d, ^3J = 20.5 Hz, *CH*=C), 83.14 (C-1), 69.60 (C-2/C-5), 68.90 (Cp), 68.26 (C-3/C-4), 60.50 (*C*H_2CH$_3$), 30.10 (d, $^1J_{P(V)}$ = 66.6 Hz, CH_2-P^V), 27.71 (d, $^1J_{P(III)}$ = 11.4 Hz, CH_2-P^{III}), 27.54 (dd, $^2J_{P(III)}$ = $^3J_{P(V)}$ = 14.5 Hz, *C*$H_2CH_2P^{III}$), 23.06 (dd, $^2J_{P(V)}$ = 15.5 Hz, $^3J_{P(III)}$ = 3.5 Hz, *C*$H_2CH_2P^V$), 14.13 (CH_2*C*H$_3$). − ^{31}P NMR ($CDCl_3$): δ = 7.32 (s, P^V), −16.61 (s, P^{III}). − MS (EI, 70 eV); *m/z* (%): 723 (30) [M^+], 606 (36), 241 (100), 183 (40), 121 (39). − $C_{43}H_{43}FeNO_2P_2$ (723.62): calcd. C 71.37, H 5.99, N 1.94; found C 71.51, H 6.08, N 1.85.



4

4: 21%, orange prisms, m.p. 78−80°C, R_f = 0.464. − IR (Nujol): ν = 1693, 1591, 1413, 1213, 1108, 807 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.64 (ddd, 4 H, ^3J_P = 12.0 Hz, ^3J = 8.1 Hz, ^4J = 1.5 Hz), 7.42−7.33 (m, 6 H), 7.28−7.23 (m, 10 H), 6.43 (d, 1 H, ^4J = 7.8 Hz, CH=C), 5.06 (pseudo-t, 2 H, *J* = 1.8 Hz, 2-H/5-H), 4.50

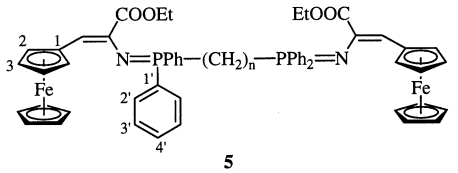
(pseudo-t, 2 H, J = 1.7 Hz, Cp′), 4.29−4.26 (m, 4 H, Cp′), 4.24 (pseudo-t, 2 H, J = 1.8 Hz, 3-H/4-H), 4.11 (s, 5 H, Cp), 3.98 (dd, 2 H, J = 3.0, 1.8 Hz, Cp′), 3.89 (q, 2 H, ^3J = 7.2 Hz, CH_2CH$_3$), 1.05 (t, 3 H, ^3J = 7.2 Hz, CH$_2$CH_3). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 167.85 (d, ^3J = 7.9 Hz, CO), 138.65 (d, ^1J = 9.5 Hz, C-1′′), 134.37 (d, ^1J = 103.6 Hz, C-1′), 134.25 (d, ^2J = 6.5 Hz, CH=C), 133.34 (d, ^2J = 19.5 Hz, C-2′′), 131.72 (d, ^2J = 9.5 Hz, C-2′), 130.43 (d, ^4J = 3.0 Hz, C-4′), 128.45 (C-4′′), 128.08 (d, ^3J = 6.5 Hz, C-3′′), 127.73 (d, ^3J = 12.0 Hz, C-3′), 115.01 (d, ^3J = 22.0 Hz, CH=C), 83.43 (C-1), 77.14 (d, ^1J = 8.0 Hz, CP^{III}), 76.81 (d, ^1J = 115.6 Hz, CP^{V}), 74.39 (d, J = 12.0 Hz), 73.91 (d, ^2J = 14.5 Hz), 73.31 (d, ^3J = 3.6 Hz), 72.92 (dd, J = 10.5 Hz, J = 2.0 Hz), 69.61 (C-2/C-5), 68.96 (Cp), 68.10 (C-3/C-4), 60.46 (CH$_2$CH$_3$), 14.18 (CH$_2$$CH_3$). − ^{31}P NMR (CDCl$_3$): δ = 4.40 (s, P^V), −19.04 (s, P^{III}). − MS (EI, 70 eV); *m/z* (%): 851 (100) [M$^+$], 602 (59), 305 (54), 121 (28). − $C_{49}H_{43}Fe_2NO_2P_2$ (851.48): calcd. C 69.12, H 5.09, N 1.64; found C 69.25, H 5.23, N 1.53.



3

Reaction of β-Ferrocenylvinyl Azide **1** *with (E)-1,2-Bis(diphenylphosphanyl)ethene:* To a cooled (−15°C) solution of compound **1** (0.50 g, 1.53 mmol) in 10 ml of dry diethyl ether, a solution of (*E*)-1,2-bis(diphenylphosphanyl)ethene (0.61 g, 1.53 mmol) in 10 ml of dry CH_2Cl_2 was added dropwise under nitrogen, and the reaction mixture was stirred for 15 h at this temperature. The solvent was then removed in vacuo and the residue was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:5) as eluent to give **3**: 46%, red prisms, m.p. 55−57°C, R_f = 0.41. − IR (Nujol): ν = 1695, 1588, 1430, 1105, 805 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 7.73 (ddd, 4 H, ^3J_P = 11.7 Hz, ^3J = 8.1 Hz, J = 2.1 Hz), 7.51−7.30 (m, 16 H), 7.10 (ddd, 1 H, J_P = 22.8 Hz, J_P = 21.3 Hz, ^3J = 18.6 Hz, =CH−P), 6.81 (ddd, 1 H, J_P = 21.6 Hz, J_P = 11.1 Hz, =CH−P), 6.49 (d, 1 H, ^4J_P = 7.5 Hz, CH=C−N), 4.90 (pseudo-t, 2 H, J = 1.8 Hz, 2-H/5-H), 4.17 (pseudo-t, 2 H, J = 1.8 Hz, 3-H/4-H), 4.06 (s, 5 H, Cp), 3.87 (q, 2 H, ^3J = 6.9 Hz, CH_2CH$_3$), 1.02 (t, 3 H, ^3J = 6.9 Hz, CH$_2$CH_3). − ^{13}C NMR{^{1}H} (CDCl$_3$): δ = 167.69 (d, ^3J = 7.5 Hz, CO), 148.41 (d, $^1J_{P(III)}$ = 23.4 Hz, =CHP^{III}), 135.53 (d, $^1J_{P(III)}$ = 10.0 Hz, C-1′′), 134.73 (dd, $^1J_{P(V)}$ = 87.0 Hz, $^2J_{P(III)}$ = 10.5 Hz, =CHP^V), 133.70 (d, ^2J = 19.5 Hz, C-2′′), 133.37 (d, $^1J_{P(V)}$ = 106.2 Hz, C-1′), 131.52 (d, $^2J_{P(V)}$ = 9.2, C-2′), 130.79 (d, $^4J_{P(V)}$ = 3.0 Hz, C-4′), 129.27 (C-4′′), 128.68 (d, $^3J_{P(III)}$ = 7.5 Hz, C-3′′), 128.23 (d, $^3J_{P(V)}$ = 12.0 Hz, C-3′), 116.60 (d, $^3J_{P(V)}$ = 21.5 Hz, CH=C−N), 82.93 (C-1), 69.72 (C-2/C-5), 68.94 (C$_p$), 68.34 (C-3/C-4), 60.57 (CH$_2$CH$_3$), 14.17 (CH$_2$$CH_3$), CH=$C$N signal overlapped. − ^{31}P NMR{^{1}H} (CDCl$_3$): δ = 1.04 (d, P^V), −7.27 (d, P^{III}), $^3J_{PP}$ = 20.0 Hz. − MS (EI, 70 eV); *m/z* (%): 693 (100) [M$^+$], 224 (35). − $C_{41}H_{37}FeNO_2P_2$ (693.55): calcd. C 71.00, H 5.38, N 2.02; found C 70.87, H 5.55, N 2.11.

Preparation of Bis(iminophosphoranes) **5** *and* **6**. − *General Procedure:* To a cooled (−15°C) solution of compound **1** (0.50 g, 1.53 mmol) in 10 ml of dry diethyl ether, a solution of the appropriate diphosphane (0.75 mmol) in 10 ml of dry diethyl ether was added under nitrogen, and the reaction mixture was stirred for 15 h at this temperature. The separated solid was collected by filtration, air-dried, and chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent.



5

5a: 45%, red prisms, m.p. 180−182°C, R_f = 0.178. − IR (Nujol): ν = 1690, 1597, 1413, 1213, 1110, 807 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 7.70 (br. s, 8 H), 7.40−7.15 (m, 12 H), 6.39 (d, 0.6 H, ^4J_P = 7.5 Hz, CH=C), 6.14 (d, 1.4 H, ^4J_P = 7.7 Hz, CH=C), 4.92 (br. s, 4 H, 2-H/5-H), 4.54 (t, 2 H, ^2J = 13.9 Hz, CH$_2$P), 4.29 (br. s, 4 H, 3-H/4-H), 4.08 (s, 10 H, Cp), 3.84−3.42 (m, 4 H, CH_2CH$_3$), 1.20 (t, 2 H, ^3J = 7.0 Hz, CH$_2$CH_3), 1.05 (t, 4 H, ^3J = 6.9 Hz, CH$_2$CH_3). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 167.32 (t, ^3J + ^5J = 8.4 Hz, CO), 135.18 (d, ^1J = 110.6 Hz, C-1′), 133.12 (d, ^2J = 7.5 Hz, CH=C), 131.22 (t, ^2J + ^4J = 9.8 Hz, C-2′), 130.02 (s, C-4′), 127.95 (t, ^3J + ^5J = 12.3 Hz, C-3′), 116.30 (m, CH=C), 83.12 (C-1), 69.63 (C-2/C-5), 68.83 (Cp), 68.17 (C-3/C-4), 60.22 (CH$_2$CH$_3$), 60.54 (CH$_2$CH$_3$), 31.43 (quint, ^1J + ^1J = 108.0 Hz, CH$_2$P), 15.26 (CH$_2$$CH_3$), 14.06 (CH$_2$$CH_3$). − ^{31}P NMR (CDCl$_3$): δ = −2.64 (s, P^V). − MS (FAB); *m/z* (%): 979 (100) [M$^+$ + 1], 978 (46) [M$^+$], 224 (21). − $C_{55}H_{52}Fe_2N_2O_4P_2$ (978.68): calcd. C 67.50, H 5.36, N 2.86; found C 67.44, H 5.50, N 2.70.

5b: 75%, red prisms, m.p. 228−231°C, R_f = 0.205. − IR (Nujol): ν = 1685, 1595, 1411, 1211, 1105, 805 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 7.71 (br. s, 4 H, 2′-H), 7.38 (br. s, 6 H, 3′-H/4′-H), 6.46 (br. s, 1 H, CH=C), 4.93 (s, 2 H, 2-H/5-H), 4.23 (s, 2 H, 3-H/4-H), 4.01 (s, 5 H, Cp), 3.78 (q, 1.6 H, ^3J = 6.9 Hz, CH_2CH$_3$), 3.47 (q, 0.4 H, ^3J = 6.9 Hz, CH_2CH$_3$), 2.76 (s, 2 H, CH$_2$P), 1.20 (t, 0.6 H, ^3J = 6.9 Hz, CH$_2$CH_3), 0.99 (t, 2.4 H, ^3J = 6.9 Hz, CH$_2$CH_3). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 167.66 (t, ^3J + ^6J = 6.3 Hz, CO), 134.01 (t, ^2J + ^5J = 7.1 Hz, CH=C), 133.24 (quint, C-1′), 131.12 (t, ^2J + ^5J = 9.0 Hz, C-2′), 130.67 (s, C-4′), 128.26 (t, ^3J + ^6J = 11.5 Hz, C-3′), 116.24 (t, ^3J + ^6J = 20.5 Hz, CH=C), 82.96 (C-1), 69.65 (C-2/C-5), 68.91 (Cp), 68.29 (C-3/C-4), 65.80 (CH$_2$CH$_3$), 60.44 (CH$_2$CH$_3$), 23.13 (quint, ^1J + ^2J = 130.2 Hz, CH$_2$P), 15.24 (CH$_2$$CH_3$), 14.04 (CH$_2$$CH_3$). − ^{31}P NMR (CDCl$_3$): δ = 8.60 (s, P^V). − MS (FAB); *m/z* (%): 993 (71) [M$^+$ + 1], 992 (30) [M$^+$], 510 (100), 307 (59). − $C_{56}H_{54}Fe_2N_2O_4P_2$ (992.71): calcd. C 67.76, H 5.48, N 2.82; found C 67.60, H 5.45, N 2.57.

5c: 89%, red prisms, m.p. 62−65°C, R_f = 0.100. − IR (Nujol): ν = 1697, 1593, 1417, 1216, 1105, 805 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 7.64 (ddd, 8 H, ^3J_P = 11.1 Hz, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 2′-H), 7.42−7.24 (m, 12 H, 3′-H/4′-H), 6.46 (d, 2 H, ^4J_P = 7.5 Hz, CH=C), 4.90 (pseudo-t, 4 H, J = 1.8 Hz, 2-H/5-H), 4.19 (pseudo-t, 4 H, J = 1.8 Hz, 3-H/4-H), 4.04 (s, 10 H, Cp), 3.93 (q, 3.2 H, ^3J = 7.2 Hz, CH_2CH$_3$), 3.46 (q, 0.8 H, ^3J = 6.9 Hz, CH_2CH$_3$), 2.73 (dd, 4 H, ^2J_P = 18.0 Hz, ^4J_P = 10.2 Hz, CH$_2$P), 1.73 (m, 2 H, CH$_2$CH$_2$P), 1.20 (t, 1.2 H, ^3J = 6.9 Hz, CH$_2$CH_3), 1.05 (t, 4.8 H, ^3J = 7.2 Hz, CH$_2$CH_3). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 168.06 (d, ^3J = 6.8 Hz, CO), 134.06 (d, ^2J = 6.8 Hz, CH=C), 133.98 (d, ^1J = 101.1 Hz, C-1′), 130.97 (d, ^2J = 9.0 Hz, C-2′), 130.40 (d, ^4J = 2.4 Hz, C-4′), 128.23 (d, ^3J = 11.5 Hz, C-3′), 116.10 (d, ^3J = 21.0 Hz, CH=C), 83.10 (C-1), 69.67 (C-2/C-5), 68.90 (Cp), 68.20 (C-3/C-4), 65.82 (CH$_2$CH$_3$), 60.53 (CH$_2$CH$_3$), 30.27 (dd, ^1J = 64.0 Hz, ^3J = 10.9 Hz, CH$_2$P), 15.22 (m, CH$_2$CH$_2$P), 14.04 (CH$_2$$CH_3$). − ^{31}P NMR (CDCl$_3$): δ = 6.73 (s, P^V) − MS (FAB); *m/z* (%): 1006 (100) [M$^+$], 725 (38), 334 (25), 223 (64). − $C_{57}H_{56}Fe_2N_2O_4P_2$

(1006.73): calcd. C 68.01, H 5.61, N 2.78; found C 68.13, H 5.70, N 2.55.

5d: 79%, orange prisms, m.p. 160−163°C, R_f = 0.071. − IR (Nujol): ν = 1693, 1595, 1417, 1216, 1107, 808 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.80−7.65 (m, 4 H, 2′-H), 7.45−7.38 (m, 6 H, 3′-H + 4′-H), 6.42 (d, 1 H, ^4J_P = 7.2 Hz, CH=C), 4.91 (br. s, 2 H, 2-H/5-H), 4.20 (br. s, 2 H, 3-H/4-H), 4.08 (s, 5 H, Cp), 3.90 (q, 1.8 H, ^3J = 7.1 Hz, CH_2CH_3), 3.46 (q, 0.2 H, ^3J = 7.0 Hz, CH_2CH_3), 2.53 (br. s, 2 H, CH_2P), 1.57 (br. s, 2 H, CH_2CH_2P), 1.20 (t, 0.3 H, ^3J = 7.0 Hz, CH_2CH_3), 1.05 (t, 2.7 H, ^3J = 7.1 Hz, CH_2CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 168.00 (d, ^3J = 7.1 Hz, CO), 134.26 (d, ^2J = 7.1 Hz, CH=*C*), 133.92 (d, ^1J = 99.5 Hz, C-1′), 131.05 (d, ^2J = 9.0 Hz, C-2′), 130.54 (d, ^4J = 2.5 Hz, C-4′), 128.31 (d, ^3J = 11.6 Hz, C-3′), 115.80 (d, ^3J = 20.8 Hz, *C*H=C), 83.11 (C-1), 69.58 (C-2/C-5), 68.89 (Cp), 68.17 (C-3/C-4), 65.80 (CH_2CH_3), 60.49 (CH_2CH_3), 30.07 (d, ^1J = 66.4 Hz, CH_2P), 23.05 (dd, ^2J = 16.0 Hz, ^3J = 3.1 Hz, CH_2CH_2P), 14.13 (CH_2CH_3). − ^{31}P NMR ($CDCl_3$): δ = 7.36 (s, P^V). − MS (FAB); *m/z* (%): 1021 (100) [M^+ + 1], 723 (15), 307 (18), 224 (30). − $C_{58}H_{58}Fe_2N_2O_4P_2$ (1020.76): calcd. C 68.25, H 5.73, N 2.74; found C 68.40, H 5.65, N 2.56.

6: 54%, orange prisms, m.p. 103−105°C, R_f = 0.054. − IR (Nujol): ν = 1700, 1590, 1410, 1213, 1105, 807 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.70−7.50 (m, 4 H, 2′-H), 7.40−7.24 (m, 6 H, 3′-H + 4′-H), 6.43 (d, 1 H, ^4J = 7.7 Hz, CH=C), 5.04 (s, 2 H, 2-H/5-H), 4.59 (s, 2 H, 3-H/4-H), 4.23 (s, 4 H, Cp′), 4.11 (s, 5 H, Cp), 3.85 (q, 1.2 H, ^3J = 7.0 Hz, CH_2CH_3), 3.46 (q, 0.8 H, ^3J = 7.0 Hz, CH_2CH_3), 1.20 (t, 1.2 H, ^3J = 7.0 Hz, CH_2CH_3), 1.01 (t, 1.8 H, ^3J = 7.0 Hz, CH_2CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.77 (d, ^3J = 7.8 Hz, CO), 134.41 (d, ^1J = 104.0, C-1′), 134.14 (d, ^2J = 6.7 Hz, CH=*C*), 131.64 (d, ^2J = 9.6 Hz, C-2′), 130.45 (d, ^4J = 2.5 Hz, C-4′), 127.74 (d, ^3J = 12.0 Hz, C-3′), 115.04 (d, ^3J = 22.3 Hz, *C*H=C), 83.32 (C-1), 69.56 (C-2/C-5), 68.96 (Cp), 68.10 (C-3/C-4), 77.18 (d, ^1J = 115.9 Hz, CP^V), 74.57 (d, ^3J = 12.4 Hz), 73.75 (d, ^3J = 10.2 Hz), 65.79 (CH_2CH_3), 60.44 (CH_2CH_3), 15.25 (CH_2CH_3), 14.14 (CH_2CH_3). − ^{31}P NMR ($CDCl_3$): δ = 5.34 (s). − MS (FAB); *m/z* (%): 1149 (89) [M^+ + 1], 602 (100), 305 (58). − $C_{64}H_{58}Fe_3N_2O_4P_2$ (1148.67): calcd. C 66.92, H 5.09, N 2.44; found C 66.85, H 5.21, N 2.30.

(E)-1,2-Bis[(α-ethoxycarbonyl-β-ferrocenyl)vinylimino-diphenylphosphoranyl]ethene (**7**): To a cooled (−15°C) solution of compound **1** (0.50 g, 1.53 mmol) in 10 ml of dry diethyl ether, a solution of (*E*)-1,2-bis(diphenylphosphanyl)ethene (0.30 g, 0.77 mmol) in 10 ml of dry CH_2Cl_2 was added dropwise under nitrogen, and the mixture was stirred for 15 h at this temperature. The solvent was then removed in vacuo and the remaining solid was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (2:7) as eluent to give **7**: 9%, red prisms, m.p. 175−178°C, R_f = 0.27. − IR (Nujol): ν = 1682, 1594, 1409, 1209, 1110, 1041 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.82−7.70 (m, 4 H), 7.54−7.30 (m, 7 H, aryl H + =CHP), 6.53 (quint, 1 H, *J* = 3.6 Hz, CH=CN), 4.92 (br. s, 2 H, 2-H/5-H), 4.21 (br. s, 2 H, 3-H/4-H), 4.08 (s, 5 H, Cp), 3.88 (q, 2 H, ^3J = 6.9 Hz, CH_2CH_3), 1.03 (t, 3 H, ^3J = 6.9 Hz, CH_2CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.54 (t, ^3J_P + ^6J_P = 7.5 Hz, CO), 141.16 (quint, ^1J_P + ^2J_P = 131.1 Hz, $=CHP^V$), 132.64 (quint, ^1J_P + ^4J_P = 106.2 Hz, C-1′), 131.58 (t, ^2J_P + ^5J_P = 9.5 Hz, C-2′), 131.00 (br. s, C-4′), 128.30 (t, ^3J_P + ^6J_P = 12.0 Hz, C-3′), 116.93 (t, ^3J_P + ^6J_P = 21.6 Hz, *C*H=*C*), 82.62 (C-1), 69.70 (C-2/C-5), 68.91 (Cp), 68.37 (C-3/C-4), 60.60 (CH_2CH_3), 14.09 (CH_2CH_3), CH=*C*N signal overlapped. − ^{31}P NMR ($CDCl_3$): δ = 0.63 (s). − MS (FAB); *m/z* (%): 990 (40) [M^+], 693 (55). − $C_{56}H_{52}Fe_2N_2O_4P_2$ (990.69): calcd. C 67.89, H 5.29, N 2.83; found C 68.00, H 5.15, N 2.90.

Reaction of β-Ferrocenylvinyl Azide **1** *with Tris(diphenylphosphanylmethyl)ethane (triphos).* − *Procedure A:* To a solution of compound **1** (0.50 g, 1.53 mmol) in 10 ml of dry CH_2Cl_2, a solution of triphos (0.96 g, 1.53 mmol) in 10 ml of the same solvent was added dropwise under nitrogen. The reaction mixture was stirred at room temperature for 15 h. The solvent was then removed in vacuo and the residue was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent.

8: 21%, red prisms, m.p. 79−82°C, R_f = 0.50. − IR (Nujol): ν = 1690, 1589, 1435, 1410, 1213, 1106, 816 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.68−7.61 (m, 4 H), 7.37−7.17 (m, 26 H), 6.48 (d, 1 H, ^4J_P = 8.7 Hz, CH=C), 5.00 (pseudo-t, 2 H, *J* = 1.6 Hz, 2-H/5-H), 4.25 (pseudo-t, 2 H, *J* = 1.6 Hz, 3-H/4-H), 4.10 (s, 5 H, Cp), 3.80 (q, 2 H, ^3J = 7.1 Hz, CH_2CH_3), 3.00 (d, 2 H, $^2J_{P(V)}$ = 11.4 Hz, CH_2P^V), 2.62 (d, 2 H, $^2J_{P(III)}$ = 15.0 Hz, CH_2P^{III}), 2.42 (d, 2 H, $^2J_{P(III)}$ = 15.0 Hz, CH_2P^{III}), 0.98 (t, 3 H, ^3J = 7.1 Hz, CH_2CH_3), 0.88−0.85 (m, 3 H, CH_3C). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.92 (d, ^3J = 8.4 Hz, CO), 139.83 (quint, ^1J_P + ^5J_P = 29.5 Hz, C-1′′), 137.14 (d, ^1J = 103.3 Hz, C-1′), 134.28 (d, ^2J = 6.8 Hz, CH=*C*), 133.08 (d, ^2J = 20.5 Hz, C-2′′)*, 132.95 (d, ^2J = 20.4 Hz, C-2′′)*, 130.40 (d, ^2J = 8.6 Hz, C-2′), 129.90 (d, ^4J = 2.6 Hz, C-4′), 128.33 (C-4′′)**, 128.31 (C-4′′)**, 128.20 (d, ^3J = 7.0 Hz, 2 × C-3′′), 128.11 (d, ^3J = 11.5 Hz, C-3′), 115.83 (d, ^3J = 21.3 Hz, *CH*=C), 83.21 (C-1), 69.79 (C-2/C-5), 68.95 (Cp), 68.21 (C-3/C-4), 60.61 (CH_2CH_3), 42.83 (dt, $^1J_{P(III)}$ = 9.0 Hz, $^3J_{P(V)}$ = 9.0 Hz, 2 × CH_2P^{III}), 40.90 (dt, $^1J_{P(V)}$ = 58.2 Hz, $^3J_{P(III)}$ = 8.2 Hz, CH_2P^V), 39.50 (dt, $^2J_{P(III)}$ = 13.8 Hz, $^2J_{P(V)}$ = 3.5 Hz, CCH_3), 28.08 (m, CCH_3), 14.12 (CH_2CH_3). − ^{31}P NMR ($CDCl_3$): δ = 0.20 (s, P^V), −26.86 (s, P^{III}). − MS (FAB); *m/z* (%): 921 (100) [M^+], 547 (13). − $C_{56}H_{54}FeNO_2P_3$ (921.83): calcd. C 72.97, H 5.90, N 1.52; found C 73.10, H 5.78, N 1.65.

9: 7%, red prisms, m.p. 101−103°C, R_f = 0.44. − IR (Nujol): ν = 1687, 1587, 1410, 1209, 1105, 806 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.78−7.65 (m, 8 H), 7.35−7.10 (m, 22 H), 6.58 (d, 2 H, ^4J_P = 8.6 Hz, CH=C), 5.03 (br. s, 2 H, 2-H/5-H), 4.98 (br. s, 2 H, 2-H/5-H), 4.27 (br. s, 2 H, 3-H/4-H), 4.22 (br. s, 2 H, 3-H/4-H), 4.11 (s, 10 H, C_p), 3.96−3.86 (m, 4 H, 2 × CH_2CH_3), 3.38 (dd, ^2J_H = 12.0 Hz, $^2J_{P(V)}$ = 11.8 Hz, CH_2P^V), 3.19 (dd, ^2J_H = 12.0 Hz, $^2J_{P(V)}$ = 11.8 Hz, CH_2P^V), 2.58 (d, $^2J_{P(III)}$ = 1.0 Hz, CH_2P^{III}), 1.05 (t, 6 H, ^3J = 7.0 Hz, 2 × CH_2CH_3), 0.86 (m, 3 H, CH_3C). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.95 (d, ^3J = 8.3 Hz, CO), 139.83 (d, $^1J_{P(III)}$ = 11.4 Hz, C-1′′), 137.12 (d, ^1J = 102.0 Hz, C-1′)*, 136.71 (d, ^1J = 103.8 Hz, C-1′)*, 134.25 (d, ^2J = 6.8 Hz, CH=*C*), 132.95 (d, ^2J = 19.9 Hz, C-2′′), 130.54 (d, ^2J = 8.9 Hz, C-2′)**, 130.42 (d, ^2J = 8.8 Hz, C-2′)**, 129.87 (d, ^4J = 2.3 Hz, 2 × C-4′), 128.38 (C-4′′), 128.31 (d, ^3J = 7.0 Hz, C-3′′), 116.43 (d, ^3J = 21.4 Hz, *C*H=C), 83.21 (C-1), 69.93 (C-2/C-5), 68.95 (Cp), 68.26 (C-3/C-4), 60.70 (CH_2CH_3), 42.77 (m, CH_2P^{III}), 41.00 (m, CH_2P^V), 40.10 (dt, $^2J_{P(III)}$ = 14.2 Hz, $^2J_{P(V)}$ = 3.8 Hz, C−CH_3), 26.76 (m, C−CH_3), 14.21 (CH_2CH_3), 2 × C-3′ signal overlapped. − ^{31}P NMR ($CDCl_3$): δ = 0.92 (s, P^V), −26.97 (s, P^{III}). − MS (FAB); *m/z* (%): 1218 (100) [M^+], 722 (56), 423 (21). − $C_{71}H_{69}Fe_2N_2O_4P_3$ (1218.97): calcd. C 69.96, H 5.71, N 2.30; found C 70.15, H 5.90, N 2.10.

Procedure B: To a cooled (−15°C) solution of compound **1** (0.50 g, 1.53 mmol) in 10 ml of dry diethyl ether, was added a solution of triphos (0.32 g, 0.51 mmol) in 10 ml of the same solvent. The reaction mixture was stirred at this temperature for 15 h. The precipitated solid was collected by filtration and chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent to give **10** (77%), red prisms, m.p. 107−109°C, R_f = 0.375. − IR (Nujol): ν = 1690, 1590, 1415, 1205, 1105, 806 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.00−7.48 (m, 12 H), 7.38−7.00 (m, 18 H), 6.70 (d,

2 H, ^4J_P = 8.4 Hz, 2 × CH=C), 6.57 (d, 1 H, ^4J_P = 8.4 Hz, CH=C), 5.56 (br. s, 6 H, 2-H/5-H), 4.48 (br. s, 6 H, 3-H/4-H), 4.15 (s, 15 H, Cp), 4.04−3.96 (m, 6 H, 3 × CH_2CH$_3$), 3.30−3.10 (m, 6 H, 3 × CHP^V), 1.12 (t, 9 H, ^3J = 7.2 Hz, 3 × CH$_2$CH_3), 0.70 (m, 3 H, CH$_3$C). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 167.96 (d, ^3J = 7.9 Hz, CO), 134.57 (d, ^2J = 6.4 Hz, CH=*C*), 129.42 (C-4′), 128.09 (d, ^3J = 11.5 Hz, C-3′), 116.54 (d, ^3J = 21.5 Hz, *C*H=C), 83.18 (C-1), 70.01 (C-2/C-5), 68.99 (Cp), 68.22 (C-3/C-4), 60.72 (*C*H$_2$CH$_3$), 40.16 (m, CH$_2$P^V), 14.13 (CH$_2$*C*H$_3$), some signals are overlapped or absent. − ^{31}P NMR (CDCl$_3$): δ = 1.89 (s, P^V). − MS (FAB); *m/z* (%): 1517 (100) [M$^+$ + 1]. − C$_{86}$H$_{84}$Fe$_3$N$_3$O$_6$P$_3$ (1516.01): calcd. C 68.13, H 5.58, N 2.77; found C 68.25, H 5.49, N 2.65.

Reaction of β-Ferrocenylvinyl Azide **1** *with Tris[2-(diphenylphosphanyl)ethyl]phosphane (tetraphos). − Procedure A:* To a solution of compound **1** (0.25 g, 0.77 mmol) in 10 ml of dry CH$_2$Cl$_2$, a solution of tetraphos (0.5 g, 0.77 mmol) in 10 ml of the same solvent was added dropwise under nitrogen, and the reaction mixture was stirred at room temperature for 20 h. The solution was then concentrated to dryness and the residue was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (2:7) as eluent to give **11** (31%), orange prisms, m.p. 120−122°C, R_f = 0.48. − IR (Nujol): ν = 1685, 1597, 1410, 1206, 1108, 1040, 810 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 7.42−7.20 (m, 30 H), 6.37 (d, 1 H, ^4J_P = 7.2 Hz, CH=C), 4.80 (pseudo-t, 2 H, *J* = 1.8 Hz, 2-H/5-H), 4.20 (pseudo-t, 2 H, *J* = 1.8 Hz, 3-H/4-H), 4.04 (q, 2 H, ^3J = 6.8 Hz, CH_2CH$_3$), 3.94 (s, 5 H, Cp), 2.10−1.93 (m, 12 H, P^{III}CH$_2$CH$_2$P^V), 1.25 (t, 3 H, ^3J = 6.8 Hz, CH$_2$CH_3). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 168.33 (d, ^3J = 7.5 Hz, CO), 137.62 (d, $^1J_{P(III)}$ = 13.0 Hz, C-1′), 134.10 (d, $^2J_{P(V)}$ = 6.7 Hz, CH=*C*), 132.70 (d, $^2J_{P(III)}$ = 18.5 Hz, C-2′), 128.87 (C-4′), 128.55 (d, $^3J_{P(III)}$ = 7.0 Hz, C-3′), 115.58 (d, ^3J = 19.5 Hz, *C*H=C), 83.04 (C-1), 69.49 (C-2/C-5), 68.82 (Cp), 68.21 (C-3/C-4), 60.82 (*C*H$_2$CH$_3$), 24.28 (dd, $^1J_{P(V)}$ = 61.5 Hz, $^2J_{P(III)}$ = 16.5 Hz, 3 × CH$_2$P^V), 20.49 (dd, $^1J_{P(III)}$ = 14.4 Hz, $^2J_{P(V)}$ = 4.0 Hz, 3 × CH$_2$P^{III}), 14.44 (CH$_2$*C*H$_3$). − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 20.91 (q, P^V), −12.96 (d, P^{III}), $^3J_{PP}$ = 43.8 Hz. − MS (FAB); *m/z* (%): 968 (30) [M$^+$ + 1], 457 (22). − C$_{57}$H$_{57}$FeNO$_2$P$_4$ (967.84): calcd. C 74.28, H 6.06, N 1.22; found C 74.40, H 5.90, N 1.40.

Procedure B: To a cooled (−15°C) solution of compound **1** (0.50 g, 1.53 mmol) in 10 ml of dry diethyl ether, a solution of tetraphos (0.25 g, 0.38 mmol) in 10 ml of the same solvent was added dropwise under nitrogen. The resulting mixture was stirred for 15 h at this temperature. The precipitated solid was collected by filtration and chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1:3) as eluent to give **12** (28%), orange prisms, m.p. 103−106°C, R_f = 0.125. − IR (Nujol): ν = 1682, 1599, 1410, 1210, 1112, 1039, 817 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 7.85−7.75 (m, 12 H), 7.52−7.20 (m, 18 H), 6.45 (br. s, 3 H, 3 × CH=C), 6.30 (br. s, 1 H, CH=C), 4.86 (br. s, 6 H, 3 × 2-H/5-H), 4.71 (br. s, 2 H, 2-H/5-H), 4.15 (br. s, 8 H, 3-H/4-H), 4.04 (s, 20 H, Cp), 3.74 (br. s, 8 H, CH_2CH$_3$), 2.66 (br. s, 6 H, CH$_2$P), 2.14−1.85 (m, 6 H, CH$_2$P^V), 0.97 (br. s, 12 H, CH$_2$CH_3). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 168.06 (d, ^3J = 6.4 Hz, CO), 167.99 (d, ^3J = 7.0 Hz, 2 × CO), 167.67 (d, ^3J = 7.1 Hz, 1′′-CCC*CO*), 133.92 (d, ^2J = 6.8 Hz, *C*=CH), 133.61 (d, ^2J = 8.7 Hz, 1′′-CH=*C*), 132.91 (d, ^1J = 103.5 Hz, C-1′), 131.39 (d, ^2J = 9.2 Hz, C-2′), 130.73 (C-4′), 128.25 (d, ^3J = 11.6 Hz, C-3′), 117.09 (d, ^3J = 21.0 Hz, CH=*C*), 116.58 (d, ^3J = 20.5 Hz, 2 × *C*H=C), 115.21 (d, ^3J = 19.1 Hz, 1′′-*C*H=C), 83.02 (C-1), 82.85 (2 × C-1), 82.67 (C-1), 69.65 (C-2/C-5), 69.38 (C-2′′/C-5′′), 68.93 (Cp), 68.78 (Cp′′), 68.40 (C-3′′/C-4′′), 68.31 (C-3/C-4), 60.65 (*C*′H$_2$CH$_3$), 60.56 (*C*H$_2$CH$_3$), 23.92 (dm, $^1J_{P(V)}$ = 67.9 Hz, 3 × CH$_2$P^V), 20.74 (dm, $^1J_{P(V)}$ = 63.4 Hz, 3 × CH$_2$P^V). − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 21.61 (q, P^V), 7.30 (d, P^V), 6.62 (d, 2 × P^V), $^3J_{PP}$ = 50.5 Hz. − MS (FAB); *m/z* (%): 1854 (35), 510 (100). − C$_{102}$H$_{102}$Fe$_4$N$_4$O$_8$P$_4$ (1859.14): calcd. C 65.89, H 5.53, N 3.01; found C 66.05, H 5.39, N 3.13.

Synthesis Complexes **13** *and* **14**. − *General Procedure:* To a cooled (−15°C) solution of monoiminophosphorane **2a** or **8** (0.367 mmol) in 15 ml of dry toluene, a solution of dichlorobis(benzonitrile)palladium(II) (0.14 g, 0.367 mmol) in 10 ml of the same solvent was added dropwise. The resulting mixture was stirred at this temperature for 10 h. The precipitated solid was collected by filtration and recrystallized from chloroform.

13: 94%, red prisms, m.p. 170−172°C. − IR (Nujol): ν = 1688, 1613, 1412, 1259, 1149, 1034 cm^{-1}. − ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.50−8.10 (m, 4 H), 7.75−6.88 (m, 16 H), 6.15 (d, 1 H, ^4J_P = 8.2 Hz, CH=C), 5.09 (br. s, 2 H, 2-H/5-H), 4.39 (s, 5 H, Cp), 4.18 (br. s, 2 H, 3-H/4-H), 3.82 (q, 2 H, ^3J = 7.1 Hz, CH_2CH$_3$), 3.55 (br. s, 2 H, CH$_2$P), 0.96 (t, 3 H, ^3J = 7.1 Hz, CH$_2$CH_3). − ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 44.23 (d), 14.16 (d), $^2J_{PP}$ = 29.6 Hz. − MS (FAB); *m/z* (%): 822 (37) [M$^+$ − Cl], 787 (100) [M$^+$ − 2 Cl], 681 (72), 666 (93). − C$_{40}$H$_{37}$Cl$_2$FeNO$_2$P$_2$Pd (859.15): calcd. C 55.94, H 4.34, N 1.63; found C 56.10, H 4.17, N 1.49.

14: 58%, orange prisms, m.p. 247−250°C. − IR (Nujol): ν = 1683, 1590, 1415 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 8.09−8.02 (m, 4 H), 7.77−7.67 (m, 4 H), 7.48−7.31 (m, 22 H), 6.47 (d, 1 H, ^4J_P = 8.7 Hz, CH=C), 5.06 (pseudo-t, 2 H, *J* = 1.6 Hz, 2-H/5-H), 4.96 (pseudo-t, 2 H, *J* = 1.6 Hz, 3-H/4-H), 4.16 (s, 5 H, Cp), 3.70 (q, 2 H, ^3J = 7.0 Hz, CH_2CH$_3$), 2.92 (d, 2 H, $^2J_{P(V)}$ = 10.7 Hz, CH$_2$P^V), 2.49 (d, 4 H, ^2J_P = 8.1 Hz, 2 × CH$_2$PPd), 2.42 (d, 2 H, $^2J_{P(III)}$ = 14.0 Hz, CH$_2$P^{III}), 0.91 (t, 3 H, ^3J = 7.0 Hz, CH$_2$CH_3), 0.14 (s, 3 H, CH$_3$C). − ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 168.17 (d, ^3J = 8.3 Hz, CO), 137.14 (d, ^1J = 103.3 Hz, C-1′), 135.67 (t, ^2J + ^4J = 11.5 Hz, C-2′′)*, 132.97 (d, ^2J = 7.5 Hz, CH=C), 132.38 (t, ^2J + 4*J* = 10.3 Hz, C-2′′)*, 130.22 (d, ^2J = 9.1 Hz, C-2′), 130.50 (d, *J* = 2.4 Hz, C-4′), 131.88 (C-4′′), 128.75 (t, ^2J + ^5J = 11.1 Hz, C-3′′), 128.39 (t, ^3J = 11.7 Hz, C-3′), 128.16 (t, ^2J + ^5J = 10.6 Hz, C-3′′), 118.51 (d, ^3J = 21.4 Hz, *C*H=C), 82.33 (C-1), 69.92 (C-2/C-5), 68.99 (Cp), 68.21 (C-3/C-4), 60.81 (*C*H$_2$CH$_3$), 45.79 (dt, $^1J_{P(V)}$ = 57.6 Hz, ^3J + ^5J = 9.5 Hz, CH$_2$P^V), 37.24 (dt, ^1J + ^3J = 18.5 Hz, $^3J_{P(V)}$ = 9.0 Hz, 2 × CH$_2$P), 39.20 (d, $^2J_{P(V)}$ = 3.6 Hz, *C*−CH$_3$), 28.15 (m, C−*C*H$_3$), 13.72 (CH$_2$*C*H$_3$). − ^{31}P NMR (CDCl$_3$): δ = 0.10 (s, P^V), 15.60 (s, PPd). − MS (FAB); *m/z* (%): 1099 (11) [M$^+$], 1063 (43) [M$^+$ − Cl], 1027 (37), 906 (46). − C$_{56}$H$_{54}$Cl$_2$FeNO$_2$P$_3$Pd (1099.43): calcd. C 61.19, H 4.95, N 1.27; found C 61.31, H 5.07, N 1.04.

X-ray Crystallographic Studies: Crystal data are given in Table 3. Crystals of **5d** suitable for X-ray diffraction were prepared by slow difussion of *n*-hexane in a dichloromethane solution. Slow concentration of a solution of compound **13** in chlroform affords crystals suitable for X-ray diffraction studies. Crystals of **13** · 2 CHCl$_3$ and **5d** were mounted in inert oil on a glass fibre and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). Measurements were made at −100°C using monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit-cell parameters were determined from a least-squares analysis of ca. 70 accurately centered reflections (10° < 2θ < 27°). Intensities were measured using ω scans. Absorption corrections were based on ψ scans. The structures were solved by direct methods (**13** · 2 CHCl$_3$) or by the heavy-atom method (**5d**) and refined anisotropically on F^2 (program SHELXL-93).[16] Hydrogen atoms were included using a riding model or as rigid methyl groups. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101187. Copies of the

Table 3. Crystal data for compounds **5d** and **13** · 2 $CHCl_3$

	5d	**13** · 2 $CHCl_3$
empirical formula	$C_{58}H_{58}Fe_2N_2O_4P_2$	$C_{42}H_{39}Cl_8FeNO_2P_2Pd$
M_r	1020.70	1097.53
a [Å]	10.401(1)	12.480(1)
b [Å]	11.327(2)	25.091(3)
c [Å]	11.199(2)	14.288(2)
α [°]	87.024(10)	90
β [°]	76.015(10)	93.776(10)
γ [°]	75.246(10)	90
Z	1	4
D [Mg/m^3]	1.369	1.633
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
crystal size [mm]	0.66 × 0.18 × 0.10	0.60 × 0.20 × 0.06
θ range [°]	3.12−25.00	3.22−25.00
reflections measured	5022	8805
independent reflections	4333	4453
μ [mm^{-1}]	0.701	1.316
max./min. transmission	0.746/0.793	0.792/0.699
parameters	308	514
F(000)	534	2208
max. Δρ [e Å^{-3}]	0.395	0.276
$R1$[a]	0.0338	0.0248
$wR2$[b]	0.0868	0.0462

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. − [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44(0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

[1] For selected recent references, see: K.-S. Gan, T. S. A. Hor, *Ferrocenes* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, **1995**, p 1.

[2] [2a] A. Yamaraki, T. Morimoto, K. Achiwa, *Tetrahedron: Asymmetry* **1993**, *4*, 2287−2290. − [2b] A. Mernyi, C. Kratky, W. Weissenteiner, M. Widhalm, *J. Organomet. Chem.* **1996**, *508*, 209−218.

[3] See for example: [3a] S. Hoppe, H. Weichmann, K. Jurkschat, C. Schneider-Koglin, M. Dräger, *J. Organomet. Chem.* **1995**, *505*, 63−72.

[3b] N. J. Goodwin, W. Henderson, J. K. Sarfo, *J. Chem. Soc., Chem. Commun.* **1996**, 1551−1552. − [3c] P. Barbaro, A. Togni, *Organometallics* **1995**, *14*, 3570−3573.

[4] [4a] H. C. L. Abbenhuis, U. Burckhardt, V. Gramlich, C. Köllner, P. S. Pregosin, R. Salzmann, A. Togni, *Organometallics* **1995**, *14*, 759−766. − [4b] M. Sawamura, H. Hamashima, M. Sugawara, R. Kuwano, Y. Ito, *Organometallics* **1995**, *14*, 4549−4558. − [4c] M. Sawamura, R. Kuwano, Y. Ito, *J. Am. Chem. Soc.* **1995**, *117*, 9602−9603. − [4d] N. C. Zanetti, F. Spindler, J. Spencer, A. Togni, G. Rihs, *Organometallics* **1996**, *15*, 860−866.

[5] [5a] T. B. Rauchfuss, J. L. Clements, S. F. Agnew, D. M. Roundhill, *Inorg. Chem.* **1977**, *16*, 775−778. − [5b] D. M. Roundhill, R. A. Bechtold, S. G. N. Roundhill, *Inorg. Chem.* **1980**, *19*, 284−289. − [5c] G. J. Organ, M. K. Cooper, K. Henrick, M. McPartlin, *J. Chem. Soc., Dalton Trans.* **1984**, 2377−2382. − [5d] M. C. Bonnet, B. Stitou, I. Tkatchenko, *J. Organomet. Chem.* **1985**, *279*, C1−C4. − [5e] H. Brunner, A. F. M. M. Rahman, *Chem. Ber.* **1984**, *117*, 710−724. − [5f] A. Breque, C. C. Santini, F. Mathey, J. Fischer, A. Mitschler, *Inorg. Chem.* **1984**, *23*, 3463−3467.

[6] [6a] J. P. Farr, M. M. Olmstead, F. E. Wood, A. L. Balch, *J. Am. Chem. Soc.* **1983**, *105*, 792−798. − [6b] J. P. Farr, M. M. Olmstead, A. L. Balch, *Inorg. Chem.* **1983**, *22*, 1229−1235. − [6c] A. L. Balch, *Homogeneous Catalysis with Metal Phosphine Complexes* (Ed: L. H. Pignolet), Plenum, New York, **1983**. − [6e] R. J. McNair, L. H. Pignolet, *Inorg. Chem.* **1986**, *25*, 4717−4723. − [6f] R. J. McNair, P. V. Nilsson, L. H. Pignolet, *Inorg. Chem.* **1985**, *24*, 1935−1939. − [7] [7a] W. J. Knebel, R. J. Angelici, *Inorg. Chem.* **1974**, *13*, 627−631 and 632−637. − [7b] W. J. Knebel, R. J. Angelici, O. A. Gansow, D. J. Darensbourg, *J. Organomet. Chem.* **1974**, *66*, C11−C13. − [7c] T. B. Rauchfuss, D. M. Roundhill, *J. Am. Chem. Soc.* **1974**, *96*, 3098−3105. − [7d] E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, *455*, 247−253. − [7e] G. P. C. M. Dekker, A. Buijs, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, W. J. J. Smeets, A. L. Spek, Y. F. Wang, C. H. Stam, *Organometallics* **1992**, *11*, 1937−1948.

[8] [8a] T. D. Appleton, W. R. Cullen, S. V. Evans, T.-J. Kim, J. Trotter, *J. Organomet. Chem.* **1985**, *279*, 5−21. − [8b] S. Park, D. Hedden, A. L. Rheingold, D. M. Roundhill, *Organometallics* **1986**, *5*, 1305−1311. − [8c] H.-H. Wang, A. L. Casalnuovo, B. J. Johnson, A. M. Mueting, L. H. Pignolet, *Inorg. Chem.* **1988**, *27*, 325−331. − [8d] M. P. Anderson, A. L. Casalnuovo, B. J. Johnson, B. M. Mattson, A. M. Mueting, L. H. Pignolet, *Inorg. Chem.* **1988**, *27*, 1649−1658. − [8e] K. V. Katti, R. G. Cavell, *Organometallics* **1989**, *8*, 2147−2153. − [8f] K. V. Katti, R. J. Batchelor, F. W. B. Einstein, R. G. Cavell, *Inorg. Chem.* **1990**, *29*, 808−814. − [8g] E. Shirakawa, Y. Murota, Y. Nakao, T. Hiyama, *Synlett* **1997**, 1143−1144. − [8h] H. Brunner, I. Deml, W. Dirnberger, B. Nuber, W. Reißer, *Eur. J. Inorg. Chem.* **1998**, 43−54. − [8i] E. K. van den Beuken, W. J. J. Smeets, A. L. Spek, B. L. Feringa, *J. Chem. Soc., Chem. Commun.* **1998**, 223−224.

[9] [9a] P. Molina, A. Pastor, M. J. Vilaplana, M. C. Ramírez de Arellano, *Tetrahedron Lett.* **1996**, 7829−7832. − [9b] P. Molina, A. Pastor, M. J. Vilaplana, M. D. Velasco, M. C. Ramírez de Arellano, *Organometallics* **1997**, *16*, 5836−5843.

[10] [10a] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 635−646. − [10b] Y. G. Gololobov, I. N. Zhmurova, L. F. Kasukhin, *Tetrahedron* **1981**, *37*, 437−472.

[11] [11a] J. Kiji, A. Matsumura, T. Haishi, S. Okazaki, J. Fukukawa, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2731−2733. − [11b] K. W. Katti, R. G. Cavell, *Inorg. Chem.* **1989**, *28*, 3033−3036. − [11c] M. V. Avis, M. E. van der Boom, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, *J. Organomet. Chem.* **1997**, *527*, 263−276.

[12] [12a] M. Sawamura, H. Hamashima, M. Sugawara, R. Kuwano, Y. Ito, *Organometallics* **1995**, *14*, 4549−4558. − [12b] D. A. Redfield, L. W. Cary, J. H. Nelson, *Inorg. Chem.* **1975**, *14*, 50−59. − [12c] A. W. Verstuyft, J. H. Nelson, L. W. Cary, *Inorg. Chem.* **1976**, *15*, 732−734.

[13] T. Seitz, A. Muth, G. Huttner, *Chem. Ber.* **1994**, *127*, 1837−1842.

[14] [14a] C. A. Ghilardi, P. Innocenti, S. Midollini, A. Orlandini, A. Vacca, *J. Chem. Soc., Dalton Trans.* **1995**, 1109−1113. − [14b] C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, A. Romerosa, R. Rossi, A. Vacca, *Organometallics* **1995**, *14*, 3203−3215.

[15] M. Alajarín, P. Molina, A. López-Lázaro, C. Foces-Foces, *Angew. Chem.* **1997**, *109*, 147−150; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 67−70.

[16] G. M. Sheldrick, *SHELXL-93*, University of Göttingen, **1993**.

[98075]