Organometallics **2000,** *19,* 4899−4903

Octaethyldiphosphaferrocene: An Efficient Ligand in the Palladium-Catalyzed Suzuki Cross-Coupling Reaction

Xavier Sava, Louis Ricard, François Mathey,* and Pascal Le Floch*

Laboratoire "Héteroéléments et Coordination", UMR CNRS 7653, Ecole Polytechnique,
91128 Palaiseau Cedex, France

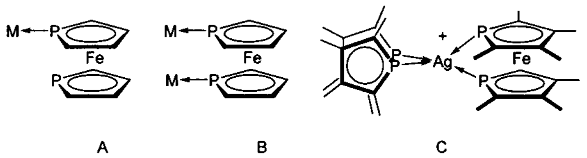
Received July 3, 2000

Syntheses of octaethyldiphosphaferrocene **4** and tetraethylphosphaferrocene **5** are presented. Tetraethylzirconacyclopentadiene **1** reacts with PCl_3 in dichloromethane to yield the 1-chlorotetraethylphosphole **2**, which upon reduction by lithium in excess, yields the teraethylphospholide anion **3**. Anion **3** was subsequently converted into **4** or **5** by treatment with $FeCl_2$ or with $[Fe(\eta^6\text{-}C_9H_{12})(\eta^5\text{-}C_5H_5)][PF_6]$ respectively. The structure of diphosphaferrocene **4** was determined. Two conformations are present in the cell: a C_2 conformation ($\alpha = 51.1°$) in which the P atom of each ring is located above the α-carbon atom of the other ring, and a C_{2h} conformation ($\alpha = 180°$) in which P atoms point in opposite directions. Reaction of ligand **4** with $[Pd(dba)_2]$ yields the bis(octaethyldiphosphaferrocene)palladium(0) complex **6**. An X-ray crystallographic study reveals that the overall geometry around palladium is nearly tetrahedral and that both ligands, whose geometry is not significantly perturbed, adopt a bridging mode involving a side-on coordination of the lone pairs. Complex **6** behaves as an efficient catalyst for the coupling reaction between phenylboronic acid and 4-bromoacetophenone in refluxing toluene. A conversion of 98% was obtained with 1×10^{-4}% of catalyst (TON = 9.80×10^5). The catalytic activity of **6** in coupling reactions between phenylboronic acid and 3-bromothiophene, 2-bromoanisole, and bromobenzene was also investigated.

Introduction

There is a continuing interest in the chemistry of phosphaferrocenes because of their use as ligands in homogeneous catalysis.[1] Many reports have emphasized the unique combination between their strong π-acceptor properties, which makes them attractive ligands for soft catalytic centers, and the planar-chiral type structure provided by the ferrocene backbone.[2] On the other hand, diphosphaferrocenes have attracted much less attention so far, and to the best of our knowledge, no report deals with their use as ligands in catalytic processes. Three bonding modes of phosphaferrocenes are known (Chart 1). Classical modes A and B, in which the ligand binds one or two metals, are by far the most widespread. Interestingly, only one example of the chelate mode C is known. In 1993, Cowley et al. reported the X-ray structure of a bis-chelate silver complex of the octamethyldiphosphaferrocene which was obtained by an electrochemical oxidation of the ligand on a silver anode.[3]

Chart 1



Assuming that the nondirectional coordination of the lone pairs would probably activate the metallic center by weakening P−metal bonds, we launched a program aimed at studying syntheses and reactivities of these diphosphaferrocene chelate complexes. In this article, we report on results obtained with palladium(0) complexes.

Results and Discussion

A first series of experiments conducted with the readily available 3,3′,4,4′-tetramethyldiphosphaferrocene showed that the substitution scheme of the ligand plays a decisive role in the formulation of complexes. Whatever the experimental conditions used, reactions of this ligand with $Pd(dba)_2$ exclusively led to the isolation of highly insoluble black compounds, most probably polymeric. To improve the solubility of complexes formed, we investigated the use of octa-alkyl-substituted derivatives. Two synthetic approaches are available for the synthesis of 1-*P* chloro and 1-*P* phenyl

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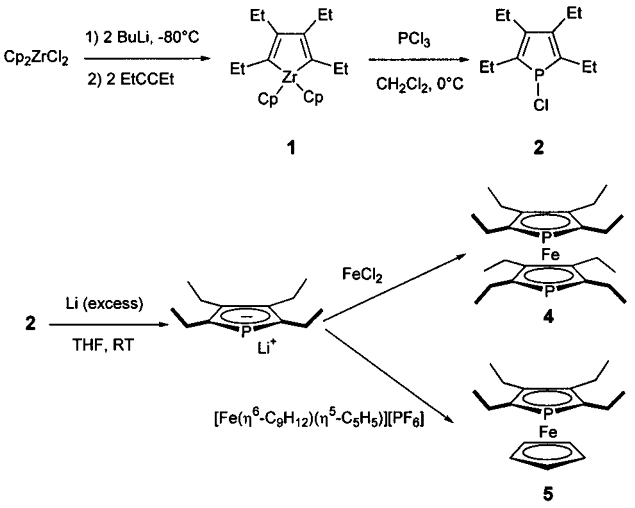
10.1021/om0005699 CCC: $19.00
Publication on Web 10/21/2000

Scheme 1



tetramethyl derivatives of phosphole: an aluminum-mediated route[4] and the classical metallacycle transfer reaction from the corresponding zirconacyclopentadiene complex,[5] a methodology that proved to be successful for syntheses of various group 14, 15, and 16 heteroles.[6] This second approach was preferred using hexyne as starting alkyne. The synthesis of diphosphaferrocene **4** was achieved via a two-step sequence. The first step is the synthesis of 1-chloro-tetraethylphoshole **2** from the tetraethylzirconacyclopentadiene **1**[7] (prepared according to Negishi's procedure)[8] using PCl$_3$ as transfer reagent. Phosphole **2** is highly moisture sensitive and was characterized only by NMR techniques. Its data compare with those reported for the tetramethyl derivative.[5] In the second step, **2** was reacted with an excess of lithium to yield the phospholide anion **3** (characterized only by ^{31}P NMR), which subsequently converted into diphosphaferrocene upon reaction with FeCl$_2$ as depicted in Scheme 1. We also investigated the synthesis of the tetraethylphosphaferrocene **5**. Reaction of phospholide **3** with the commercially available (cumene)-cyclopentadienyliron(II) hexafluorophosphate salt yielded **5** in satisfactory yield (Scheme 1). All NMR data, mass spectroscopy, and elemental analyses support formulation proposed in both cases.

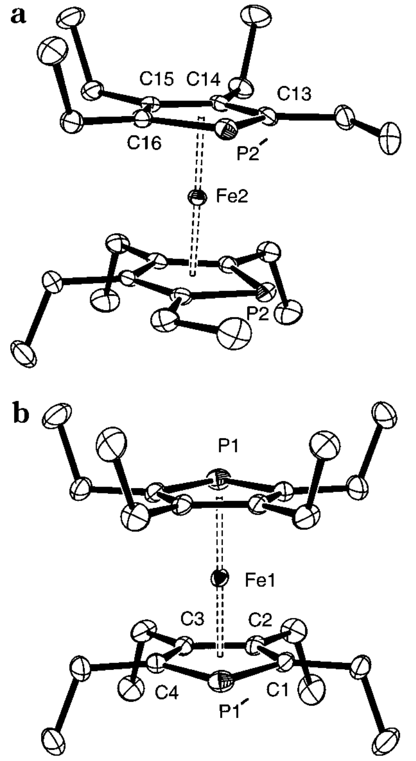


Figure 1. ORTEP drawings of the (a) C_2 and (b) C_{2h} conformation of **4**. Hydrogen atoms are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignments of ^{13}C NMR spectrum.

Definite proof of the structure of diphosphaferrocene **4** was given by an X-ray crystallographic study. Two different conformations are present in the unit cell: a C_2 conformation in which the P atom of each ring nearly eclipses the carbon adjacent to the P atom of the other ring ($\theta = 51.1°$) and a C_{2h} conformation in which the two P atoms point in opposite directions ($\theta = 180°$). The presence of these two conformations[9] lead us to propose that the barrier to rotation is probably very weak as usually observed.[9h] Another interesting feature is the location of two ethyl substituents located at the Cα carbon atoms in conformer C_2. As can be seen in Figure 1, one methyl group of a Cα ethyl substituent of each phospholyl subunit is coplanar, probably to relieve congestion with its direct ethyl neighbor. These particular structural arrangements are not maintained in solution, and NMR spectra (^{31}P, ^{1}H, ^{13}C) show that both phosphorus atoms and ethyl groups are magnetically equivalent. Apart from these particular details, the structure of **4** deserves no special comment, and bond distances and angles are quite similar in both conformations and compare with those reported for other diphosphaferrocenes.[9] One ORTEP view of each of these two conformation is presented in Figure 1, whereas the most relevant bond distances and bond angles are listed in Table 1.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ligand 4

Conformation C_{2h}			
P1′–C1	1.778(2)	P1′–C4	1.773(2)
C1–C2	1.418(2)	Ct–Fe	1.656(2)
C2–C3	1.445(2)	C1–P1′–C4	89.83(7)
C3–C4	1.426(2)		
Conformation C_2			
P2′–C13	1.783(2)	C16–P2′	1.782(1)
C13–C14	1.431(2)	Ct–Fe	1.662(2)
C14–C15	1.432(2)	C13–P2′–C16	89.92(7)
C15–C16	1.430(2)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 6

P1–C1	1.787(2)	Pd1–Fe1	3.0382(3)
C1–C2	1.424(3)	Pd1–Fe2	3.0573(3)
C2–C3	1.434(3)	C1–P1–C4	89.4(1)
C3–C4	1.424(3)	P1–Pd1–P2	100.18(2)
C4–P1	1.790(2)	P3–Pd1–P4	99.63(2)
P1–Pd1	2.3852(6)	P1–Pd1–P4	108.95(2)
P2–Pd1	2.3667(6)	P2–Pd1–Pd3	105.15(2)
P3–Pd1	2.3680(6)	P4–Pd1–P2	122.05(2)
P4–Pd1	2.3615(6)	P1–Pd1–P3	122.52(2)
Ct–FeI	1.684(3)		

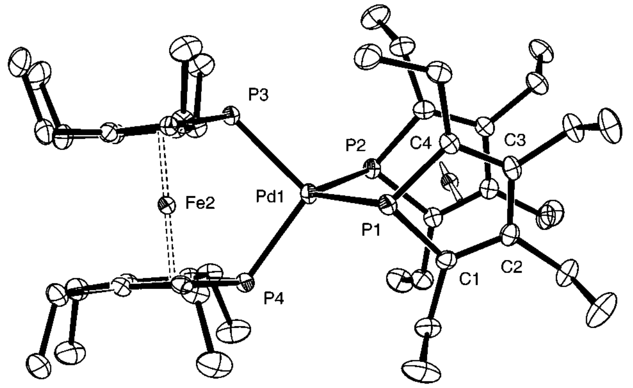
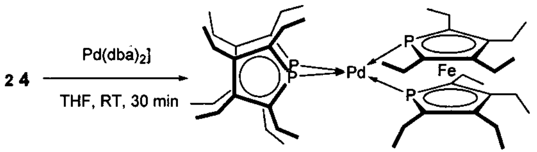


Figure 2. ORTEP drawing of one molecule of **X**. Hydrogen atoms and methyl groups are omitted for clarity. Ellipsoids are scaled to enclose 50% of the electron density. The crystallographic labeling is arbitrary and different from the numbering used for assignments of ^{13}C NMR spectra.

Scheme 2



6

The coordinating behavior of ligand **4** toward Ni and Pd(0) precursors was then investigated. In the case of Ni complexes best results were obtained using [Ni(COD)$_2$] as starting material. In THF at room temperature, with 2 equiv of **4**, a clean exchange takes place leading to the formation the bis(octaethyldiphosphaferrocene) nickel(0) complex. Unfortunately this species turned out to be too oxygen sensitive to be isolated in satisfactory yields, and characterizations were limited to ^{31}P NMR data (singlet, δ (THF) = -107.9 ppm). More convincing results were obtained with Pd complexes. The reaction of 2 equiv of **4** with [Pd(dba)$_2$] (dba = dibenzylidene acetone) in THF at room temperature yielded complex **6**, which was isolated as a green powder (see Experimental Section) (Scheme 2). The formulation of **6** was unambiguously established on the basis of NMR data. The most surprising feature is given by the ^{31}P NMR chemical shift, which is highly shielded ($\delta = -125.5$, $\Delta\delta = 59.5$ ppm) compared to other diphosphaferrocene complexes. Unfortunately, no comparison could be drawn with the isoelectronic Ag$^+$ chelate species since NMR data were not reported.[3]

The molecular structure of complex **6** was confirmed by X-ray crystallography. An ORTEP view of **6** is presented in Figure 2. Most significant bond distances and bond angles are listed in Table 2. As expected for a d^{10} complex, the overall geometry around palladium is nearly tetrahedral ($\theta = 77.3$, θ being the angle between planes $P_1{-}Pd_1{-}P_2$ and $P_3{-}Pd_1{-}P_4$). Like in the Ag$^+$ complex, both ligands act as chelate and the deviation from the ideal in-plane coordination of the lone pair at phosphorus is very important ($\theta = 50°$). This particular bonding implies that P–Pd–P angles are unusually large (about 100°) compared with those of complexes with classical phosphorus bidentate ligands. Though no theoretical calculations have been carried out yet, one may propose that this type of nondirectional bonding mode is probably very specific of molecules containing sp^2-hybridized phosphorus atoms. Indeed, in such compounds, as well as in their heavier congeners (As, Sb, Bi), the lone pair at the heteroatom shows a pronounced spherical character due to a less favored orbital mixing between 3s and 3p orbitals than between 2s and 2p as in nitrogen compounds.[10] A similar nondirectional bonding mode has already been observed in a 2,2′-biphosphinine Cu(I) complex.[11] This particular electronic situation complicates the analysis of P–Pd bond distances, and comparisons with other known complexes involving a classical axial bonding would be inappropriate. Nevertheless, at 2.3815(6)–2.3852(6) Å, these bonds appear to be quite long. Another interesting question concerns the possible existence of a Pd–Fe dative bonding between nonbonding orbitals at iron and vacant orbitals of similar symmetry at the metal, as frequently observed in ferrocene derivatives.[12] Although there is a close analogy between MO diagrams of both compounds[9a] (degenerated e_{2g} in ferrocenes, $d_{x^2-y^2}$ and d_{xy} in diphosphaferrocenes), the fact that Pd–Fe bond distances in **6** (3.0282(3) and 3.0273 (3) Å) appear to be quite long and that no orbitals at the metal (d^{10}) are available leads us to propose that such interactions are not found here.

A chemical consequence of this particular bonding situation is that ligand **4** is not a very efficient chelate. Thus, when bidentate ligands such as dppe or dppp are reacted with complex **6**, the two ligands **4** are displaced and [Pd(dppe)$_2$] or [Pd(dppp)$_2$] is formed quantitatively (eq 1).

These very particular features led us to postulate that diphosphaferrocene **4** would certainly behave as a

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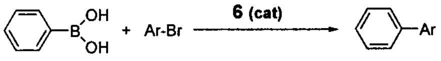
$$\mathbf{6} \xrightarrow[\text{THF, RT}]{2\,L_2} 2\,\mathbf{4} + Ni(L_2)_2 \qquad (1)$$

$$L_2 = \text{dppe, dppp}$$

hemilabile ligand in complex **6**. We therefore attempted to test its catalytic activity on the catalyzed Suzuki cross-coupling reaction,[13] which has been thoroughly studied with various palladium−phosphines systems.[14] As a model reaction, we first investigated the coupling between phenylboronic acid and 4-bromoacetophenone in the presence of K_2CO_3 as base (eq 2).



(2)

Ar = 4-MeCO-C_6H_4, 3-thienyl,
2-Me0-C_6H_4, C_6H_5.

All our experiments were conducted in toluene, as usually experimented by other authors. Various experimental conditions were tested, and the best results were obtained when preparing separately complex **6** and adding it to the mixture of arenes (see Experimental Section). Complex **6** was indeed very efficient as catalyst, and a reproducible conversion of 77% to 4′-acetylbiphenyl was obtained using 1×10^{-4}% of Pd catalyst at 110 °C for 1 h (TON = 7.70×10^5, TOF = 213.9 (mol product(mol Pd)$^{-1}$ s^{-1}). Prolonged heating for 20 h led to a nearly quantitative conversion under the same conditions. Although less effective than the remarkable *o*-(*tert*-butylphosphino)biphenyl/Pd(OAc)$_2$ system recently developed by Buchwald et al.[14a] (TON = 9.1×10^7 for the same reaction, 24 h heating), our result approaches the second highest TON reported by Bedford using the tris(2,4-di-*tert*-butylphenyl)phosphite (TON = 8.70×10^5 for 1 h reaction).[14c] As stated by other authors, the coupling between phenylboronic acid and 4′-bromoacetophenone efficiently proceeds and generally leads to high turnovers. Consequently, we extended our study to the coupling of phenylboronic acid to other substrates such as 3-bromothiophene, 2-bromoanisole, and bromobenzene (eq 2).

Also in these cases, high TONs were recorded (for 1 h reaction), thus demonstrating the versatility of our system. Results of these catalytic tests are summarized in Table 3.

Table 3. Suzuki Coupling of Aryl Bromides[a]

aryl bromide	mol % Pd	*t*/h	conversion (%)	TON
4-bromoacetophenone	0.0001	1	77	770 000
4-bromoacetophenone	0.0001	20	98	980 000
3-bromothiophene	0.005	1	80	16 000
3-bromothiophene	0.005	20	96	19 200
2-bromoanisole	0.005	1	67	13 400
2-bromoanisole	0.005	20	96	19 200
bromobenzene	0.0001	1	46	460 000

[a] Reaction conditions: 1.0 equiv of aryl bromide, 1.5 equiv of phenylboronic acid, 2.0 equiv of K_2CO_3. Temperature: 110 °C. TON are expressed in mol product (mol Pd)$^{-1}$.

The efficiency of complex **6** is difficult to rationalize without knowing the nature of the active species. Three intermediates are plausible: 14-electron complexes [Pd(**4**)$_2$] and [Pd(**4**)], in which the ligand coordinates palladium either through the lone pair of one P atom (η^1) or in a chelate fashion, respectively, and a 12-electron complex [Pd(**4**)] involving the axial-coordination of only one phosphorus atom. Recently, Fu et al. proposed that the bulkiness of P(t-Bu)$_3$[15,16] favors the formation of the 12-electron species [PdP(t-Bu)$_3$], which can be considered as the active species in the Suzuki cross-coupling reaction of arylboronic acid with aryl and vinyl halides and triflates. [14i]

In conclusion, we anticipate that diphosphaferrocene chelate complexes may display quite an unusual catalytic chemistry due to their unique combination between electronic properties and geometry. Investigations aimed at expanding the use of complexes such as **6** in catalyzed C_{sp2}−C_{sp2} bond formation processes as well as in other catalytic transformations of importance are currently underway in our laboratories.

Experimental Section

General Procedures. All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Dry hexanes was obtained by distillation from Na/benzophenone and dry CH_2Cl_2 from P_2O_5. Dry Celite was used for filtration. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. Mass spectra were obtained at 70 eV with a HP 5989 B spectrometer coupled a with HP 5890 chromatograph by the direct inlet method. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed by the "Service d'Analyse du CNRS", at Gif sur Yvette, France. [Pd(dba)$_2$] was prepared according to a published procedure.[17]

Tetraethyl-1-chlorophosphole (2). To a cooled (0 °C) dichloromethane (50 mL) solution of complex **1** (5.78 g, 15 mmol) was added via a syringe 3.4 mL of phosphorus trichloride (15 mmol). The solution was allowed to warm, and the formation of **2** was monitored by ^{31}P NMR. After 20 min the transformation was completed. After evaporation to dryness, hexane (30 mL) was added and the resulting solution was filtered over dried Celite. No further purification was undertaken, and phosphole **2** was isolated as a highly moisture sensitive yellow oil. Yield: 3.35 g (96%). ^{31}P NMR (CDCl$_3$): δ 73.4. ^{1}H NMR (CDCl$_3$): δ 1.05 (t, 6H, ^3J(H−H) = 7.60, 2 × CH$_3$), 1.19 (t, 6H, ^3J(H−H) = 6.50, 2 × CH$_3$), 2.31 (m, 4H, 2 × CH$_2$), 2.47 (m, 4H, 2 × CH$_2$). ^{13}C NMR (CDCl$_3$): δ 15.05 (d, ^4J(P−C) = 4.6, Me), 16.65 (d, ^3J(P−C) = 6.2, Me), 21.05 (d, ^2J(P−C) = 21.4, CH$_2$), 22.25 (s, CH$_2$), 144.55 (d, ^1J(P−C) =

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[16] This value does not represent the genuine cone angle but the "cone" swept out by ligand **4** when it rotates around the P−Pd bond, which was approximated to 2.25 Å.

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21.2, $C_{2,5}$), 150.35 (d, ^2J(P−C) = 11.4, $C_{3,4}$). MS (EI, *m/z* (ion, relative intensity)): 230 (M^+).

Octaethyl-1,1′-diphosphaferrocene (4). To a solution of chlorophosphole **2** (3.35 g, 14.5 mmol) in 50 mL of THF was added about 3 equiv of lithium wire (0.3 g). The formation of phospholide anion **3** was then monitored by ^{31}P NMR. After 1 h, 0.5 equiv of anhydrous iron dichloride (0.9 g, 7.2 mmol) was added at room temperature to the resulting red solution. The mixture was then allowed to stir for 30 min at 30 °C to help completion. The volume of solvents was then strongly reduced to about 5 mL, and salts were precipitated by addition of 20 mL of hexanes. After filtration over dried Celite and evaporation of the volatiles, the mixture was quickly purified by silica gel flash chromatography using a 90:10 hexanes/dichloromethane mixture. After evaporation of solvents, complex **4** was isolated as an orange-red powder. Yield: 2.65 g (81%). ^{31}P NMR ($CDCl_3$): δ −66.0. ^{1}H NMR ($CDCl_3$): δ 1.08 (t, 12H, ^3J(H−H) = 7.60, 4 × CH_3), 1.09 (t, 12H, ^3J(H−H) = 7.50, 4 × CH_3), 2.00 (m, 8H, 2 × CH_2), 2.32 (m, 4H, 4 × 1H of CH_2), 2.58 (m, 4H, 4 × 1H of CH_2). ^{13}C NMR ($CDCl_3$): δ 16.65 (s, Me), 18.90 (m, Me), 21.40 (s, CH_2), 22.65 (m, CH_2), 100.40 (s, $C_{3,4}$), 102.20 (d, ^1J(P−C) = 55.9, $C_{2,5}$). MS (CI, *m/z* (ion, relative intensity)): 446 (M^+). Anal. Calcd for $C_{24}H_{40}Fe_1P_2$: C, 64.58; H, 9.03. Found: C, 64.80; H, 9.25.

Tetraethyl-1-monophosphaferrocene (5). The preparation of the phospholide anion **3** was carried out as described above, starting from 2.76 g of chlorophosphole **2** (12.0 mmol). After checking the univocal formation of **3**, 1 equiv of iron(II) cyclopentadienyl cumene hexafluorophosphate salt (4.6 g, 12.0 mmol) was added at room temperature. The mixture was then allowed to stir for 30 min at 35 °C to help completion. The volume of solvents was then strongly reduced to about 5 mL, and salts were precipitated by addition of 30 mL of hexanes. After filtration over dried Celite and evaporation of the volatiles, the mixture was purified by silica gel flash chromatography, using a 95:5 hexane/dichloromethane mixture. After evaporation of the volatiles, complex **5** was obtained as a red powder. Yield: 2.70 g (71%). ^{31}P NMR ($CDCl_3$): δ −74.9. ^{1}H NMR ($CDCl_3$): δ 1.14 (t, 12H, ^3J(H−H) = 7.50, 2 × CH_3), 2.20 (m, 4H, 2 × CH_2), 2.54 (m, 2H, 2 × 1H of CH_2), 2.77 (m, 2H, 2 × 1H of CH_2). ^{13}C NMR ($CDCl_3$): δ 16.70 (s, Me), 17.59 (d, ^3J(P−C) = 11.2, Me), 23.05 (s, CH_2), 23.70 (d, ^2J(P−C) = 18.4, CH_2), 99.50 (s, $C_{3,4}$), 100.10 (d, ^1J(P−C) = 53.8, $C_{2,5}$). MS (CI, *m/z* (ion, relative intensity)): 316 (M^+). Anal. Calcd for $C_{17}H_{25}FeP$: C, 64.57; H, 7.97. Found: C, 64.75; H, 7.85.

Bis(octaethyldiphosphaferrocene)palladium(0) Complex (6). To a solution of diphosphaferrocene **4** (89 mg, 0.2 mmol) in 5 mL of THF was added 0.5 equiv of $[Pd(dba)_2]$ (57 mg, 0.1 mmol). After 30 min stirring, the solution turned green. The volatiles were evaporated, and dibenzylilidene acetone was extracted with acetonitrile (3 mL). Complex **6** was isolated as a green powder. Yield: 80 mg (80%). ^{31}P NMR (C_6D_6): δ −125.20. ^{1}H NMR (C_6D_6): δ 1.20 (t, 24H, ^3J(H−H) = 7.10, 8 × CH_3), 1.22 (t, 24H, ^3J(H−H) = 7.00, 8 × CH_3), 1.40 (m, 8H, 8 × 1H of CH_2), 1.97 (m, 8H, 8 × 1H of CH_2), 2.04 (m, 8H, 8 × 1H of CH_2), 2.35 (m, 8H, 8 × 1H of CH_2). ^{13}C NMR (C_6D_6): δ 17.50 (s, Me), 20.40 (s, Me), 21.60 (m, CH_2), 22.05 (s, CH_2), 99.85 (m, $C_{2,5}$), 100.90 (s, $C_{3,4}$). Anal. Calcd for $C_{48}H_{80}Fe_2P_4Pd$: C, 57.70; H, 8.07. Found: C, 57.58; H, 8.13.

General Procedure for Catalytic Cross-Coupling Reactions. Coupling of 4-Bromoacetophenone with Phenylboronic Acid. In a Schlenk flask under inert atmosphere were added 2 equiv of octaethyldiphosphaferrocene (8.9 mg, 2 × 10^{-2} mmol) in 20 mL of toluene and 1 equiv of $Pd(dba)_2$ (5.7 mg, 10^{-2} mmol). The solution was allowed to stir for 1 h. With a microsyringe, 20 μL of this solution was poured in 30 mL of toluene in a separate Schlenk flask. Then were successively added 2.0 g (10 mmol) of 4-bromoacetophenone, 1.83 g (15 mmol) of phenylboronic acid, and 2.76 g (20 mmol) potassium carbonate. The mixture was then allowed to stir for 1 h, at 110 °C.

Table 4. Crystallographic Data and Experimental Parameters for 4 and 6

	4	6
molecular formula	$C_{24}H_{40}FeP_2$	$C_{62}H_{96}Fe_2P_4Pd$
molecular wt	446.35	1183.37
cryst description (habit/size (mm))	orange cube (0.20 × 0.20 × 0.20)	deep green needle (0.18 × 0.14 × 0.10)
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
a (Å)	16.7440(5)	12.6860(4)
b (Å)	8.9870(2)	14.9980(4)
c (Å)	31.9560(11)	16.8110(5)
α (deg)	90.0000(17)	103.7540(14)
β (deg)	101.2270(16)	97.6040(13)
γ (deg)	90.0000(17)	11.3291(15)
V (Å^3)	4716.7(2)	2808.13(14)
Z	8	2
d (g cm^{-3})	1.257	1.400
F(000)	1920	1252
μ (cm^{-1})	0.782	0.980
T (K)	150.0(1)	150.0(1)
max θ (deg)	30.04	30.04
hkl ranges	0 23; 0 12; −44 44	0 17; −21 19; −23 23
no. of reflns measd	23 052	25 704
no. of indep reflns	5537	16 294
no. of reflns used	5080	12 808
R_{int}	0.032	0.027
refinement type	F^2	F^2
hydrogen atoms	mixed	mixed
no. of params refined	260	638
Flack parameter	not applicable	not applicable
reflns/params	19	20
wR2	0.1228	0.0952
R1	0.0380	0.0392
criterion	$>2\sigma$(I)	$>2\sigma$(I)
GOF	1.052	1.026
difference peak/hole (e Å^{-3})	0.311 (0.060)/ −0.288 (0.060)	1.632 (0.084)/ −1.996 (0.084)

Coupling Reactions of 2-Bromoanisole, 3-Bromothiophene, and Bromobenzene with Phenylboronic Acid. The same procedure was employed, with identical molar equivalents and temperature. Only the volume of the Pd complex solution taken and time of reaction were adapted.

X-ray Crystal Structure Determinations. Crystals of **4** were obtained by cooling a hexane solution of the compound at −20 °C and crystals of **6** by a slow diffusion of hexanes into a dichloromethane solution of the complex at room temperature. Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 4. The crystal structures were solved using SIR 97[18] and SHELXL-97.[19] ORTEP drawings were made using ORTEP III for Windows.[20]

Acknowledgment. The authors are grateful to the CNRS and the Ecole Polytechnique for financial support of this research.

Supporting Information Available: Listings containing tables of crystal data, atomic coordinates and equivalent isotropic parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen coordinates for structures of compounds **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0005699

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