Palladium pincer complexes $Pd(BH_4)[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (R = Pr^i, Bu^t) with unidentate borohydride ligand

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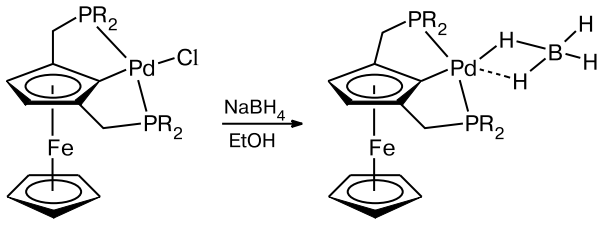
It is known[1] that the BH_4^- ligand can be involved in mononuclear transition metal complexes to form covalent bonds of different types. This ligand can be coordinated to the metal atom by one, two, or three hydrogen atoms. The two latter modes of coordination occur frequently, whereas the unidentate coordination is observed rather rarely. Palladium complexes with the η^1-BH_4 ligand have not been characterized at all.

We found that the reaction of $NaBH_4$ with the ferrocene-based P,C,P pincer complexes $PdCl[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$[2] (**1**, R = Pr^i; **2**, R = Bu^t) in refluxing ethanol afforded the corresponding borohydride complexes $Pd(BH_4)[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**3**, R = Pr^i; **4**, R = Bu^t) (Scheme 1).

Scheme 1



1, 2 **3, 4**

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

The ^1H and $^{31}P\{^1H\}$ NMR spectra are indicative of the retention of the tridentate P,C,P ligand in complexes **3** and **4**. The presence of the BH_4^- group in these complexes is evidenced by the ^1H and ^{11}B NMR spectroscopic data. For example, the ^1H NMR spectrum of complex **4** has a very broad pseudodublet at δ −0.50 ($J \approx 98$ Hz), and its ^{11}B NMR spectrum shows a quintet at δ −37.28 ($J_{B,H}$ = 83.1 Hz). The multiplicity of the ^{11}B signal is indicative of the rapid averaging of the H atoms bound to the boron atom. We failed to "freeze" the exchange process by cooling a solution of complex **4** in toluene-d_8 up to 200 K. The spectroscopic characteristics of complex **3** are very similar to those of complex **4**, which is evidence for the identical mode of coordination of the BH_4^- ligand in these complexes.

The IR spectroscopic data for complexes **3** and **4** correspond to the unidentate coordination of the BH_4^- ligand.[1,3] For example, the spectrum of complex **4** has absorption bands at 2380 (sh), 2369 (v.s), 2293 (s) (stretching vibrations of the terminal B—H bonds), and 1064 (s) cm^{-1} (BH_4 bending vibrations). The structure of complex **4** was established by single-crystal X-ray diffraction study (Fig. 1).

In molecule **4**, the palladium center has a distorted square-planar geometry. Three coordination sites are occupied by the P,C,P ligand, and the fourth site is occupied by the H atom of the borohydride ligand; the Pd—H(1) distance is 2.00(4) Å. The P(1)—Pd—P(2) angle (160.72(3)°) is close to those found earlier[2] in complexes **1** and **2**. Like in other P,C,P pincer complexes based on ferrocene, the chelated metal atom deviates from the plane of the Cp ring in the direction opposite to the iron atom (deviation of Pd is 0.361 Å). The Cp rings are noncoplanar (angle between the planes of these rings is 4.2°) and adopt an eclipsed conformation.

In complex **4**, the Pd...B distance (2.614(7) Å) is too long to assume the presence of the Pd—B bond, unlike the $Ti(BH_4)_3(PMe_3)_2$ complex,[4] in which the Ti atom is bound to two BH_4^- groups (Ti—B, 2.27(1) Å). The analogous short M...B distances are also observed in the complexes in which the metal atom is bound to two hydrogen atoms of the BH_4^- group. For instance, this distance in

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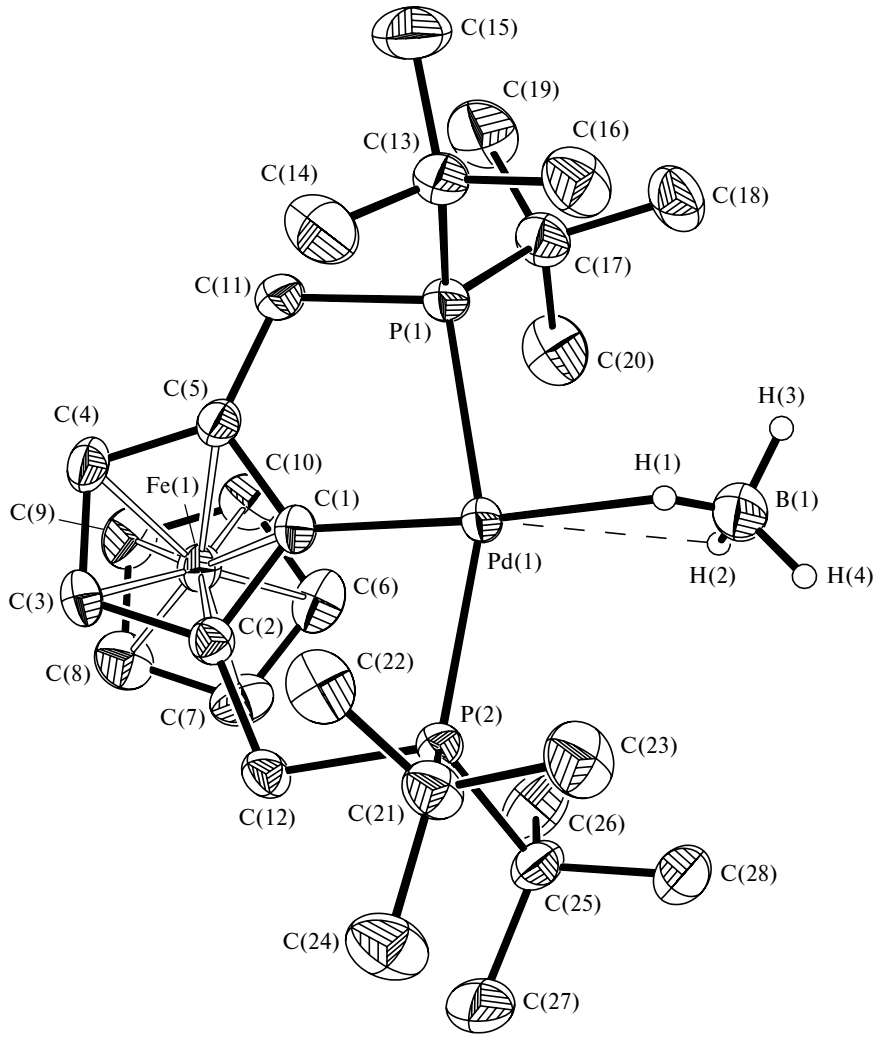

Fig. 1. Structure of complex **4**.

$Co(\eta^2\text{-}BH_4)(triphos)$ **5** is 2.29 Å. However, it should be noted that the Pd...B distance in complex **4** is smaller than the corresponding distances in other η^1-BH_4 derivatives of metals. For example, the Fe...B distance in the $Fe(\eta^1\text{-}BH_4)(H)(dmpe)_2$ compound[6] is 2.84 Å. This fact as well as the rather short distance between the palladium atom and one of the terminal hydrogen atoms of the BH_4^- group (Pd...H(2), 2.56(5) Å) provide evidence that the bond between Pd and BH_4^- in the crystal of **4** involves not only the Pd—H(1) interaction but also the "incipient Pd...H(2) bonding interaction."

In solution, averaging of the hydrogen atoms of the BH_4^- groups in complexes **3** and **4** should proceed through the stepwise formation of η^1- and η^2-coordinated borohydride structures accompanied by rotation of the unidentate BH_4^- group about the Pd—HBH_3 bond.

It should be noted that the complexes synthesized in the present study are very stable. Complex **4** not only withstands refluxing in ethanol but is also inert with respect to triethylamine. An attempt to eliminate borane as the $Et_3N \cdot BH_3$ adduct to form the palladium hydride complex failed. However, complexes **3** and **4** in chloroform solutions were gradually transformed into the starting chloro complexes **1** and **2**, respectively.

The BH_4^- ion is isoelectronic to the CH_4 molecule and, like neutral boranes $L \cdot BH_3$ ($L = NR_3$, PR_3), forms stable complexes with transition metals.[1,7] Since transition metal complexes with alkanes[8,9] are extremely unstable, the complexes with BH_4^- and $L \cdot BH_3$ are commonly considered as models for alkane σ-complexes. It is likely that the structural features of the binding of the BH_4^- ion with the Pd atom in complex **4** model the early step of the oxidative addition of alkanes to the metal center in pincer complexes.

All operations associated with the synthesis of complexes **3** and **4** were carried out under argon. The ^1H, ^{31}P, and ^{11}B NMR spectra were recorded on a Bruker AMX-400 instrument (400.13, 161.98, and 128.38 MHz, respectively). The IR spectra were measured on a Nicolet Magna 750 instrument. The mass spectra were obtained on a Finnigan LCQ instrument.

Tetrahydroborato{2,5-bis(di-*tert*-butylphosphinomethyl)ferrocen-1-yl}palladium(II) (4). Sodium borohydride (350 mg) was added to a solution of the $PdCl[\{2,5\text{-}(Bu^t_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ complex (96 mg, 0.15 mmol) in ethanol (40 mL). The reaction mixture was refluxed for 1 h and then cooled, after which $NaBH_4$ (100 mg) was added to the yellow-orange solution and the mixture was refluxed for 1 h. The solution was separated by decantation, the white precipitate was washed several times with ethanol, and the extracts were concentrated on a rotary evaporator. The residue was dried *in vacuo* and extracted with dichloromethane. Then hexane was added to the extract. The solution was concentrated to 3—4 mL and kept in a freezer for 2 h. The virtually colorless mother liquor was removed using a pipette. The residue was washed with hexane and dried *in vacuo* to prepare an orange crystalline powder in a yield of 68.2 mg (73%). ^{1}H NMR ($CDCl_3$), δ: –0.50 (br.d, 4 H, BH_4, J = 98 Hz); 1.23 (t, 18 H, Me, $J_{H,P}$ = 6.7 Hz); 1.53 (t, 18 H, Me, $J_{H,P}$ = 7.2 Hz); 2.53 (dt, 2 H, $C\underline{H}_aH_bP$, $J_{H,H}$ = 17.0 Hz, $J_{H,P}$ = 4.5 Hz); 3.01 (br.d, 2 H, $CH_a\underline{H}_bP$, $J_{H,H}$ = 17.0 Hz); 3.95 (s, 5 H, C_5H_5); 4.22 (s, 2 H, FeC_5H_2). $^{31}P\{^1H\}$ NMR, δ: 91.39 (s, 2 P). ^{11}B NMR, δ: –37.28 (quint, 1 B, $J_{B,H}$ = 83.1 Hz). IR (KBr), ν/cm^{-1}: 2380 sh, 2369 v.s, 2293 s, 1064 s. MS: 608 [$M^+ - BH_3$].

Tetrahydroborato{2,5-bis(diisopropylphosphinomethyl)ferrocen-1-yl}palladium(II) (3) was prepared analogously in 45% yield. Selected characteristics of the ^{1}H NMR (C_6D_6) spectrum, δ: 0.27 (br.d, 4 H, J = 97.7 Hz); $^{31}P\{^1H\}$ NMR, δ: 78.05 (s, 2 P); ^{11}B NMR: –37.76 (quint, 1 B, $J_{B,H}$ = 81.3 Hz).

X-ray diffraction study. Complex **4**, $C_{28}H_{51}BFeP_2Pd$, M = 622.69, space group $P2_1/c$, a = 10.977(1) Å, b = 18.634(2) Å, c = 15.632(2) Å, β = 109.312(2)°, V = 3017.5(5) Å^3, Z = 4, the final reliability factors R_1 = 0.0440 (based on F for 5266 observed reflections with $I > 2\sigma(I)$), wR_2 = 0.0928 (based on F^2 for all 8751 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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