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Synthesis and structures of palladium P,C,P pincer complexes based on ferrocene

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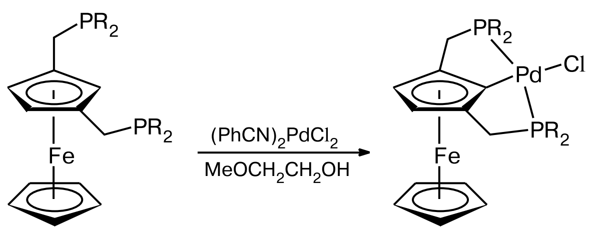
As part of our continuing studies of P,C,P pincer complexes based on metallocenes,[1—3] we synthesized new palladium pincer complexes based on ferrocene. The reaction of 1,3-bis(dialkylphosphinomethyl)ferrocenes $\{1,3\text{-}(R_2PCH_2)_2C_5H_3\}Fe(C_5H_5)$[1] (**1**, R = Pr^i; **2**, R = Bu^t) with $PdCl_2(PhCN)_2$ in hot 2-methoxyethanol afforded the $PdCl[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ complexes (**3**, R = Pr^i; **4**, R = Bu^t) (Scheme 1) as air-stable yellow crystalline compounds. Complexes **3** and **4** are thermally stable and withstand heating at 150 °C over a long period of time. The conclusions about the structures of complexes **3** and **4** were based on the results of NMR spectroscopy and mass spectrometry. The $^{31}P\{^1H\}$ NMR spectra of complexes **3** and **4** have one singlet at δ 71.87 (**3**) and 85.78 (**4**), respectively, which is indicative of the equivalence of the phosphorus nuclei. In the ^1H NMR spectra of complexes **3** and **4**, the signals of the cyclopentadienyl protons are observed as two singlets at δ 4.01 (5 H), 4.23 (2 H) (**3**), and 3.94 (5 H), 4.23 (2 H) (**4**), which provides evidence that the ferrocene moiety underwent cyclometallation.

Scheme 1



1, 2 **3, 4**

1, 3: R = Pr^i; **2, 4:** R = Bu^t

The structures of complexes **3** and **4** were confirmed by single-crystal X-ray diffraction study. These complexes can be used as convenient models for estimating the steric accessibility of the chelated metal atom in P,C,P pincer complexes based on metallocenes not only due to their stability but also because of the presence of the only auxiliary ligand (Cl) at the Pd atom. The recent study[3] of alkane dehydrogenation with the iridium complexes $IrH_2[^RP,C,P^{Fe}]$ has generated the necessity of evaluating the accessibility of the catalytic center to a substrate. Unfortunately, we failed to prepare single crystals of the iridium dihydride complexes suitable for X-ray diffraction analysis. The structural study of complexes **3** and **4** is of interest by itself, because these compounds are potential catalysts, for example, of the Heck reaction and related coupling reactions giving rise to the C—C bond.

According to the X-ray diffraction data, the pincer ligands in complexes **3** and **4** have similar structures (Fig. 1). The palladium atom has a distorted square-planar geometry; the P(1)—Pd—P(2) angle in **3** and **4** is 160.39(6) and 157.57(4)°, respectively.

An interesting structural feature of complexes **3** and **4** is the orientation of the alkyl groups at the phosphorus atoms. In both complexes, both groups at the P atoms located above the cyclometallated Cp ring are in a pseudoaxial orientation. These complexes are structurally different from the P,C,P pincer complexes based on benzene, *viz.*, $PdCl[2,6\text{-}(R_2PCH_2)_2C_6H_3]$,[4—6] in which one of the groups at the P atoms on each side of the cyclometallated benzene ring is pseudoaxial, whereas another group is pseudoequatorial. This difference is conveniently illustrated in Fig. 2, where structures **A** and **B** correspond to the benzene- and ferrocene-based complexes, respectively, projected along the Cl—Pd—C line. As a result of these structural differences, the chelated metal atom in the ferrocene-based complexes is sterically less accessible to a substrate from the exo position compared to their benzene analogs. This structural feature is necessary to take into account in the synthesis of P,C,P pincer com-

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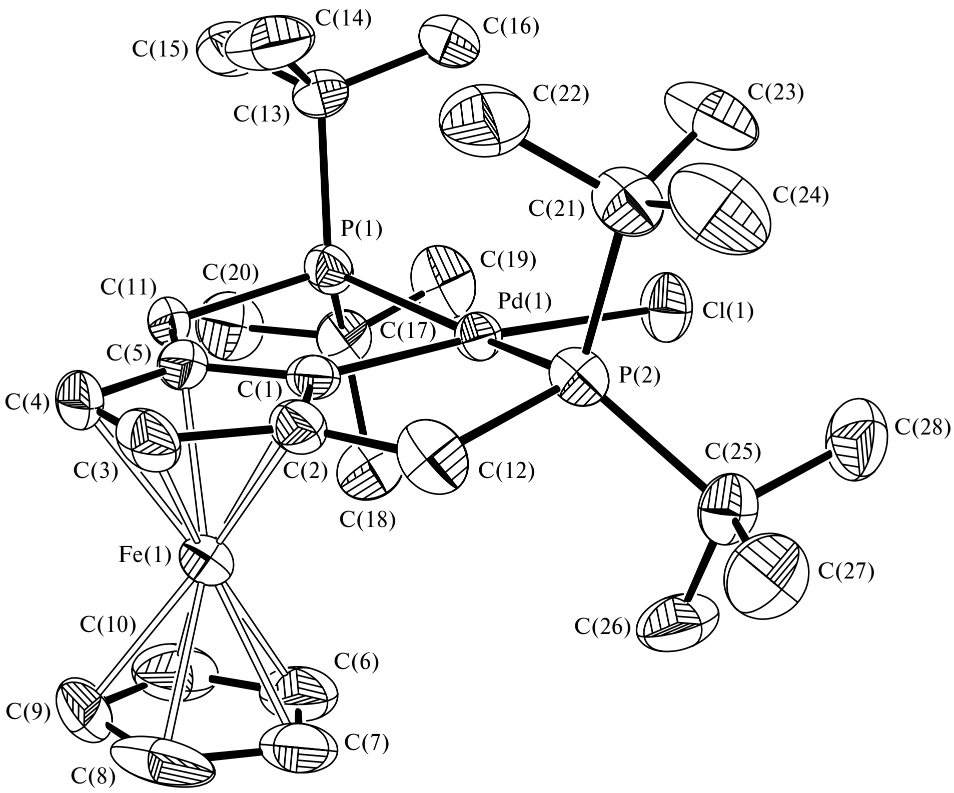

Fig. 1. Structure of complex **4**.

plexes based on metallocenes, which can be used as catalysts.

All operations associated with the synthesis of complexes **3** and **4** were carried out under argon. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 and 161.98 MHz, respectively) in $CDCl_3$. The mass spectra were measured on a Finnigan LCQ instrument.

Chloro{2,5-bis(diisopropylphosphinomethyl)ferrocen-1-yl}palladium(II) (3). The $PdCl_2(PhCN)_2$ complex (440 mg, 1.154 mmol) was added to a suspension of 1,3-bis(diisopropylphosphinomethyl)ferrocene (515 mg, 1.154 mmol) in anhydrous 2-methoxyethanol (50 mL). The reaction mixture was stirred at 125 °C for 3 h. Then the resulting orange solution was cooled and filtered through celite to remove a black powder. The solvent was distilled off on a rotary evaporator and the residue was crystallized from an *n*-hexane—CH_2Cl_2 mixture. The yield of **3** was 320 mg (47%). $^{31}P\{^1H\}$ NMR, δ: 71.87 (s, 2 P). ^1H NMR, δ: 1.07 (*pseudo*-q, 6 H, $CH\underline{H}_3$, J = 7.8 Hz); 1.33 (*pseudo*-q,

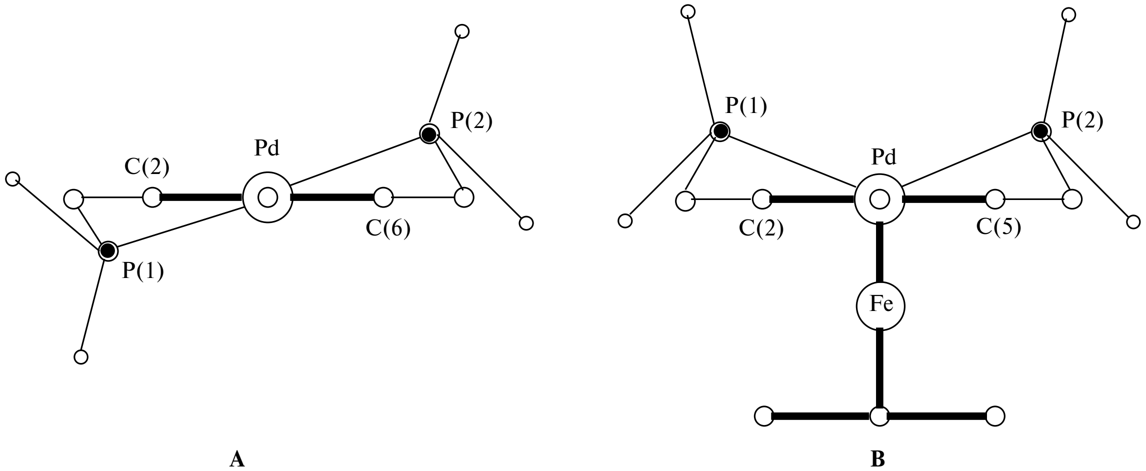

Fig. 2. Schematic representation of the $PdCl[2,6-(R_2PCH_2)_2C_6H_3]$ (**A**) and $PdCl[\{2,5-(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**B**) complexes projected along the Cl—Pd—C axis.

12 H, CHC$\underline{H}_3$, J = 7.4 Hz); 1.53 (*pseudo*-q, 6 H, CHC$\underline{H}_3$, J = 8.1 Hz); 2.18 (m, 2 H, C$\underline{H}$CH$_3$); 2.29 (m, 2 H, C$\underline{H}_a$H$_b$P); 2.53 (m, 2 H, C$\underline{H}$CH$_3$); 2.76 (m, 2 H, CH$_a$$\underline{H}_b$P); 4.01 (s, 5 H, C_5H_5); 4.23 (s, 2 H, C_5H_2). MS, m/z (%): 588 [M$^+$] (100).

Chloro{2,5-bis(di-*tert*-butylphosphinomethyl)ferrocen-1-yl}palladium(II) (4) was prepared analogously in 65.2% yield. ^{31}P{^{1}H} NMR, δ: 85.78 (s, 2 P). ^{1}H NMR, δ: 1.27 and 1.55 (both virt.t, 18 H each, Me); 2.48 (dt, 2 H, C$\underline{H}_a$H$_b$P, $J_{H,H}$ = 16.5 Hz, $J_{H,P}$ = 1.5 Hz); 2.89 (br.d, 2 H, CH$_a$$\underline{H}_b$P, $J_{H,H}$ = 16.5 Hz); 3.94 (s, 5 H, C_5H_5); 4.23 (s, 2 H, C_5H_2). MS, m/z (%): 642 [M]$^+$ (100). Found (%): C, 52.35; H, 7.28. $C_{28}H_{47}ClFeP_2Pd$. Calculated (%): C, 52.38; H, 7.33.

X-ray diffraction study. Complex **4**, $C_{28}H_{47}ClFeP_2Pd$, M = 643.30, space group *Pbca*, a = 17.2290(6) Å, b = 16.4470(5) Å, c = 21.3131(7) Å, V = 6039.4(3) Å^3, Z = 8, the final reliability factors R_1 = 0.0471 (based on F for 3538 observed reflections with $I > 2\sigma(I)$), wR_2 = 0.1026 (based on F^2 for all 7291 independent reflections). X-ray diffraction study was carried out in the Center of X-ray Diffraction Studies of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

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