Article
Steric and Electronic Effect of Cp-Substituents on the Structure of the Ruthenocene Based Pincer Palladium Borohydrides

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Abstract: Ruthenocene-based PCP\textsubscript{tBu} pincer ligands were used to synthesize novel pincer palladium chloride Rc\textsuperscript{F}[PCP\textsubscript{tBu}]PdCl (2a) and two novel palladium tetrahydroborates Rc\textsuperscript{F}[PCP\textsubscript{tBu}]Pd(BH\textsubscript{4}) (3a) and Rc\textsuperscript{*}[PCP\textsubscript{tBu}]Pd(BH\textsubscript{4}) (3b), where Rc\textsuperscript{F}[PCP\textsubscript{tBu}] = \kappa\textsuperscript{3}{\{2,5-(tBu\textsubscript{2}PCH\textsubscript{2})\textsubscript{2}C\textsubscript{5}H\textsubscript{2}\}}Ru(Cp\textsuperscript{F}) (Cp\textsuperscript{F} = C\textsubscript{5}Me\textsubscript{4}CF\textsubscript{3}), and Rc\textsuperscript{*}[PCP\textsubscript{tBu}] = \kappa\textsuperscript{3}{\{2,5-(tBu\textsubscript{2}PCH\textsubscript{2})\textsubscript{2}C\textsubscript{5}H\textsubscript{2}\}}Ru(Cp\textsuperscript{*}) (Cp\textsuperscript{*} = C\textsubscript{5}Me\textsubscript{5}). These coordination compounds were characterized by X-ray, NMR and FTIR techniques. Analysis of the X-ray data shows that an increase of the steric bulk of non-metalated cyclopentadienyl ring in 3a and 3b relative to non-substituted Rc[PCP\textsubscript{tBu}]Pd(BH\textsubscript{4}) analogue (3c; where Rc[PCP\textsubscript{tBu}] = \kappa\textsuperscript{3}{\{2,5-(tBu\textsubscript{2}PCH\textsubscript{2})\textsubscript{2}C\textsubscript{5}H\textsubscript{2}\}}Ru(Cp), Cp = C\textsubscript{5}H\textsubscript{5}) pushes palladium atom from the middle plane of the metalated Cp ring in the direction opposite to the ruthenium atom. This displacement increases in the order 3c < 3b < 3a following the order of the Cp-ring steric volume increase. The analysis of both X-ray and IR data suggests that BH\textsubscript{4} ligand in both palladium tetrahydroborates 3a and 3b has the mixed coordination mode \eta\textsuperscript{1,2}. The strength of the BH\textsubscript{4} bond with palladium atom increases in the order Rc[PCP\textsubscript{tBu}]Pd(BH\textsubscript{4}) < Rc\textsuperscript{*}[PCP\textsubscript{tBu}]Pd(BH\textsubscript{4}) < Rc\textsuperscript{F}[PCP\textsubscript{tBu}]Pd(BH\textsubscript{4}) that appears to be affected by both steric and electronic properties of the ruthenocene moiety.

Keywords: pincer; ligand; palladium; ruthenocene; tetrahydroborate

1. Introduction

The chemistry of transition metal complexes with pincer-type ligands has been actively studied since the 1970s [1]. Such complexes feature a unique balance of stability and reactivity, which can be controlled by the systematic modification of ligands, and thus a huge potential for the use in organic synthesis and catalysis [2–12]. A continuous search for more active and selective catalysts, including asymmetric ones, has led to the appearance of new bimetallic complexes of transition metals with pincer ligands of sandwich-type containing cyclometalated five- [13–22] (A) and six-membered [23–30] (B) aromatic rings (Scheme 1).
The presence of a transition metal in the sandwich moiety allows varying the charge of the bimetallic complex and significantly affects the electrochemical characteristics of the chelated η1-metal center [23]. For example, in comparison with neutral precursors, the presence of a positive charge in bimetallic ruthenium–palladium complexes leads to a decrease in the electron density on the chelated palladium atom and contributes to an increase in its catalytic activity in Suzuki cross-coupling reactions [19,24,26]. It can be assumed that the introduction of electron-withdrawing groups into the sandwich core of the bimetallic complex can favorably affect the catalytic properties of the chelated metal atom. On the other hand, it is well known that in addition to the electronic factor, the catalytic activity of metal complexes is strongly affected by steric factors determining the spatial availability of the metal center for the substrate [8,15,16,31]. In the case of bimetallic PCP complexes of sandwich-type, the steric accessibility of the chelated metal atom is determined not only by the volume of organic groups R at the phosphorus donor atoms and the P-M-P angle but also by the presence of substituents in the non-metalated ring [17,23,25]. Thus, the presence of five methyl groups in the cyclopentadienyl ligand significantly increases its steric volume and donor ability in comparison with the unsubstituted Cp ring (Cp = η5-C5H5). Replacing one of the methyl groups in the Cp* ligand (Cp* = η5-C5Me5) with CF3 group (CpX = C5HMe3CF3) slightly increases the volume of the five-membered ring, but keeps the electronic effect of the ligand at the level of unsubstituted cyclopentadienyl [32–35].

An interesting feature of palladium chloride complexes based on ferrocene and ruthenocene is their ability to react with NaBH4 to form the corresponding tetrahydroborate complexes Fc[PCPbf][Pd(BH4)] and Rc[PCPbf][Pd(BH4)] (where Fc[PCPbf] and Rc[PCPbf] = κ3-(2,5-(tBu2PCH2)2C5H2)M(Cp), M = Fe, Ru) [15,36]. Rc[PCPbf][Pd(BH4)] complex, which we have recently studied [36], proved to be a useful starting compound for the production of highly reactive palladium hydride Rc[Pcpbf][PdH]. However, despite a high potential of complexes of this type, the sterically loaded palladium pincer complexes remain almost unexplored. In this work, we report on the synthesis of two new palladium borohydride pincer complexes based on substituted ruthenocenes. The use of Cp* and CpX ligands and comparison with the non-substituted Cp analogues allows accessing the steric and electronic effects of sandwich moiety on the properties of PCPbf chelated palladium.

2. Results and Discussion

2.1. Synthesis

1,3-disubstituted ruthenocene bisphosphine with a CpX ligand in the metallocene core {1,3-(tBu2PCH2)2C5H2}Ru(CpX) (1) was synthesized by phosphination of the corresponding diol (1,3-(HOCH2)2C5H2)Ru(CpX) in acetic acid according to the previously published procedure [37]. The cyclometation of 1 with PdCl2(PhCN)2 in 2-methoxyethanol under reflux for 3 h (Scheme 2) yields the new palladium complex RcX[Pcpbf][PdCl] (2a) (where RcX[Pcpbf] = κ3-(2,5-(tBu2PCH2)2C5H2)Ru(C5Me3CF3)).
As the reaction proceeds, a finely dispersed, unidentified, bright yellow precipitate and impurities are formed that significantly complicate the subsequent isolation of the target cyclometalation product. To facilitate the isolation of 2a, two equivalents of triethylamine were introduced into the reaction mixture after 3 h of reflux, which was continued for another 2 h. This approach led to the formation of a significant amount of palladium black, however, it allowed simplifying the purification procedure and gave the product with 31% yield. Note that the analogues palladium complex based on pentamethylruthenocene \( \text{Rc}[\text{PCP}t\text{Bu}]\) (2b) (where \( \text{Rc}[\text{PCP}t\text{Bu}] = \kappa^3\{2,5-(t\text{Bu}_2\text{PCH}_2)\text{C}_5\text{H}_2\}\text{Ru}(\text{C}_5\text{Me}_3) \)) was previously obtained under similar conditions with 30% yield. Apparently, the serious steric hindrance in the bisphosphine molecule created by the presence of five substituents in the cyclopentadienyl ring and tert-butyl groups at the donor phosphorus atoms hampers the cyclometalation reaction. For comparison, [PCP\text{Bu}] complexes of palladium based on ferrocene, ruthenocene, and benzene can be obtained under comparable conditions with much higher yields [1,15,17]. It has been reported that in the preparation of benzene-based [POCOP\text{Bu}] palladium complex the replacement of the most frequently used PdCl\(_2\)(PhCN)\(_2\) as a cyclometalating agent with palladium(II) chloride leads to an increase in the yield of the reaction product from 31 to 80% [38]. Unfortunately, the use of PdCl\(_2\) as a cyclometalation reagent in the reaction with \( \text{Rc}^\text{F}[\text{PCP}t\text{Bu}] \) (1) led to the formation of complex 2a only in trace amounts. Compound 2a is a pale yellow, air-stable powder. It was characterized by multinuclear NMR spectroscopy, and its purity was confirmed by elemental analysis.

The \( ^{31}\text{P}[\text{H}] \) and \( ^{19}\text{F} \) NMR spectra of complex 2a contain a single signal from two equivalent phosphorus nuclei and three equivalent fluorine nuclei at \( \delta 82.07 \) ppm and \( -52.74 \) ppm, respectively. In the \( ^1\text{H} \) NMR, the proton signal of the metallated cyclopentadienyl ring is observed as a singlet at 4.22 ppm (2H). The signal of the six protons of two methyl groups located at the 2',5' positions of the \( \text{Cp}^\text{F} \) ligand appears as a broadened multiplet at \( \delta 1.89 \) ppm and the proton signals of two other methyl groups of the same ligand as a singlet at \( \delta 1.77 \) ppm. Geminal methylene protons of CH\(_2\)\(^\text{P}t\text{Bu} \) groups are not equivalent and appear as doublets of virtual triplets at \( \delta 2.45 \) and 2.51 ppm. Resonances of methyl protons of nonequivalent tert-butyl groups are observed in the form of two virtual triplets at \( \delta 1.33 \) ppm and 1.47 ppm in accordance with the expected structure.

The reaction of \( \text{Rc}^\text{F}[\text{PCP}t\text{Bu}]\text{PdCl} \) (2a) and \( \text{Rc}^\text{F}[\text{PCP}t\text{Bu}]\text{PdCl} \) (2b) with an excess of NaBH\(_4\) in refluxing ethanol leads to the formation of the corresponding tetrahydroborates complexes \( \text{Rc}^\text{F}[\text{PCP}t\text{Bu}]\text{Pd(BH}_4 \) (3a) and \( \text{Rc}^\text{F}[\text{PCP}t\text{Bu}]\text{Pd(BH}_4 \) (3b) (Scheme 3).

The complete conversion of the starting chlorides 2 into borohydrides 3 can be reached in 8 h, adding extra NaBH\(_4\) to the reaction mixture every hour. Monitoring of the formation of complex 3b using NMR spectroscopy showed that after 3 h of reflux the ratio of the reaction product to the starting compound is approximately 3:1. The formation of palladium hydride complexes was not observed. For comparison, the pincer chloropalladium complexes based on ferrocene \( \text{Fc}[\text{PCP}t\text{Bu}]\text{PdCl} \) [15] and ruthenocene \( \text{Rc}[\text{PCP}t\text{Bu}]\text{PdCl} \) [36] are completely converted to the corresponding tetrahydroborates in 2 h. Complexes 3a and 3b were isolated in analytically pure form with 90% and 93% yield, respectively, as bright yellow crystalline powders. They are stable at room temperature in the solid state but are sensitive to air and thermally unstable in solution. In chloroform, 3a and 3b rapidly transform.
into the chloropalladium precursors 2a and 2b. In general, sterically loaded borohydride complexes 3a and 3b are less stable than the previously obtained ruthenocene analogue Rc[PCPttBu]Pd(BH₄) (3c) [36]. Compounds 3a and 3b were fully characterized by NMR, IR, and elemental analysis. The presence of BH₄ ligand coordinated to the palladium atom is confirmed by ¹H and ¹¹B NMR spectroscopy. The BH₄ protons appear in the ¹H NMR spectrum as a strongly broadened multiplet at δH 0.13 and 0.21 ppm for 3a and 3b in C₆D₆, respectively. ¹¹B[¹H] NMR spectra exhibit broadened signals at δ ≈−34.54 and −34.73, respectively. The broadening of the BH₄ group signals in the ¹H NMR spectra indicates a rapid averaging in solution of hydrogen atoms bound to boron. The ³¹P[¹H] NMR spectra of complexes 3a and 3b exhibit singlets at δP 87.44 and 87.07, respectively, indicating the equivalence of two phosphorus nuclei.

![Diagram of complexes 2a and 3a](image)

Scheme 3. Synthesis of borohydrides 3a and 3b.

2.2. X-Ray Diffraction Study

The structures of complexes 3a and 3b are very similar as confirmed by single-crystal XRD analysis (Figures 1 and 2). They feature palladium atoms in a distorted square-planar environment with an angle P(1)-Pd(1)-P(2) equal to 155.67(2) and 158.87(5)°, respectively. Palladium atom deviates from the middle plane of the metalated Cp ring in the direction opposite to the ruthenium atom by 0.541(3) and 0.489(9) Å, respectively. For comparison, in the Rc[PCPttBu]Pd(BH₄) complex (3c) the distance between the palladium atom and the plane of the Cp ring is 0.322 Å [36]. In both structures, the phosphorus atoms P(1) and P(2) rise above the Cp ring plane to different degrees: by 0.888(3) and 0.591(3) Å in case of 3a, 0.708(10) and 0.501(11) Å in case of 3b. The presence of five organic substituents in the non-metalated Cp ring makes the cyclopentadienyl rings noticeably non-coplanar. The angle between the planes of the cyclopentadienyl rings is 8.75(8) and 9.9(2)° in 3a and 3b, respectively. Similar values of this angle are reported for palladium chloride complex Rc*[PCPtBu]PdCl (2b) [17].

It is known that the BH₄ anion can be coordinated to a transition metal atom in a monodentate (η¹), bidentate (η²), or tridentate (η³) fashion [39]. According to our X-ray diffraction data, in complexes 3a and 3b the BH₄ group is located in the syn position to the metallocene core relative to the Pd-C(1) bond line. The distance Pd-H(1) is 1.86(2) and 1.82(5) Å, respectively. These values significantly exceed the Pd-H bond length (1.53–1.75 Å) in the known palladium hydride pincer complexes [38,40,41] and are comparable to the values found for the ruthenocene-based complex Rc[PCPttBu]Pd(BH₄) 3c (1.87(2) Å) [36]. The distance of the Pd atom to the second nearest hydrogen atom H(2) in structures 3a, 3b is 2.46(2) and 2.34(6) Å, respectively (for comparison, d(Pd-H(2)) = 2.54(3) Å in 3c [36]) that is below the sum of Pd-H van der Waals radii. The difference between the distances Pd-H(1) and Pd-H(2) in 3a and 3b Δd(Pd···H) = 0.60(2) and 0.52(5) Å is slightly lower than in 3c. These values are comparable to Δd(Pd···H) in the previously described palladium borohydride complexes and fall in the reported range 0.2–0.67 Å [15,36,42,43]. An analysis of the above data votes for the monodentate η¹ type of BH₄ binding to palladium atom with more pronounced secondary Pd···H interaction relative to 3c. However, according to our DFT calculations for complex 3c the elongated Pd-H(2) contact makes an important additional contribution to the total binding of the BH₄ fragment to the palladium atom [36]. We believe
that in complexes 3a and 3b, featuring even shorter Pd-H(2) distances, the coordination of the BH₄ ligand to the palladium atom can be described as the intermediate η¹,² type similar to 3c.

Figure 1. Two views of the compound 3а with thermal ellipsoids at 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.9844(18), Pd(1)–P(1) 2.3447(5), Pd(1)–P(2) 2.3679(5), Pd(1)–B(1) 2.531(2), Pd(1)–H(1) 1.86(2), Pd(1)–H(2) 2.46(2); C(1)–Pd(1)–H(1) 167.9(6), Pd(1)–H(1)–B(1) 118(4), Pd(1)–H(2)–B(1) 90(3), C(1)–Pd(1)–B(1) 165.62(8), P(1)–Pd(1)–P(2) 155.67(2).

Figure 2. Two views of the compound 3b in representation of atoms via thermal ellipsoids at 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.990(5), Pd(1)–P(1) 2.3409(13), Pd(1)–P(2) 2.3453(13), Pd(1)–H(1) 2.34(6), Pd(1)–H(2) 2.34(6); C(1)–Pd(1)–H(1) 166.8(18), Pd(1)–H(1)–B(1) 118(4), Pd(1)–H(2)–B(1) 90(3), C(1)–Pd(1)–B(1) 170.0(2), P(1)–Pd(1)–P(2) 158.87(5).

In complexes 3a and 3b, the Pd⋯B distance exceeds the sum of the covalent radii of Pd and B atoms (ca. 2.2 Å) being 2.531(2) and 2.560 (7) Å, respectively. For comparison, in complex 3c, the Pd⋯B distance is 2.587(3) Å [36]. Obviously, a decrease in the Pd⋯B distance in the series of compounds 3 indicates an increase in the strength of the BH₄ bond with the palladium atom. For comparison, in the recently described monodentate and bidentate borohydride complexes supported by benzene based pincer ligands, the Pd⋯B distance varies in the range 2.42–2.47 Å [42,43]. It is interesting to note that the angle C(1)-Pd(1)-B(1) is 170.3(1)° in the complex R₀(PC₄Bu)Pd(BH₄) (3c) [36] and 170.0(2)° in R₁[PC₄Bu]Pd(BH₄) (3b), while in R₂[PC₄Bu]Pd(BH₄) (3a) it is 165.62(8)°.
Presumably, the additional (relative to complexes 3b and 3c) deviation of 4.4–4.7° from linearity in 3a is due to the greater steric pressure of the bulky axial tert-butyl groups at phosphorus atoms on the borohydride ligand. Indeed, the distance between the central carbon atoms C(16) and C(21) of the axial tert-butyl groups in complexes 3a and 3b is 5.573(3) and 5.759(6) Å, respectively. For comparison, the same distance in complex 3c is 6.006(3) Å [36]. Thus, despite the bulky CF₃ group is in the remote position relative to Pd(BH₄) fragment, it affects the overall geometry of this pincer complex: the decreased inclination of two Cp rings puts three methyl groups close to tert-butyls pushing both tBu₂P fragments above the plane of cyclometalated ring away from to the ruthenium atom. That, in turn, expels BH₄ moiety below the same plane decreasing the C(1)-Pd(1)-B(1) angle.

2.3. IR Spectra

Vibrational spectra are often used to determine the type of BH₄ group coordination to transition metal [39,44]. The IR spectra of complexes 3a and 3b are similar to the spectrum of the previously published Ru[PCP(tBu)]Pd(BH₄) (3c) complex (Figures S14–S17). In agreement with the crystallographic data, they indicate the presence of a secondary Pd···H interaction in addition to the primary Pd-H bond both in the crystalline state and in solution. In the spectra of solid samples of complexes 3a and 3b, the stretching vibration ν(B-H) of the terminal B-H bonds is observed in the frequency range 2363–2388 cm⁻¹ either as a split band (in case of 3a) or as a band with a shoulder (3b). Probably, the splitting is associated with the isotopic effect of ¹⁰B-H/¹³B-H [39] vibrations. In the CH₂Cl₂ solution of complexes 3a and 3b, the same vibration appears as a non-split strong band at 2376 and 2372 cm⁻¹, respectively. Note that, in the series of complexes 3, a shift of this band to a higher frequency region is observed (Table 1), which may indicate an increase in the contribution of the bidentate form of BH₄ coordination [39,44]. The stretching bands ν(B-H) of moderate intensity are observed in the IR spectrum of solid samples 3a and 3b at 2296 and 2291 cm⁻¹, respectively. The stretching vibrations ν(B-H) of a bridging hydrogen atom Pd-H-B in the spectra of complexes 3a, 3b appear as wide bands of moderate intensity at 2019 and 2025 cm⁻¹ and a high-intensity band in the lower frequency region at 1838 and 1846 cm⁻¹, respectively. It should be noted that ν(B-H) stretching vibrations in the low-frequency region at 1700-2000 cm⁻¹ are rarely observed in the IR spectra of M(η₁-BH₄) complexes, but as a rule always present in the spectra of M(η²-BH₄) complexes [44]. The bands of bending vibrations δ(BH) in the spectra of complexes 3a, 3b are observed at 1054 and 1060 cm⁻¹, respectively, that is in the frequency range characteristic rather for the η¹-bound BH₄ ligand [39,44].

Table 1. Selected FTIR data for complexes 3a–3c (band positions in cm⁻¹).

|                  | 3a(KBr) | 3b(KBr) | 3c(KBr) [36] | 3a(CH₂Cl₂) | 3b(CH₂Cl₂) |
|------------------|---------|---------|--------------|------------|------------|
| ν(B-H)           | 2388, 2363 | 2374 | 2364 | 2376 | 2372 |
| ν¹(B-H)          | 2296 | 2291 | 2292 | 2289 | 2287 |
| δ₁(B-H)          | 2019 | 2025 | 1993 | 2019 | 2008 |
| δ₂(B-H)          | 1838 | 1840 | 1840 | 1840 | 1841 |
| δ(BH)            | 1054 | 1060 | 1062 | 1062 | 1062 |

3. Materials and Methods

3.1. General Considerations

All synthetic work was performed under a purified argon atmosphere using standard Schlenk techniques. The solvents were dried and degassed by standard methods under an argon atmosphere. Deuterated solvents were freshly distilled under argon prior to use. The starting compounds 1,3-bis(di-tert-butylphosphinomethyl)-1’-t(trifluoromethyl)-2’,3’,4’,5’-(tetramethyl)-ruthenocene (1) [37] and 2,5-bis(di-tert-butylphosphinomethyl)-1’,2’,3’,4’,5’-(pentamethyl)-ruthenocene-1-yl)palladium chloride (2b) [17] were prepared by known procedures.
3.2. Crystallographic Data

Crystals of 3a (C32H38BF3P2PdRu, M = 792.01) are monoclinic, space group P21/c, at 120 K: a = 18.5494(6), b = 12.0953(4), c = 15.8197(5) Å, β = 90.2560(10)°, V = 3549.3(2) Å³, Z = 4 (Z′ = 1), dcalc = 1.482 g cm⁻³, µ(MoKα) = 10.59 cm⁻¹, F(000) = 1632. Crystals of 3b (C33H39BF3P2PdRu, M = 783.03) are orthorhombic, space group P212121, at 120 K: a = 11.3765(5), b = 15.0316(6), c = 21.0022(9) Å, V = 3591.5(3) Å³, Z = 4 (Z′ = 1), dcalc = 1.365 g cm⁻³, µ(MoKα) = 10.30 cm⁻¹, F(000) = 1536. Intensities of 72725 and 36743 reflections were measured with a Bruker APEX2 DUO CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, 2θ < 58°] for 3a and 3b, respectively; 9442 and 9578 independent reflections [Rint = 0.0522 and 0.0518] were used in a further refinement. Using Olex2 [45], the structures were solved with the ShelXT structure solution program [46] using Intrinsic Phasing and refined with the XL refinement package [47] using Least-Squares minimization. Hydrogen atoms of the BH groups were located from difference Fourier synthesis and refined freely in the isotropic approximation. Positions of all other atoms were calculated, and they were refined within the riding model. For 3a, the refinement converged to wR2 = 0.0535 and GOF = 1.023 for all the independent reflections (R1 = 0.0235 was calculated against F for 8034 observed reflections with I > 2σ(I)). For 3b, the refinement converged to wR2 = 0.0729 and GOF = 1.009 for all the independent reflections (R1 = 0.0394 was calculated against F for 8230 observed reflections with I > 2σ(I)). CCDC 1993081 and 1993082 contain the supplementary crystallographic information for 3a and 3b, respectively. Crystal data and structure refinement parameters for 3a, 3b are summarized in Table S1.

3.3. Synthesis

3.3.1. Preparation of [2,5-Bis(di-tert-butylphosphinomethyl)-1′-(trifluoromethyl)-2′,3′,4′,5′-(tetramethyl) ruthenocen-1-yl]palladium(II) chloride PdCl2[2,5-(tBu2PCH2)2C5H2]2Ru(C5Me5CF3)] (2a)

PdCl2(PhCN)2 (270 mg, 0.703 mmol) was added to a suspension of bisphosphine 1 (470 mg, 0.700 mmol) in 2-methoxyethanol (20 mL). The mixture was refluxed with stirring for 3 hr, then triethylamine (0.20 mL, 1.45 mmol) was rapidly added to the boiling solution using a syringe and the mixture was refluxed for additional 2 hr. After cooling the resulting solution was diluted with dichloromethane (1:1) and filtered through celite. Then the solvents were removed in vacuo, and the residue was purified on an alumina column (elucent hexane-dichloromethane (2:1)). Recrystallization of the residue from ethanol gave pale-yellow solid of the product. Yield: 175 mg (31%). 1H NMR (400.13 MHz, CDCl3, 294 K): 1.33 (vt, 18H, JHp = 13.1, (CH3)3), 1.47 (vt, 18H, JHp = 14.6, (CH3)3), 1.77 (s, 6H, 3,4-C5(CH3)2(CH3)2CF3), 1.89 (br. m, 6H, 2,5-C5(CH3)2(CH3)2CF3), 2.45 (dvt, 2H, JHH = 16.6, JHp = 6.3, CH3Hap), 2.51 (dvt, 2H, JHH = 16.6, JHp = 8.7, CH3Hap), 4.22 (s, 2H, C5H2). 31P[1H] NMR (161.98 MHz, CDCl3, 294 K): 82.07 (s, 2P). 19F NMR (376.50 MHz, CDCl3, 294 K): -52.74 (s, 3F, CF3).
C₅(CH₃)₄CF₃), 97.26 (vt, 2C, J₇P = 29.3, 2,5-C₅H₂), 118.98 (s, 1C, 1-C₅H₂), 128.27 (q, 1C, J₇P = 270.0, CF₃). Anal. Calc. for C₅₃H₄₅F₃₂Cl₂PdRu (Mr = 812.75): C, 48.76; H, 6.71; P, 7.62; Cl, 4.36%. Found: C, 48.54; H, 6.82; P, 7.49; Cl, 4.48%.

3.3.2. General Procedure for Preparation of Palladium Tetrahydroborate Complexes 3a and 3b

NaBH₄ (100 mg, 2.63 mmol) was added to a solution of complexes 2a or 2b (110–120 mg) in 20 mL of ethanol-benzene (10:1) mixture at room temperature. The mixture was refluxed for 8 h, adding 50 mg (1.32 mmol) of NaBH₄ to the mixture every hour. The reaction mixture was then cooled and evaporated in vacuo to a minimum volume. Distilled water (20 mL) was added to the residue, the resulting suspension was stirred at room temperature for 1 h. The reaction mass was extracted (4 × 10 mL) with hexane-benzene (3:1). The solvents were evaporated in vacuo. Recrystallization of the residue from toluene-hexane (1:1) mixture gave solid products (3a or 3b), which were additionally dried in vacuo at room temperature.

Preparation of [2,5-Bis(di-tert-butylphosphinomethyl)-1′-(trifluoromethyl)-2′,3′,4′,5′-(tetramethyl)-ruthenocen-1-yl]palladium(II) tetrahydroborate Pd(BH₄)[(2,5-(Bu₂PCH₂)₃C₅H₅)Ru(C₅Me₅CF₃)] (3a)

Complex 3a obtained from 118 mg (0.145 mol) of complex 2a as a yellow powder. Yield: 104 mg (90%). ¹H NMR (400.13 MHz, C₅D₅₀, 293 K): 0.13 (br. m, 4H, BH₄), 1.15 (vt, 18H, J₁₂P = 13.4, C(CH₃)₃), 1.40 (vt, 18H, J₁₂P = 14.4, C(CH₃)₃), 1.66 (s, 6H, 3,4-C₅(CH₃)₂(CH₂)₂CF₃), 1.95 (br. m, 6H, 2,5-C₅(CH₃)₂(CH₂)₂CF₃), 2.08 (dvt, 2H, J₁HH = 16.6, J₁HP = 9.2, CH₃H₂P), 2.32 (dvt, 2H, J₁HH = 16.6, J₁HP = 5.9, CH₃H₂P), 4.25 (s, 2H, C₅H₂). ¹¹B¹[H] (128.38 MHz, C₅D₅₀, 295 K): −34.54 (br.s, 1B, BH₄). ¹³P¹[H] NMR (121.49 MHz, C₅D₅₀, 293 K): 87.44 (s, 2P). ¹⁹F NMR (376.50 MHz, C₅D₅₀, 295 K): −52.05 (s, 3F, CF₃). ¹³C¹[H] NMR (150.93 MHz, C₅D₅₀, 294 K): 10.57 (s, 2C, 3,4-C₅(CH₃)₂(CH₂)₂CF₃), 11.44 (br. m, 2C, 2,5-C₅(CH₃)₂(CH₂)₂CF₃), 23.36 (vt, 2C, J₇P = 20.3, CH₂), 29.55 (vt, 6C, J₇P = 7.1, C(CH₃)₃), 29.63 (vt, 6C, J₇P = 6.0, C(CH₃)₃), 34.70 (vt, 2C, J₇P = 14.4, C(CH₃)₃), 35.27 (vt, 2C, J₇P = 11.4, C(CH₃)₃), 71.43 (vt, 2C, J₇P = 16.5, 3,4-C₅H₂), 77.03 (q, 1C, J₇P = 35.3, C-CF₃), 82.65 (s, 2C, C₅(CH₃)₄CF₃), 87.45 (s, 2C, C₅(CH₃)₄CF₃), 97.82 (vt, 2C, J₇P = 28.8, 2,5-C₅H₂), 121.77 (s, 1C, 1-C₅H₂), 129.22 (q, 1C, J₇P = 269.9, CF₃). FTIR (KBr pellet, ν in cm⁻¹): 2376 (s(σ), B-H), 2363 (s, B-H), 2296 (s, B-H), 2019 (br. w, B-H₃-Pd), 1838 (br. s, B-H₃-Pd), 1054 (s, δ(BH₄)). FTIR (CH₂Cl₂, ν in cm⁻¹): 2376 (s(σ), B-H), 2289 (s, B-H), 2019 (br. w, B-H₃-Pd), 1840 (s, B-H₃-Pd), 1062 (s, δ(BH₄)). Anal. Calc. for C₅₃H₄₃BF₃₂PdRu (Mₐ = 792.06): C, 50.04; H, 7.38%. Found: C, 50.29; H, 7.48%.

Preparation of [2,5-Bis(di-tert-butylphosphinomethyl)-1′,2′,3′,4′,5′-(pentamethyl)ruthenocen-1-yl]palladium(II) tetrahydroborate Pd(BH₄)[(2,5-(Bu₂PCH₂)₃C₅H₅)Ru(C₅Me₅CF₃)] (3b)

Complex 3b obtained from 114 mg (0.150 mol) of complex 2b as a yellow powder. Yield: 103 mg (93%). ¹H NMR (400.13 MHz, C₅D₅₀, 295 K): 0.21 (br.m, 4H, BH₄), 1.20 (vt, 18H, J₁₂P = 13.0, C(CH₃)₃), 1.47 (vt, 18H, J₁₂P = 14.3, C(CH₃)₃), 1.84 (s, 15H, C₅(CH₃)₅), 2.15 (dvt, 2H, J₁HH = 16.5, J₁HP = 9.1, CH₃H₂P), 2.38 (dvt, 2H, J₁HH = 16.5, J₁HP = 5.9, CH₃H₂P), 3.95 (s, 2H, C₅H₂). ¹¹B¹[H] (128.38 MHz, C₅D₅₀, 295 K): −34.73 (br.s, 1B, BH₄). ¹³P¹[H] NMR (161.98 MHz, C₅D₅₀, 295 K): 87.07 (s, 2P). ¹³C¹[H] NMR (150.93 MHz, C₅D₅₀, 293 K): 11.49 (s, 5C, C₅(CH₃)₅), 23.42 (vt, 2C, J₇P = 20.4, CH₂), 29.71 (m, 12C, C(CH₃)₃), 34.67 (vt, 2C, J₇P = 14.3, C(CH₃)₃), 35.22 (vt, 2C, J₇P = 11.1, C(CH₃)₃), 71.43 (vt, 2C, J₇P = 16.9, 3,4-C₅H₂), 83.99 (s, 5C, C₅(CH₃)₅), 95.84 (vt, 2C, J₇P = 29.1, 2,5-C₅H₂), 120.55 (s, 1C, 1-C₅H₂). FTIR (KBr pellet, ν in cm⁻¹): 2374 (s(σ), B-H), 2291 (s, B-H), 2025 (br. w, B-H₃-Pd), 1851 (s, B-H₃-Pd), 1060 (s, δ(BH₄)). FTIR (CH₂Cl₂, ν in cm⁻¹): 2372 (s(σ), B-H), 2287 (s, B-H), 2008 (br. w, B-H₃-Pd), 1841 (s, B-H₃-Pd), 1062 (s, δ(BH₄)). Anal. Calc. for C₅₃H₄₃BF₃₂PdRu (Mₐ = 738.09): C, 53.70; H, 8.33; P, 8.39%. Found: C, 53.84; H, 8.38; P, 8.13%.
4. Conclusions

Thus, our work demonstrated that the introduction of the bulky C₅Me₅CF₃ (C₅f) and C₅Me₅(C₅f*) ligands in the sandwich scaffold of the ruthenocene-based PCP[tBu] pincer palladium complexes does not preclude the formation of the corresponding palladium tetrahydroborate pincer complexes. The two novel sterically loaded pincer palladium tetrahydroborates Rc-[PCP[tBu]]Pd(BH₄) (3a) and Rc*[PCP[tBu]]Pd(BH₄) (3b) were synthesized and fully characterized by X-ray, NMR, and FTIR techniques. The X-ray diffraction study of 3a and 3b revealed that an increase of the steric bulk of non-metalated cyclopentadienyl ring in 3a and 3b relative to non-substituted Rc[PCP[tBu]]Pd(BH₄) analogue (3c) pushes palladium atom from the middle plane of the metalated Cp ring in the direction opposite to the ruthenium atom. This displacement increases in the order 3c < 3b < 3a following the order of the Cp-ring steric volume increase. The analysis of both X-ray and IR data suggests that BH₄ ligand in both palladium tetrahydroborates 3a and 3b has the mixed coordination mode η¹² similar to that in 3c in which the primary Pd-H contact of 1.82–1.87Å is accompanied by the secondary interaction Pd···H of 2.34–2.54Å. Pd···B distances decrease in the order: Rc[PCP[tBu]]Pd(BH₄) > Rc*[PCP[tBu]]Pd(BH₄) > Rc²[PCP[tBu]]Pd(BH₄) that suggests the increase in the strength of the BH₄ bond with the palladium atom that appears to be affected by both steric and electronic properties of the ruthenocene moiety.

Supplementary Materials: The following are available online, Table S1: Crystal data and structure refinement parameters for 3a, 3b. Figure S1: ¹H NMR spectrum (400.13 MHz) of 2a in CDCl₃. Figure S2: ³¹P[¹H] NMR spectrum (161.98 MHz) of 2a in CDCl₃. Figure S3: ¹⁹F NMR spectrum (376.50 MHz) of 2a in CDCl₃. Figure S4: ¹³C[¹H] NMR spectrum (150.93 MHz) of 2a in CDCl₃. Figure S5: ¹H NMR spectrum (400.13 MHz) of 3a in C₆D₆. Figure S6: ¹¹B[¹H] NMR spectrum (128.38 MHz) of 3a in C₆D₆. Figure S7: ³¹P[¹H] NMR spectrum (121.49 MHz) of 3a in C₆D₆. Figure S8: ¹⁹F NMR spectrum (376.50 MHz) of 3a in C₆D₆. Figure S9: ¹³C[¹H] NMR spectrum (150.93 MHz) of 3a in C₆D₆. Figure S10: ¹H NMR spectrum (400.13 MHz) of 3b in C₆D₆. Figure S11: ¹¹B[¹H] NMR spectrum (128.38 MHz) of 3b in C₆D₆. Figure S12: ³¹P[¹H] NMR spectrum (161.98 MHz) of 3b in C₆D₆. Figure S13: ¹³C[¹H] NMR spectrum (150.93 MHz) of 3b in C₆D₆. Figure S14: FTIR spectra of 3a in KBr pellet. Figure S15: FTIR spectra of 3b in KBr pellet. Figure S16: FTIR spectra of 3a in the CH₂Cl₂ solution. Figure S17: FTIR spectra of 3b in the CH₂Cl₂ solution.

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