Organometallics **2004,** *23,* 4585−4593 4585

Ferrocene-Based Pincer Complexes of Palladium: Synthesis, Structures, and Spectroscopic and Electrochemical Properties

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Received April 13, 2004

Palladium P,C,P pincer complexes based on ferrocene were synthesized for the first time. The reaction of the 1,3-bis((dialkylphosphino)methyl)ferrocenes $\{1,3\text{-}(R_2PCH_2)_2C_5H_3\}Fe(C_5H_5)$ (**2a**, R = Pr^i; **2b**, R = Bu^t) with $PdCl_2(NCPh)_2$ in refluxing 2-methoxyethanol leads to the corresponding pincer complexes $PdCl[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**3a**,**b**). The ferrocene-based binuclear compound **3b** reacts with $[Cp_2Fe]PF_6$ to form the ferrocenium-based pincer complex $\{PdCl[\{2,5\text{-}(Bu^t{}_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}PF_6$ (**4b**), and this is the first example of ferrocene-based phosphine chelate oxidation centered on the iron atom. Treatment of complexes **3a**,**b** with $NaBH_4$ in refluxing ethanol affords the complexes $Pd(BH_4)[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**5a**, R = Pr^i; **5b**, R = Bu^t), containing a BH_4^- group coordinated to the metal in the rarely occurring unidentate mode. The structures of **3a**,**b** and **5b** were confirmed by X-ray analyses. Cyclic voltammetric investigations of complexes **2b** and **3a**,**b** are also reported. The structural and spectroscopic features of the palladium ferrocene-based pincer complexes are discussed and compared with those of related compounds.

Introduction

Transition-metal complexes with tridentate monoanionic ligands, so-called "pincer" ligands,[1] of general formula $[2,6\text{-}(ECH_2)_2C_6H_3]^-$, where E is a neutral two-electron donor such as NR_2, PR_2, AsR_2, OR, or SR, show interesting and rich chemistry.[2] The first pincer complexes were synthesized on a base of 1,3-bis((di-*tert*-butylphosphino)methyl)benzene by Moulton and Shaw[3] as early as 1976, but interest and activity in this area have rapidly increased, especially during the past decade. The presence of one metal−carbon σ bond and two chelating donor atoms are responsible for the high thermal stability of pincer complexes. The highly protective environment for the multiply bound metal and possibilities to tune the properties of the metal center gave impetus to extensive research on the use of pincer complexes as homogeneous catalysts,[2] as well as crystalline switches and sensors.[2c]

Pincer complexes catalyze various transformations of organics, such as Kharasch addition,[4] Heck olefin arylation,[5] Suzuki aryl coupling,[6] enantioselective aldol type condensation of methyl isocyanoacetate and aldehydes,[7] transfer hydrogenation of ketones,[8] polymerization of phenylacetylene,[9] and alkane dehydrogenation.[2d,10] It is remarkable that palladium P,C,P pincer

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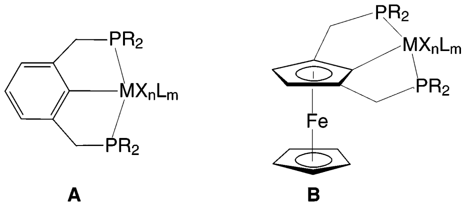
10.1021/om0497285 CCC: $27.50
Publication on Web 08/31/2004

Chart 1



A **B**

complexes catalyze the Heck reaction with turnover numbers (TON) as high as 500 000.[5a] Hydridoiridium P,C,P pincer complexes proved to be the most active (TON up to 1200) among all known homogeneous catalysts for alkane dehydrogenation.[10e]

Although impressive progress has been achieved in this area, the majority of pincer complexes have not find industrial applications for a variety of reasons. For example, the reaction rates are still insufficient, asymmetric aldol addition gives only moderate (65%) ee's of the product, the rates of alkane dehydrogenation by iridium complexes are also insufficient, and product inhibition and isomerization of the primarily formed 1-alkenes into internal isomers take place.

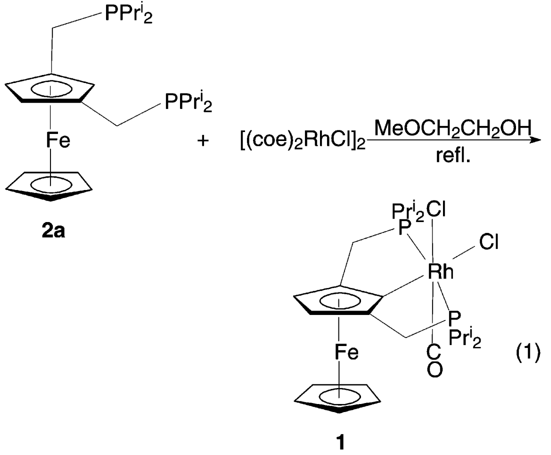
It is obvious that a search for approaches to the design of novel pincer complexes is a topical problem. One way of solving this problem is to substantially modify the pincer ligand, including a change of its electronic and steric properties.

It is rather remarkable that there have been no reports until recently on attempts to design pincer complexes based on aromatic homocyclic systems other than benzene: viz. the cyclopentadienyl ring of metallocenes. At the same time, the design of conceptually novel bimetallic pincer systems based on metallocene seems to be very attractive. We believe that metallocene-based pincer complexes of type **B** could possess electronic and steric features which distinguish them from their benzene analogues **A** and are attractive from the viewpoint of their use in catalysis (Chart 1).

These features are as follows.[11] First, the central atom of the metallocene unit in metallocene-based pincer complexes is located in the vicinity (β-position) of the catalytic center, the chelated metal atom M; this arrangement can facilitate tuning of electronic effects on the atom M by varying the metallocene central atom (Fe, Ru, and Os). Second, the iron atom in ferrocene can be involved in a rapid and reversible redox reaction, thus providing an additional possibility to tune the electron density at the catalytic center. Third, the sandwich nature of ferrocene allows one to design *planar-chiral* molecules (the known benzene-based P,C,P chiral ligands usually possess elements of *central chirality at the benzylic positions*, which are remote from the catalytic center M), in which the chirality of the P,C,P' ligand results from the presence of different substituents at the P donor atoms; the presence of the $Fe(C_5H_5)$ fragment provides the additional possibility of tuning the stereochemistry around the catalytic center. This may prevent isomerization of 1-alkenes, primary products of the iridium-catalyzed alkane dehydrogenation, into less valuable internal alkenes. It should be also noted that the iron group metallocenes possess high thermal stability.

The possibility of designing metallocene-based P,C,P pincer complexes was not evident, since the P donor atoms in 1,3-bis((diorganylphosphino)methyl)metallocenes are more remote from each other as compared to those in the benzene analogues. Metallocene-based pincer complexes might be expected to be formed only at the expense of a deviation of the bond angles at the C(2) and C(5) centers in pincer complexes from the standard value of 126° for the cyclopentadienyl ring.

In early 2002, we published[11] preliminary results on the synthesis and X-ray structure of the first representative of ferrocene-based P,C,P pincer complexes, the rhodium derivative *cis*-$RhCl_2(CO)[\{2,5\text{-}(Pr^i{}_2PCH_2)_2C_5H_2\}\text{-}Fe(C_5H_5)]$ (**1**) (eq 1).



(1)

Simultaneously, van Koten, Brown, and co-workers[12] published a brief report on the synthesis of the rhodium pincer complex $RhH(Cl)[\{2,5\text{-}(Bu^t{}_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (a mixture of *endo*- and *exo*-H isomers). Thus, it was demonstrated that it is possible to synthesize metallocene-based pincer complexes. As expected, the X-ray diffraction study of complex **1** revealed that the formation of the metallocene-based complex led to a decrease (by ~5°) of the bond angles at C(2) and C(5) atoms in fused metallacycles as compared to the standard value.[11] The formation of complex **1** gave impetus to a further search for procedures for the synthesis of precursors of metallocene-based pincer ligands such as P,CH,P and P,CH,N,[11] and hydridoiridium P,C,P pincer complexes based on ferrocene and ruthenocene.[13a,b]

Our interest in the generation of metallocene-based pincer complexes was stimulated by the reports of Kaska, Jensen, and Goldman with co-workers on the extraordinary catalytic activity of iridium pincer com-

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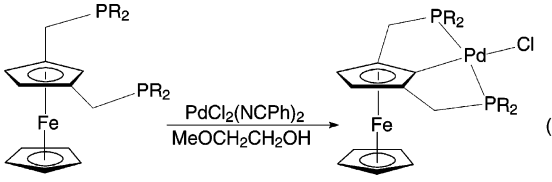
plexes $IrH_2[2,6\text{-}(R_2PCH_2)_2C_6H_3]$ (R = Bu^t, Pr^i) in alkane dehydrogenation.[10f,g] It seemed extremely interesting to produce metallocene-based analogues of these complexes, $IrH_2[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}M'(C_5H_5)]$ ($IrH_2[^RP,C,P^{M'}$; M′ = Fe, Ru),[13a,b] and to evaluate their properties as catalysts for the dehydrogenation of alkanes and organics containing alkyl groups. Since accessibility of the catalytic center for substrates is one of the most important factors in catalysis, it was desirable to possess X-ray structural data on the steric environment of the Ir atom in metallocene-based hydridoiridium complexes. Unfortunately, we failed to prepare single crystals of the complexes $IrH_2[^RP,C,P^{M'}]$ and $IrH_4[^RP,C,P^{M'}]$ suitable for an X-ray diffraction study. For this reason, we have initiated the study of the chloropalladium complexes $PdCl[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**3a**, R = Pr^i; **3b**, R = Bu^t) as model compounds. In addition, complexes **3a**,**b** are of independent interest as potential catalysts for the Heck and related carbon−carbon coupling reactions.

This account represents the first full paper on metallocene-based P,C,P pincer complexes of platinum-group metals and includes details of the synthesis of ferrocene-based P,CH,P diphosphines, P,C,P pincer complexes of palladium, their crystal structures, and spectroscopic and redox properties. Some of these results have been published as preliminary communications.[13c,d]

Results and Discussion

Synthesis of Chloropalladium Ferrocene-Based P,C,P Pincer Complexes. The starting 1,3-bis((dialkylphosphino)methyl)ferrocenes $\{1,3\text{-}(R_2PCH_2)_2C_5H_3\}Fe(C_5H_5)$ (**2a**, R = Pr^i; **2b**, R = Bu^t) were obtained by the reaction of 1,3-bis(hydroxymethyl)ferrocene with the corresponding dialkylphosphines HPR_2 in hot acetic acid. Cyclometalation of diphosphines **2a** and **2b** with $PdCl_2(NCPh)_2$ in 2-methoxyethanol at 120 °C gives the chloropalladium pincer complexes **3a**,**b**, respectively (eq 2).



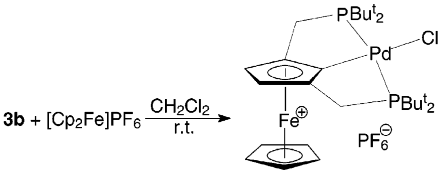
(2)

2a, R=Pr^i
2b, R=Bu^t

3a, R=Pr^i
3b, R=Bu^t

Chloropalladium complexes form orange air- and heat-stable crystalline solids (they remain unchanged after heating in solution at 150 °C for several hours). Compounds **3a**,**b** were characterized by NMR and mass spectrometry and by elemental analysis. A single resonance was observed for the two equivalent phosphorus nuclei in the $^{31}P\{^1H\}$ NMR spectrum, at δ 71.87 (**3a**) and 85.78 ppm (**3b**). In the ^1H NMR spectra, the resonances of the cyclopentadienyl protons of the ferrocene unit are revealed as two singlets of relative intensities of 5H and 2H, indicating the cyclometalation of the substituted ring. The methylene protons of the CH_2PR_2 groups are nonequivalent and are revealed as a doublet of triplets. In the ^1H NMR spectrum of complex **3b**, the methyl protons of the *tert*-butyl groups gave two virtual triplets at δ 1.28 ($^3J_{PH}$ = 6.5 Hz, 18H) and 1.55 ppm ($^3J_{PH}$ = 7.0 Hz, 18H), in accord with the expected structure. For complex **3a** the methyl protons of the isopropyl groups are observed as three pseudo quadruplets at δ 1.07, 1.33, and 1.53 ppm with relative intensities of 6H, 12H, and 6H, respectively. A similar spectral pattern was observed earlier[11] for the isopropyl groups in the spectrum of complex **1**. The $^{13}C\{^1H\}$ NMR spectrum of **3b** is also in accordance with the expected structure, with the cyclopentadienyl resonances being observed at δ 114.28 (vt, J_{PC} = 20.1 Hz, 1C, C(1)), 92.75 (vt, J_{PC} = 13.9 Hz, 2C, C(2,5)), and 63.76 ppm (vt, J_{PC} = 81 Hz, 2C, C(3,4)).

Formation of the Complex $\{PdCl[\{2,5\text{-}(Bu^t_2PCH_2)\text{-}C_5H_2\}Fe(C_5H_5)]\}PF_6$ (4b). Complex **3b** reacts with the equivalent amount of $[Cp_2Fe]PF_6$ in methylene chloride at room temperature to form the green ferrocenium-based pincer complex $\{PdCl[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}PF_6$ (**4b**) in ~80% yield (eq 3). This is the first example of ferrocene-based phosphine chelate oxidation centered on the iron atom.

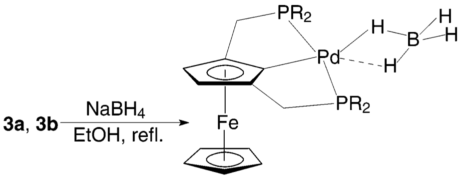


(3)

4b

Complex **4b** is poorly soluble in chloroform but readily soluble in methylene chloride. The NMR spectral data of **4b** indicate its paramagnetic character. In the ^1H NMR spectrum, the methyl protons of the *tert*-butyl groups are observed at δ −10.24 and 7.30 ppm, and the methylene group protons of $CH_2PBu^t_2$ appear at δ −115.49 (very broad) and −25.87 ppm (broad). In the $^{31}P\{^1H\}$ NMR spectrum of **4b**, there is a singlet at δ 93.9 ppm (2P, PBu^t_2) and a septet at −150.0 ppm (1P, PF_6, J_{PF} = 709.5 Hz). The ferrocenium nature of complex **4b** follows also from its electrochemical behavior, as compared to the redox characteristics obtained from an electrochemical study of complex **3b** (see below).

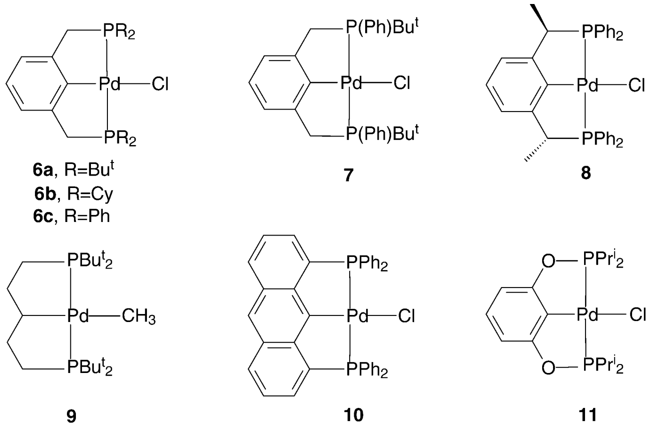
Formation of the Complexes $Pd(BH_4)[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (5a, R = Pr^i; 5b, R = Bu^t). Our initial attempts to synthesize a hydridopalladium complex by the reaction of **3b** with $LiAlH_4$ were unsuccessful, because the reaction was accompanied by the destruction of the pincer complex to form the free diphosphine **2b**. However, we found that when $NaBH_4$ was used as a reducing agent, both of the chloro complexes **3a**,**b** yield the corresponding tetrahydroborate derivatives of palladium, complexes $Pd(BH_4)[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**5a**, R = Pr^i; **5b**, R = Bu^t) (eq 4).



(4)

5a, R=Pr^i
5b, R=Bu^t

Chart 2



The ^1H and $^{31}P\{^1H\}$ NMR spectral data indicate that the tridentate P,C,P pincer ligand is retained in complexes **5a**,**b**. The presence of the $BH_4{}^-$ ligand is evident from the ^1H and ^{11}B NMR spectra. The ^1H NMR spectrum of **5b** contains a very broad signal centered at δ -0.50 ppm. The ^{11}B NMR spectrum consists of a quintet at δ -37.28 ppm, with coupling constant $J_{BH} =$ 83.1 Hz; the multiplicity of the signal indicates fast averaging of all four H atoms bound to the B atom. The IR spectrum of **5b** contains the B$-$H stretching bands at 2380 (sh), 2369 (vs), and 2293 (s) and an intense absorption at 1064 cm^{-1} (BH_3 deformation); the last band is characteristic of the unidentate $BH_4{}^-$ ligand.[14]

It is known that the $BH_4{}^-$ ion can form transition-metal complexes, in which it coordinates the metal by three, two, and one hydrogen atoms.[14] While the first two bonding modes are quite common, the unidentate coordination mode very rarely occurs. To our knowledge, palladium complexes with the η^1-BH_4 ligand have not been characterized earlier.

X-ray Diffraction Study of Complexes 3a,b and 5b. It was of interest to study the structures of ferrocene-based P,C,P pincer complexes **3a**,**b** and to compare their geometric features with those of known benzene-based analogues and related pincer complexes of palladium. The X-ray structures of several P,C,P pincer palladium complexes have been described previously (Chart 2). These include chloro complexes **6a**,[15a] **6b**,[15b] and **6c**,[15c] complexes **7**[5e] and **8**[15d] containing chiral P,C,P ligands, complexes **9**[16a] and **10**[16b] based on 1,5-bis(di-*tert*-butylphosphino)pentane and 1,8-bis(diphenylphosphino)anthracene pincer ligands, and the phosphinito P,C,P pincer complex **11**.[16c] The structures of cationic complexes containing ancillary two-electron donor ligands at the Pd atom, $[Pd(OH_2)\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}]BF_4$ (**12**; two crystallographic isomers),[15a] $[Pd(OH_2)\{(Bu^t{}_2PCH_2CH_2)_2CH\}]BPh_4$[16a] (**13**), $[Pd(NH_2Ph)\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}]BF_4$[17a] (**14**), and $[Pd(PEt_3)\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3\}]BF_4$,[17b] (**15**), have also been determined.

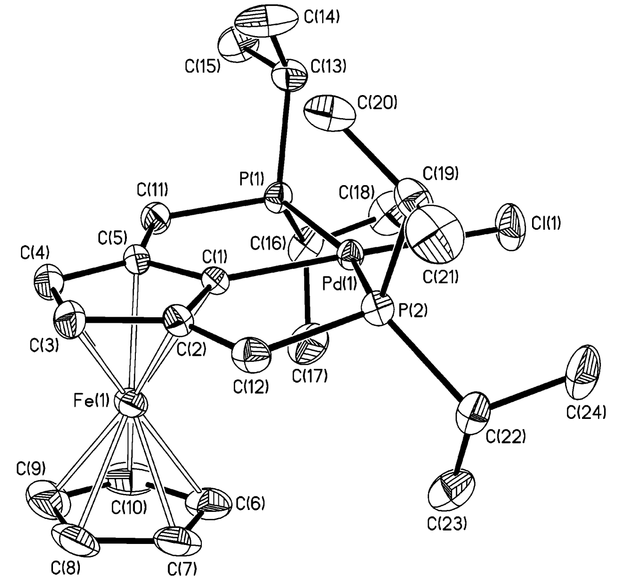


Figure 1. Molecular structure of **3a**.

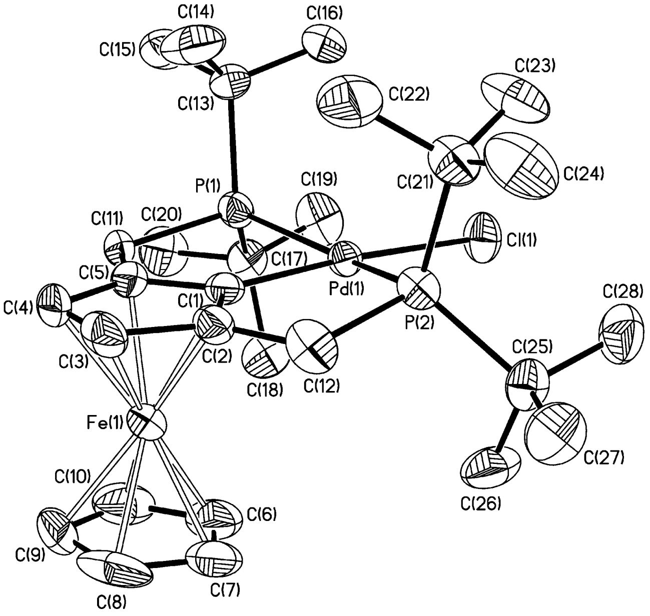


Figure 2. Molecular structure of **3b**.

The molecular structures of **3a**,**b** are illustrated in Figures 1 and 2, respectively, while the selected bond distances and angles are listed in Table 1. As may be seen from Figures 1 and 2, the structures of both molecules are very similar and contain the Pd atom in a distorted-square-planar geometry, with P(1)$-$Pd$-$P(2) angles in **3a**,**b** being equal to 160.39(6) and 157.57(4)°, respectively. These values are markedly smaller than the corresponding angles in benzene-based pincer complexes **6**$-$**10**, where they are in the 162.0(1)$-$166.2(1)° range. They are also smaller relative to the two forms of complex **12**, 166.26(8) and 167.6(1)°, and similar to

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Table 1. Selected Geometrical Parameters for Complexes 3a,b

	3a	3b		3a	3b
Bond Lengths (Å)					
Pd(1)−Cl(1)	2.400(2)	2.403(1)	C(1)−C(5)	1.417(8)	1.425(5)
Pd(1)−C(1)	1.964(5)	1.961(4)	C(2)−C(3)	1.436(8)	1.421(5)
Pd(1)−P(1)	2.318(2)	2.342(1)	C(2)−C(12)	1.494(8)	1.502(6)
Pd(1)−P(2)	2.305(2)	2.337(1)	C(3)−C(4)	1.430(9)	1.430(6)
P(1)−C(11)	1.842(6)	1.857(4)	C(4)−C(5)	1.416(8)	1.414(6)
P(2)−C(12)	1.835(6)	1.858(4)	C(5)−C(11)	1.513(8)	1.525(6)
C(1)−C(2)	1.433(7)	1.420(6)			
Bond Angles (deg)					
C(1)−Pd(1)−Cl(1)	179.0(2)	175.5(1)	C(1)−C(2)−C(3)	107.0(5)	108.2(4)
C(1)−Pd(1)−P(1)	80.9(2)	80.8(1)	C(1)−C(2)−C(12)	120.6(5)	119.1(4)
C(1)−Pd(1)−P(2)	81.1(2)	80.7(1)	C(3)−C(2)−C(12)	132.5(5)	132.7(4)
P(1)−Pd(1)−P(2)	160.39(6)	157.57(4)	C(2)−C(3)−C(4)	108.0(5)	108.1(4)
P(1)−Pd(1)−Cl(1)	99.70(6)	99.77(4)	C(5)−C(4)−C(3)	108.2(5)	107.4(4)
P(2)−Pd(1)−Cl(1)	98.48(6)	99.65(4)	C(4)−C(5)−C(1)	108.3(5)	108.8(4)
C(11)−P(1)−Pd(1)	106.4(2)	106.1(2)	C(4)−C(5)−C(11)	132.0(5)	130.2(4)
C(12)−P(2)−Pd(1)	106.7(2)	104.7(2)	C(1)−C(5)−C(11)	119.6(5)	121.0(4)
C(2)−C(1)−C(5)	108.6(5)	107.5(4)	C(5)−C(11)−P(1)	106.5(4)	104.8(3)
C(2)−C(1)−Pd(1)	124.8(4)	126.7(3)	C(2)−C(12)−P(2)	105.8(4)	106.7(3)
C(5)−C(1)−Pd(1)	126.4(4)	125.7(3)			

those in the cationic complexes **14** and **15**, 160.8(3) and 158.1(1)°, respectively. (In **9**, **10**, **11**, and **13** the P(1)−Pd−P(2) angles are 166.2(1), 166.2(1), 160.380(6) and 157.770(7) (for two independent molecules), and 167.1(1)°, respectively).

As in the case of rhodium complex **1**, the formation of palladium complexes **3a**,**b** leads to a decrease in the bond angles at C(2) and C(5) in the fused metallacycles (C(1)−C(2)−C(12) = 120.6(5)°, C(1)−C(5)−C(11) = 119.6(5)° for **3a**; C(1)−C(2)−C(12) = 119.1(4)°, C(1)−C(5)−C(11) = 121.0(4)° for **3b**). In complexes **3a**,**b** the Pd atom deviates from the plane of the cyclopentadienyl ring and lies 0.147 and 0.069 Å above the ring in **3a**,**b**, respectively.

The distinguishing features of **3a**,**b** in comparison with benzene systems are also an increase of the Pd−P bond distances. Thus, the Pd−P distance (average 2.3391(12) Å) in **3b** is markedly longer than in its benzene analogue **6a**, 2.3025(6) Å. In benzene-based P,C,P pincer complexes the two chelating five-membered metallacycles are strained and adopt an envelope conformation with the methylene carbon at the flap. As a result, the plane of the aromatic ring is tilted from the coordination plane. Thus, in **6c**, for example, the coordination plane defined by Pd, Cl, C(1), P(1), and P(2) forms an angle of 19.85(5)° with the cyclometalated benzene ring, and the P(1) and P(2) atoms are situated at the opposite sides of the benzene plane.[15c] As a consequence, at each side of the benzene ring of **6c** one of the phenyl groups at the P atom is pseudoaxial and the other is pseudoequatorial. In contrast to **6c** and other benzene-based P,C,P pincer complexes, the two pseudoaxial groups in metallocene-based pincer complexes **3a**,**b** are located at the opposite sides of the cyclometalated cyclopentadienyl ring with respect to the two pseudoequatorial groups (see Figure 3). The phosphorus atoms P(1) and P(2) are located on the same side of the plane containing the substituted cyclopentadienyl ring, opposite to the iron atom. This deviation is probably due to a close contact between the hydrogen atoms of the methyl groups in the P(1) and P(2) substituents and the hydrogen atoms of the unsubstituted cyclopentadienyl ring. Thus, the chelated metal atom M is more shielded against the attack from the exo position in the metallocene-based pincer complexes than in the benzene-based systems. Evidently, this peculiarity should be kept in mind for the design of metallocene-based P,C,P pincer complexes as catalysts for various reactions.

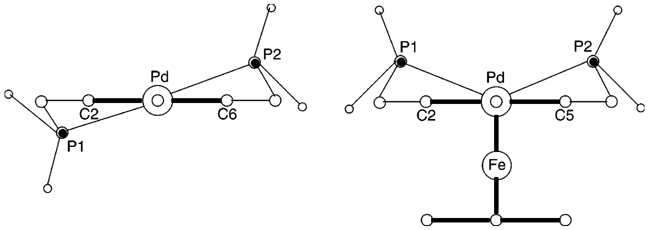

Figure 3. Schematic views of P,C,P pincer complexes (left, benzene-based; right, ferrocene-based) along the Cl−Pd−C(1) axis. The Cp ring deviation from the Pd−Cl axis is omitted for clarity.

There are some other structural features in complexes **3a**,**b**. Thus, the Pd−Cl distances (2.4002(17) and 2.4030(11) Å, respectively) are longer than for **6c** (2.367(3) Å) and close to those for **6a** (2.3969(6) Å) and **6b** (2.427(2) Å), which contain bulky alkyl groups at the P atoms.[15a,b] It cannot be ruled out that weakening of the Pd−Cl bond in **3a**,**b** is the result of steric congestion by the bulky isopropyl or *tert*-butyl groups. It should be noted in this respect that the angles C(1)−Pd−Cl in complexes **3a**,**b** are 178.89(17) and 175.46(12)°, respectively, and this difference may also originate from steric congestion by the bulkier *tert*-butyl groups.

The molecular structure of complex **5b** is illustrated in Figure 4; the main bond lengths and angles are presented in Table 2. The structural features of the pincer ligand of molecule **5b** are similar to those of complex **3b**; in both complexes the cyclopentadienyl rings deviate from being parallel by 4.2 and 4.5°, respectively, and have an eclipsed conformation. The coordination geometry of Pd in **5b** is essentially square planar with a slight distortion toward tetrahedral, with a P(1)−Pd−P(2) angle of 160.72(3)°. The palladium atom coordinates only one of the BH_4^- group hydrogen atoms, with a Pd−H(1) distance of 2.00(4) Å. As in other metallocene-based P,C,P pincer complexes, the chelated metal atom in **5b** deviates from the plane of the cyclopentadienyl ring, and the Pd atom lies 0.361 Å

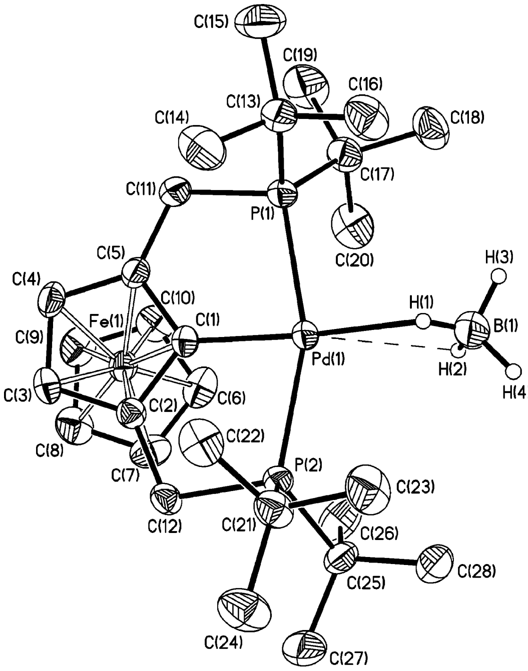

Figure 4. Molecular structure of **5b**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Complex 5b

Pd(1)−P(1)	2.3526(9)	P(1)−C(11)	1.854(3)
Pd(1)−P(2)	2.3521(9)	P(2)−C(12)	1.861(3)
Pd(1)−C(1)	1.980(3)	C(1)−C(2)	1.433(4)
Pd(1)...B(1)	2.614(7)	C(1)−C(5)	1.424(4)
Pd(1)−H(1)	2.00(4)	C(2)−C(3)	1.439(4)
Pd(1)...H(2)	2.56(5)	C(2)−C(12)	1.499(4)
B(1)−H(1)	0.92(4)	C(3)−C(4)	1.421(5)
B(1)−H(2)	1.14(5)	C(4)−C(5)	1.424(4)
B(1)−H(3)	0.94(5)	C(5)−C(11)	1.491(5)
B(1)−H(4)	0.98(6)		
C(1)−Pd(1)−P(1)	80.67(9)	C(2)−C(1)−Pd(1)	125.2(2)
C(1)−Pd(1)−P(2)	80.97(9)	C(1)−C(2)−C(3)	107.4(3)
C(1)−Pd(1)−B(1)	173.6(3)	C(1)−C(2)−C(12)	120.8(3)
P(1)−Pd(1)−P(2)	160.72(3)	C(3)−C(2)−C(12)	131.8(3)
P(1)−Pd(1)−B(1)	99.1(1)	C(4)−C(3)−C(2)	107.9(3)
P(2)−Pd(1)−B(1)	99.9(1)	C(3)−C(4)−C(5)	108.5(3)
Pd(1)−H(1)−B(1)	123(3)	C(4)−C(5)−C(1)	107.9(3)
C(11)−P(1)−Pd(1)	105.2(1)	C(4)−C(5)−C(11)	132.0(3)
C(12)−P(2)−Pd(1)	105.6(1)	C(1)−C(5)−C(11)	120.0(3)
C(5)−C(1)−C(2)	108.3(3)	C(5)−C(11)−P(1)	106.9(2)
C(5)−C(1)−Pd(1)	125.7(2)	C(2)−C(12)−P(2)	106.2(2)

above the ring. The three atoms C(1), Pd, and B form an angle of 173.6(3)°, and the Pd−H(1)−B angle is 123.3°. It should be mentioned that in transition-metal complexes with the unidentate BH_4^- ligand, $M-H_b-B$ angles vary in a broad range. Thus, in $FeH(\eta^1\text{-}BH_4)(dmpe)_2$[18a,b] and *trans*-$RuH(\eta^1\text{-}BH_4)(Me_8[16]aneS_4)$[19] the $M-H_b-B$ angles are 161.7 and 164(1)°, respectively, while in $Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$[20a] and $Cu(\eta^1\text{-}BH_4)$(triphos)[21] those angles are substantially smaller: 121.7(4) and 121(3)°, respectively. Intermediate $M-H_b-B$ angles were observed for the complexes $Ag(\eta^1\text{-}BH_4)(PMePh_2)_3$[22] and $V(\eta^1\text{-}BH_4)_2(dmpe)_2$,[23] while the isostructural complexes $M(\eta^1\text{-}BH_4)(CO)(NO)(PMe_3)_3$ (M = Mo, W)[24] contain two independent molecules, in which the $M-H_b-B$ angles are 128.5, 142.4° and 138.5, 146.6°, respectively.

The Pd···B distance of 2.614(7) Å is too long to suppose Pd−B bonding in complex **5b**. For comparison, in the complex $Ti(BH_4)_3(PMe_3)_2$,[25] containing unique "agostic" or "side-on" bonding of the Ti atom with two BH_4^- groups, the Ti−B distance is 2.27(1) Å. A similar short M−B distance was also observed for complexes where the metal atom was bound to two hydrogen atoms of the BH_4^- group: for example 2.29 Å in $Co(\eta^2\text{-}BH_4)$(triphos).[26] However, it may be noted that the Pd···B distance in **5b** is markedly shorter in comparison to other $\eta^1\text{-}BH_4$ derivatives of transition metals; for example 2.833(4), 2.84, and 2.895(16) Å in the complexes $V(\eta^1\text{-}BH_4)_2(dmpe)_4$,[23] $FeH(\eta^1\text{-}BH_4)(dmpe)_2$,[18] and $RuH(\eta^1\text{-}BH_4)(Me_8[16]aneS_4)$,[19] respectively. This fact as well as the relatively short distance between the palladium atom and one of the three terminal hydrogen atoms of the BH_4^- group, Pd···H(2) = 2.56(5) Å, allows us to describe the latter contact as an "incipient Pd−H bonding interaction" as was proposed for the complex $Cu(\eta^1\text{-}BH_4)(PMePh_2)_3$.[20a] In the related complex $Hf_2H_3(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]_2$, the bonding of one of the BH_4^- groups is intermediate between the η^1 and η^2 modes (the Hf−H distances are 1.93 and 2.43 Å).[20b] Evidently, equilibration of the hydrogen atoms of the BH_4^- group in the solution of **5b** should include stepwise formation of η^1 and η^2 structures accompanied by rotation of the unidentate BH_4^- group.

It is known that the BH_4^- ion and electronically neutral boran-Lewis base adducts $BH_3{\cdot}L$ are isoelectronic with alkanes and form relatively stable complexes with transition metals.[14a,27] At the same time, the alkane σ-complexes of transition metals are extremely unstable and only recently have become available for observation under specific conditions.[28] Shimoi and coworkers showed that properties of metal complexes with unidentate borane−Lewis base adducts embodied those of alkane complexes.[27]

Several modes of metal−alkane interactions were suggested for alkane σ-complexes (Chart 3), intermediates in alkane oxidative addition reactions.

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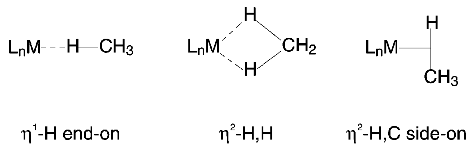
Chart 3



Although alkane activation was not observed for Pd(II) in pincer complexes, it is reasonable to regard the interaction of the chelated, sterical crowded Pd atom with BH_4^- in **5b** as modeling an earlier stage of alkane oxidative addition to the Ir atom in Ir[^{R}P,C,P$^{M'}$], catalytic species for alkane dehydrogenation. Remarkably, the distances between the Pd atom and two hydrogen atoms of the BH_4^- group in **5b** (Pd−H(1) = 2.00(4) Å and Pd−H(2) = 2.56(5) Å) and corresponding Ir−H bond distances of 2.017 and 2.554 Å, calculated for the hypothetical intermediate agostic complex of ethane with Ir[2,6-$(H_2PCH_2)_2C_6H_3$], are very similar.[27c]

Electrochemical Studies of 2b and 3a,b. As mentioned earlier,[11] one of the peculiarities of the ferrocene-based pincer complexes is their potential to undergo a rapid and reversible redox process centered on the iron atom. We suppose that upon altering the redox state of the iron atom in ferrocene-based pincer complexes we can modify the chemical and catalytic reactivity of the chelated metal atom M, situated at the position β to the iron atom. There is some resemblance to α-ferrocenylcarbenium ions, the enhanced stability of which results from the direct interaction between the iron atom and the carbenium ion center, also situated at the position β to iron. Therefore, by altering the iron oxidation state within the pincer ligand, we can enhance the rate of either oxidative addition or reductive elimination at M. Thus, it is known that an increase in the electron density at the metal favors oxidative addition, whereas oxidation of metal complexes containing σ-bonded ligands leads to enhanced tendency toward reductive elimination by the loss of σ-bonded ligands.[29]

The redox properties of the ligand **2b** and the complexes **3a**,**b** were investigated by cyclic voltammetry. The results (see Figure 5) demonstrate that diphosphine and both complexes display reversible oxidation processes. All waves have a ΔE_p value equal to or smaller than that measured for an internal ferrocene standard, in agreement with their nature as one-electron redox processes. The free ligand **2b** is oxidized at $E_{1/2} = -0.11$ V vs ferrocene; i.e., its oxidation is slightly more facile than that of ferrocene, in line with the expected electron-donating effect of the two $CH_2PBu^t_2$ arms on the cyclopentadienyl ring. The palladium complexes **3a**,**b** show oxidation potentials very close to each other ($E_{1/2}$ = −0.21 and −0.22 V vs ferrocene, respectively), slightly *more negative* than the corresponding free ligands. The small shift with respect to the free ligand suggests that the processes are once again Fe-based. In addition, square-planar Pd(II) complexes do not show reversible electrochemistry at potentials close to that of ferrocene.[30] The observation that the redox potentials shift to more negative values relative to the free ligand is interesting. It means that the global effect of phosphorus coordination and metalation makes the Fe center more electron rich. The donation from the P donors to the Pd center decreases the electron density at the P atoms, and the transmission of this electronic change to the ferrocene moiety through the CH_2PR_2 should make the ferrocene less electron rich. This means that the replacement of a cyclopentadienyl C−H bond by a C−Pd bond more than compensates for this effect, transmitting more electron density to the Fe center.

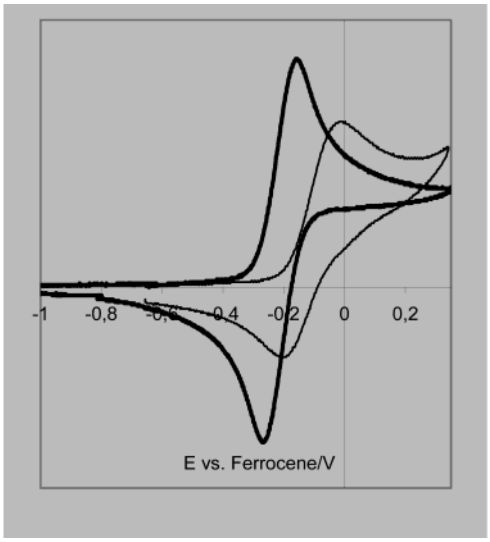


Figure 5. Cyclic voltammograms of compounds **2b** (thinner line) and **3b** (thicker line) in THF solution. The scan rate was 100 mV s^{-1}.

Conclusions

We have presented here the synthesis, structures, and electrochemical properties of palladium ferrocene-based P,C,P pincer complexes, obtained by cyclometalation of 1,3-bis((dialkylphosphino)methyl)ferrocenes. These include tetrahydroborato derivatives, the first palladium complexes containing a unidentate BH_4^- ligand. The X-ray diffraction study of chloropalladium pincer complexes **3a** and **3b** reveals some interesting structural features, including the steric environment of the chelated metal atom, which distinguishes them from their benzene analogues. The structural peculiarity of the BH_4^- ion bonding with the palladium atom in **5b** can be considered as modeling an earlier stage of alkane oxidative addition to the metal center in Ir[^{R}P,C,P$^{M'}$], catalytic species for alkane dehydrogenation.

Unexpected effects of the cyclometalation process on the Fe-based redox properties have been observed for the pincer complexes **3a**,**b**. At the moment, we are extending our work by probing the effect of the iron oxidation state on the reactivity and catalytic properties of the chelated metal atom in ferrocene-based pincer complexes.

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Experimental Section

All manipulations were carried out under an argon atmosphere. The ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer. FTIR spectra were recorded on a Nicolet Magna 750 spectrophotometer, and mass spectra were measured on a Finnigan LCQ instrument. Cyclic voltammograms were recorded with an EG&G 362 potentiostat connected to a Macintosh computer through MacLab hardware/sofware. The electrochemical cell was fitted with an Ag−AgCl reference electrode, a 1 mm diameter Pd-disk working electrode, and a platinum-wire counter electrode. $[Bu_4N]PF_6$ (ca. 0.1 M) was used as the supporting electrolyte in THF. All potentials are reported relative to the ferrocene/ferrocenium couple. Ferrocene was added and measured as an internal standard at the end of each experiment. The compound 1-(ethoxycarbonyl)-3-formylferrocene was prepared as described in the literature.[31]

Synthesis of $\{1,3\text{-}(HOCH_2)_2C_5H_3\}Fe(C_5H_5)$. A solution of 1-(ethoxycarbonyl)-3-formylferrocene (150 mg, 0.524 mmol) in ether (30 mL) was added dropwise to a suspension of $LiAlH_4$ (60 mg, 15.7 mmol) in ether (30 mL). The solution was stirred at room temperature for 4.5 h. Then water (50 mL) was added, and the water layer was separated and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4. The solvents were evaporated under vacuum, and the resulting yellow oil was purified on an alumina column (eluent methanol). Recrystallization of the residue from methanol gave orange-yellow crystals of the product. Yield: 100 mg (77.5%). Mp: 115−116 °C; lit.[32] mp 115−116 °C. ^{1}H NMR (acetone-d_6): δ 4.11 (s, 5H, C_5H_5), 4.13 (d, 2H, $J = 1.1$ Hz, HC_5H_2), 4.25 (t, 1H, $J = 1.1$ Hz, HC_5H_2), 4.29 (s, 4H, CH_2OH).

Synthesis of $\{1,3\text{-}(Pr^i_2PCH_2)_2C_5H_3\}Fe(C_5H_5)$ (2a). The phosphine $HPPr^i_2$ (602 mg, 5.10 mmol) was added to a solution of the dicarbinol $\{1,3\text{-}(HOCH_2)_2C_5H_3\}Fe(C_5H_5)$ (502 mg, 2.04 mmol) in acetic acid (40 mL). The solution was stirred at 95 °C for 3 h. The solvent was removed under vacuum, and the residue was extracted with dichloromethane (60 mL). The extract was washed with a saturated aqueous Na_2CO_3 solution (50 mL). The layers were separated, and the aqueous solution was extracted with CH_2Cl_2 (2×50 mL). The combined organic solutions were evaporated, and the residue was dissolved in anhydrous methanol. Crystallization at −78 °C gave air-sensitive light yellow crystals (yellow-brown oil at room temperature). Yield: 409 mg (45%). The product appears to be analytically pure, as indicated by NMR. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 9.14 (s, 2P). ^{1}H NMR ($CDCl_3$): δ 0.96−1.04 (m, 24H, $CH(CH_3)_2$), 1.6−1.7 (m, 4H, $CH(CH_3)_2$), 2.48 (br s, 4H, CH_2P), 4.01 (s, 2H, C_5H_2H), 4.02 (s, 5H, C_5H_5), 4.13 (s, 1H, C_5H_2H).

Synthesis of $\{1,3\text{-}(Bu^t_2PCH_2)_2C_5H_3\}Fe(C_5H_5)$ (2b). The phosphination of 1,3-bis(hydroxymethyl)ferrocene (500 mg, 2.03 mmol) with $HPBu^t_2$ (600 mg, 4.10 mmol) was done according to the procedure described above for the synthesis of **2a**. Precipitation of the product by addition of methanol to the concentrated solution in dichloromethane gave air-sensitive light yellow needles. Yield: 613 mg (60%). The product appears to be analytically pure, as indicated by NMR. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.46 (s, 2P). ^{1}H NMR ($CDCl_3$): δ 1.07 (2d, 36H, $J_{P,H} = 10.7$ Hz, $C(CH_3)_3$), 2.53 (d, $J = 2.3$ Hz, 4H, CH_2P), 4.02 (s, 5H, C_5H_5), 4.11 (s, 2H, C_5H_2H), 4.31 (s, 1H, C_5H_2H). MS: m/z 502 [M^+].

Synthesis of $PdCl[\{2,5\text{-}(Pr^i_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (3a). $PdCl_2(NCPh)_2$ (440 mg, 1.154 mmol) was added to the suspension of 1,3-bis((diisopropylphosphino)methyl)ferrocene (**2a**; 515 mg, 1.154 mmol) in dry 2-methoxyethanol (50 mL). The mixture was stirred at 125 °C for 3 h. After it was cooled, the orange solution was filtered and solvent was removed under vacuum. The residue was crystallized from a *n*-hexane−CH_2Cl_2 mixture. Yield: 320 mg (47%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 71.87 (s, 2P). ^{1}H NMR ($CDCl_3$): δ 1.07 (vq, $J = 7.8$ Hz, 6H, $CH(CH_3)_2$), 1.33 (vq, $J = 7.4$ Hz, 12H, $CH(CH_3)_2$), 1.53 (vq, $J = 8.1$ Hz, 6H, $CH(CH_3)_2$), 2.18 (m, 2H, $CH(CH_3)_2$), 2.29 (m, 2H, CH_AH_BP), 2.53 (m, 2H, $CH(CH_3)_2$), 2.76 (m, 2H, CH_ACH_BP), 4.01 (s, 5H, C_5H_5), 4.23 (s, 2H, C_5H_2). MS: m/z 588 [M^+]. Anal. Calcd for $C_{24}H_{39}ClFeP_2Pd$ (587.2): C, 49.09; H, 6.69. Found: C, 49.04; H, 6.71.

Synthesis of $PdCl[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (3b). This compound was obtained by the procedure described above for **3a**. Yield: 65.2%. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 85.78 (s, 2P). ^{1}H NMR ($CDCl_3$): δ 1.28 (vt, $J = 6.5$ Hz, 18H, CH_3), 1.55 (vt, $J = 7.0$ Hz, 18H, CH_3), 2.48 (dt, $J_{HH} = 16.5$ Hz, $J_{PH} = 2.0$ Hz, 2H, CH_ACH_BP), 2.90 (dt, $J_{HH} = 16.5$ Hz, $J_{PH} = 1.1$ Hz, 2H, CH_ACH_BP), 3.94 (s, 5H, C_5H_5), 4.23 (s, 2H, C_5H_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 24.99 (vt, $J_{PC} = 10.3$ Hz, 2C, CH_2P), 29.33 (“t”, 6C, CH_3), 29.41 (“t”, 6C, CH_3), 35.06 (v.t, $J_{PC} = 6.7$ Hz, 2C, CMe_3), 35.37 (vt, $J_{PC} = 5.4$ Hz, 2C, CMe_3), 63.76 (vt, $J_{PC} = 8.1$ Hz, 2C, C(3,4)), 70.62 (s, 5C, C_5H_5), 92.75 (vt, $J_{PC} = 13.9$ Hz, 2C, C(2,5)), 114.28 (vt, $J_{P,C} = 20.1$ Hz, 1C, C(1)). MS: m/z 641 [M^+]. Anal. Calcd for $C_{28}H_{47}ClFeP_2Pd$ (641.5): C, 52.34; H, 7.33. Found: C, 52.35; H, 7.28.

Synthesis of $\{PdCl[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}PF_6$ (4b). $[Cp_2Fe]PF_6$ (87.1 mg, 0.263 mmol) was added to a stirred solution of $PdCl[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**3b**; 169 mg, 0.263 mmol) in dichloromethane (20 mL). The solution rapidly changed color to green. After the solution was stirred for 1 h, the solvent was removed under vacuum, and the residue was extracted with toluene (6×10 mL) to remove ferrocene. The green residue was dried under vacuum. Yield: ca. 80%. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 93.9 (s, 2P), −150.0 (sept., $^{1}J_{P,F} = 709.5$ Hz, 1, PF_6). ^{1}H NMR (CD_2Cl_2): δ −115.50 (br, 2H, CH_AH_BP), −25.87 (br, 2H, CH_AH_BP), −10.24 (s, 18H, $C(CH_3)_3$), 7.03 (s, 18H, $C(CH_3)_3$), 24.42 (br, 5H, C_5H_5), 29.52 (br, 2H, C_5H_2). Anal. Calcd for $C_{28}H_{47}ClF_6FeP_3Pd \cdot CH_2Cl_2$ (873): C, 39.86; H, 5.61; F, 13.05. Found: C, 39.93; H, 5.51; F, 12.91.

Synthesis of $Pd(BH_4)[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (5b). To a solution of $PdCl[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**3b**; 96 mg, 0.15 mmol) in 40 mL of ethanol was added $NaBH_4$ (350 mg), and the mixture was refluxed for 1 h. After the yellow-orange solution was cooled, additional $NaBH_4$ (100 mg) was added and the solution was refluxed for another 1 h. After the solution was cooled, the solvent was decanted and the white residue was washed several times with ethanol. The combined ethanol solutions were evaporated to dryness under vacuum. The residue was extracted with dichloromethane, *n*-hexane was added, and the solution was concentrated to a small volume (3−4 mL) and cooled to −20 °C for 2 h. The almost colorless supernatant was removed by pipet, and the solid was washed with hexane and dried under vacuum, to yield an orange crystalline powder. Yield: 68.2 mg (73%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 91.39 (s, 2P). ^{1}H NMR ($CDCl_3$): δ −0.50 (v. broad, 4H, BH_4), 1.23 (t, $J_{HP} = 6.7$ Hz, 18H, CH_3), 1.53 (t, $J_{HP} = 7.2$ Hz, 18H, CH_3), 2.53 (dt, $J_{HH} = 17.0$ Hz, $J_{HP} = 4.5$ Hz, 2H, CH_AH_BP), 3.01 (dt, $J_{HH} = 17.0$ Hz, $J_{HP} = 2.5$ Hz, 2H, CH_AH_BP), 3.95 (s, 5H, C_5H_5), 4.22 (s, 2H, C_5H_2). ^{11}B NMR ($CDCl_3$): δ −37.28 (quint, $J_{BH} = 83.1$ Hz). IR (KBr): 2380 (sh), 2369 (vs), 2293 (s), 1064 (s) cm^{-1}. MS: m/z 608 ($M^+ - BH_3$). Satisfactory elemental analysis could not be obtained, despite several attempts. The product, however, appears to be analytically pure, as indicated by NMR.

Synthesis of $Pd(BH_4)[\{2,5\text{-}(Pr^i_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (5a). This compound was obtained by the procedure described above for **5a**, starting from 128.6 mg of **3a** and 400 mg of $NaBH_4$ in 40 mL of ethanol. Yield: 59.2 mg, 45%. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 78.05 (s, 2P). ^{1}H NMR (C_6D_6): δ 0.27 (v. broad, 4H, BH_4) (pseudo q, $J_{BH} = 97$, $J_{BH} = 55$ Hz), 0.89 (vq, $J = 7.6$ Hz, 6H, $CHCH_3$), 1.00 (vq, $J = 6.4$ Hz, 6H, $CHCH_3$), 1.26 (vq, $J = 7.8$ Hz, 6H, $CHCH_3$), 1.53 (vq, $J = 8.0$ Hz, 6H, $CHCH_3$),

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Table 3. Summary of Crystal Structure Determination for Complexes 3a,b and 5b

	3a	**3b**	**5b**
formula	$C_{24}H_{39}ClP_2FePd$	$C_{28}H_{47}ClP_2FePd$	$C_{28}H_{51}BP_2FePd$
mol wt	587.19	643.30	622.69
cryst color, habit	yellow prism	orange prism	orange prism
cryst size, mm	0.30 × 0.20 × 0.10	0.20 × 0.18 × 0.10	0.55 × 0.40 × 0.20
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$Pbca$	$P2_1/c$
temp, K	295(2)	295(2)	295(2)
a, Å	12.018(2)	17.2290(6)	10.977(1)
b, Å	14.031(4)	16.4470(5)	18.634(2)
c, Å	15.439(3)	21.3131(7)	15.632(2)
β, deg			109.312(2)
V, Å^3	2603(1)	6039.4(3)	3017.5(5)
Z	4	8	4
d_{calcd}, g/cm^3	1.498	1.415	1.371
μ, cm^{-1} (Mo Kα, $\lambda = 0.710\ 73$ Å)	14.82	12.85	11.97
diffractometer	Enraf-Nonius CAD4	SMART 1000 CCD	SMART 1000 CCD
scan technique	$\theta - 5/3\theta$	ω and φ	ω and φ
$2\theta_{max}$, deg	56	56	60
no. of rflns collected	3502	44 813	28 100
no. of indep rflns (R_{int})	3502	7291 (0.0767)	8751 (0.0435)
no. of obsd rflns ($I > 2\sigma(I)$)	2588	3538	5266
R1[a]	0.0362	0.0471	0.0440
wR2[b]	0.0776	0.1026	0.0928

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

1.73 (m, 2H, C*H*CH$_3$), 2.04 (dt, $J_{HH} = 16.6$ Hz, $J_{HP} = 4.3$ Hz, 2H, CH_AH$_B$P), 2.49 (m, 2H, C*H*CH$_3$), 2.70 (dt $J_{HH} = 16.6$ Hz, $J_{HP} \approx 1.2$ Hz, 2H, CH$_A$$H_B$P), 4.11 (s, 5H, C_5H_5), 4.25 (s, 2H, C_5H_2). ^{11}B NMR (C_6D_6): δ −37.65 (quint, $J_{BH} = 81.3$ Hz). Satisfactory elemental analysis could not be obtained. The product appears to be analytically pure, as indicated by NMR.

X-ray Diffraction Studies. X-ray-quality crystals of **3a**,**b** and **5b** were grown by slow crystallization from *n*-hexane/CH_2Cl_2 and CH_2Cl_2/ethanol, respectively. Details of the data collection and structure refinement are presented in Table 3. The data were corrected for Lorentz and polarization effects. An absorption correction was not deemed necessary, because the single-crystal samples were carefully chosen, rather small, well formed, and essentially isometric, and the quality of the obtained results and the low absorption coefficient values justified no necessity for absorption corrections. All structures have been solved by direct methods and refined by the full-matrix least-squares procedure with anisotropic thermal factors for all non-hydrogen atoms. The H atoms of the BH_4 group in **5b** were located in difference syntheses and refined isotropically; the other H atoms in **5b** as well as all H atoms in **3a** and **3b** were placed at calculated positions and included in the structure factor calculation in the riding motion approximation. The absolute structure for **3a** was defined by the Flack parameter[33] refinement ($x = 0.00(4)$). The SHELXTL-97 program package[34] was used throughout the calculations.

Acknowledgment. We are grateful to the Russian Foundation for Basic Research (Grant Nos. 03-03-32138 and 03-03-32499), to PowerNova Technologies Corp., to INTAS (Grant No. 00-00179), to the European Commission's RTN Program (Grant No. HPRN-CT-2002-00176), to the Leading Scientific School (Grant No. SS-1060.2003.03), and to the Council of the President of Russian Federation on the Grants (Grant No. MK-2212.2004.3), for support of this work.

Supporting Information Available: X-ray crystallographic data for **3a**,**b** and **5b** as CIF files and figures giving NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0497285

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