Synthesis and comparative X-ray diffraction study of first ruthenocene-based pincer palladium complexes, PdCl[{2,5-($Bu^t_2PCH_2)_2C_5H_2$}Ru(Cp´)] (Cp´ = C_5H_5 or C_5Me_5)

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First ruthenocene-based palladium complexes PdCl[{2,5-($Bu^t_2PCH_2)_2C_5H_2$}Ru(Cp´)] (Cp´ = C_5H_5 (**4**) or C_5Me_5 (**5**)) were synthesized. Comparative single-crystal X-ray diffraction study of complexes **4** and **5** showed that the deviations of the cyclopentadienyl rings in these complexes from being parallel are 2.6 and 10.1°, respectively. In addition, the shift of the palladium atom relative to the plane of the metallated cyclopentadienyl ligand is 0.007 Å for **4** and 0.336 Å for **5**. These differences in the structures of complexes **4** and **5** are due to close contacts between the pseudoequatorial *tert*-butyl groups at the phosphorus atoms and the unmetallated cyclopentadienyl ring.

Key words: 1,3-disubstituted ruthenocene derivatives, pincer palladium complexes, steric effects, X-ray diffraction analysis.

Recently, we have begun studies of metallocene-based pincer transition metal complexes.[1] These studies were initiated primarily in an effort to design homogeneous catalytic systems for alkane dehydrogenation related to the known benzene-based pincer P,C,P complexes[2] IrH_2[2,6-($R_2PCH_2)_2C_6H_3$] (R = Bu^t or Pr^i). It was of interest to find answers to the following three questions: whether it is possible to synthesize metallocene-based pincer P,C,P complexes, whether these complexes will be sufficiently thermally stable for their use in catalysis (taking into account strong steric strain in fused five-membered metallacycles), and whether the IrH_2[{2,5-($Bu^t_2PCH_2)_2C_5H_2$}M(C_5H_5)] complexes (IrH_2[$^{Bu^t}$P,C,P^M], M = Fe (**1**) or Ru (**2**)) will catalyze alkane dehydrogenation. Positive answers to all theses questions were obtained.[1,3,4] Moreover, recently we have demonstrated that complexes **1** and **2** exhibit unprecedented activity in alkane dehydrogenation.[4] For example, the turnover numbers (TONs) for cyclooctane dehydrogenation in the presence of *tert*-butylethylene as a hydrogen acceptor at 180 °C for 8 h with the use of complexes **1** and **2** and the known[5] pincer bis(phosphinite) iridium complex IrH_2[2,6-($Bu^t_2PO)_2C_6H_3$] were 3300, 2571, and 1843, respectively.

With the aim of explaining high catalytic activity of complexes **1** and **2** and a substantial difference in the activity of these "isostructural" complexes, we studied the electronic and steric properties of the Ir[P,C,P] fragments in our complexes and the known benzene-based iridium complexes[4] and analyzed the role of the steric factors based on X-ray diffraction data for pincer iridium and palladium complexes[4] (stable metallocene-based pincer palladium complexes proved to be convenient models[3] for studying activation of alkanes by the catalytically active Ir[^{R}P,C,P^M] species). It was found that steric accessibility of the chelated metal atom to a substrate may be the key factor responsible for catalytic activity of pincer iridium complexes.

Steric accessibility of the chelated iridium atom in pincer complexes is determined by the following two factors: the P—Ir—P angle and the bulkiness of the alkyl groups R at the donor phosphorus atoms.[4] We found that there is also the third steric factor in metallocene-based pincer complexes associated with the contact between the pseudoequatorial groups R at the phosphorus atoms and the unmetallated cyclopentadienyl ring. This contact causes a deviation of the cyclopentadienyl rings from being parallel and a shift of the chelated metal atom relative to the plane of the metallated cyclopentadienyl ring.[4] The above-mentioned steric effects would be expected to be different for "isostructural" ferrocene- and ruthenocene-based complexes due to the difference in the interring

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distance in ferrocene and ruthenocene (3.32 and 3.682 Å, respectively)[6,7]. Actually, X-ray diffraction studies of PdCl[$^{Bu^t}$P,C,P^{Fe}] (**3**) and PdCl[$^{Bu^t}$P,C,P^{Ru}] (**4**) demonstrated that the deviation of the cyclopentadienyl rings from being parallel is 4.5 and 2.6°, respectively.[3,4] In addition, the Pd atom in complex **3** deviates upward from the plane of the cyclopentadienyl ring by 0.069 Å, whereas the analogous deviation of the Pd atom in complex **4** is as small as 0.007 Å.

Therefore, the steric factor in metallocene-based pincer complexes associated with the contact between the pseudoequatorial organyl groups and the unmetallated cyclopentadienyl ring can influence both the accessibility of the catalytic center to a substrate and stability of various intermediates of the catalytic cycle, thus determining the overall rate of the catalytic reaction.

Evidently, the sandwich nature of metallocene-based pincer ligands opens new possibilities for the design of organometallic compounds with the finely controlled catalytic properties by both varying the nature of the central atom of metallocene and introducing substituents of different bulkiness into the unmetallated cyclopentadienyl ring.

In this connection, it was of interest to synthesize related metallocene-based pincer complexes, which differ in the steric demands of the unmetallated cyclopentadienyl ligand (for example, C_5H_5 and C_5Me_5) and reveal the influence of this difference on the structural characteristics and catalytic activity of the pincer system. In the present investigation, we synthesized the palladium complexes PdCl[{2,5-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5H_5)] (**4**) and PdCl[{2,5-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5Me_5)] (**5**) and performed a comparative X-ray diffraction study of these complexes.

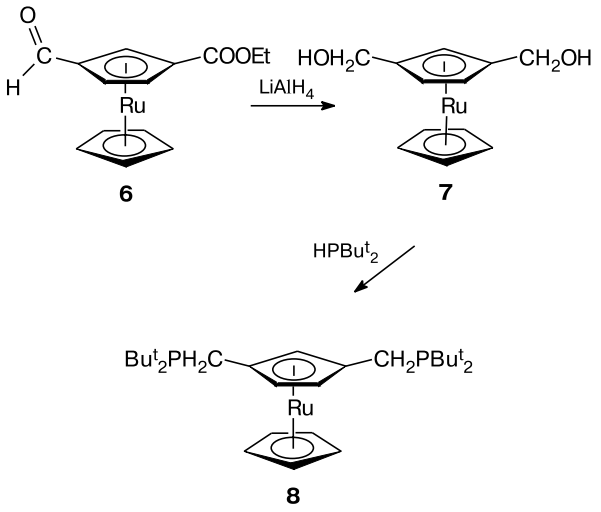
Results and Discussion

Synthesis of palladium complexes 4 and 5. We developed different procedures for the synthesis of diphosphine derivatives of ruthenocene, which are precursors of the pincer ligands of complexes **4** and **5**.

Reduction of 3-ethoxycarbonyl-1-formylruthenocene[8] (**6**) with lithium aluminum hydride in diethyl ether afforded 1,3-bis(hydroxymethyl)ruthenocene (**7**), whose phosphorylation with $HPBu^t_2$ in hot acetic acid gave the corresponding diphosphine[1,4] (**8**) (Scheme 1).

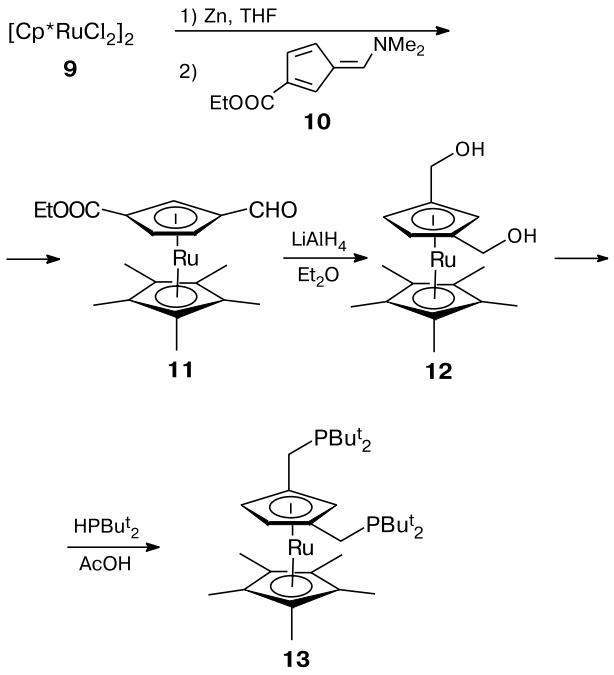
A precursor of the pincer ligand of complex **5** was synthesized with the use of the reaction sequence presented in Scheme 2. The dimeric ruthenium complex [(C_5Me_5)$RuCl_2$]$_2$ (**9**) (see Refs 9 and 10) was treated with zinc dust in THF at 40 °C. Then 2-ethoxycarbonyl-6-dimethylaminopentafulvene[8] (**10**) was added to the solution, which presumably[11] contained [(C_5Me_5)RuCl]$_n$. The reaction mixture was refluxed for several hours.

Scheme 1



The removal of the solvent and chromatographic purification on a silica gel column afforded Ru{1-(CHO)-3-(COOEt)C_5H_3}(C_5Me_5) (**11**). Reduction of the latter with $LiAlH_4$ produced the corresponding diol Ru{1,3-(CH_2OH)$_2C_5H_3$}(C_5Me_5) (**12**), whose phosphorylation afforded diphosphine Ru{1,3-($Bu^t_2PCH_2$)$_2C_5H_3$}(C_5Me_5) (**13**).

Scheme 2

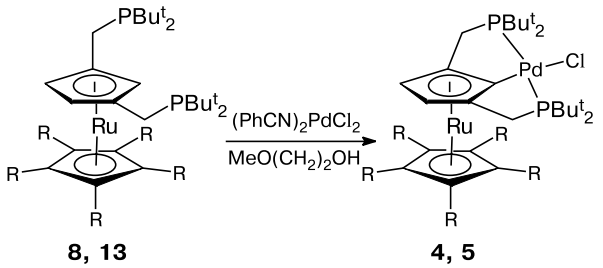


The newly formed ruthenocene derivatives were characterized by ^{1}H NMR spectroscopy. Diphosphine **13** was

additionally characterized by ^{31}P NMR spectroscopy. The reaction products are crystalline compounds with various tints of yellow.

Cyclopalladation of diphosphines **8** and **13** was carried out under the conditions, which we have used earlier for the synthesis of ferrocene-based pincer chloropalladium complexes by the reaction of the corresponding diphosphine with $PdCl_2(NCPh)_2$ in 2-methoxyethanol[3,12] (Scheme 3).

Scheme 3



8, 13 **4, 5**

R = H (**4, 8**), Me (**5, 13**)

Palladium complexes **4** and **5** are air-stable crystalline yellowish compounds. These compounds were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectra of complexes **4** and **5** show a signal for two equivalent ^{31}P nuclei at δ 84.52 and 81.96, respectively. The formation of the cyclopalladated complex is evidenced by the presence of a singlet for two cyclopentadienyl protons at δ 3.89 in the ^1H NMR spectrum of complex **5**. The structures of complexes **4** and **5** were confirmed by a single-crystal X-ray diffraction study, which revealed interesting differences in the structures of these complexes.

X-ray diffraction study of complexes 4 and 5. It was of interest to compare the crystal structures of complexes **4** and **5**, in particular, to elucidate the influence of the introduction of five methyl substituents into the cyclopentadienyl ring on the mutual inclination of the cyclopentadienyl ligands and the position of the palladium atom relative to the plane of the cyclometallated five-membered ring.

The structures of complexes **4** and **5** are very similar (Fig. 1) and contain the palladium atom in a distorted square-planar environment. The P(1)—Pd(1)—P(2) angles in complexes **4** and **5** are 157.94(3) and 157.87(3)°, respectively (Table 1). In both complexes, the C(1)—Pd(1) distances are also similar (1.961(3) and 1.972(3) Å for **4** and **5**, respectively). The C(1)—Pd(1)—Cl(1) angle is 175.24(1)° and 176.84(9)° in **4** and **5**, respectively. Presumably, the deviation from linearity is due to the steric effect of the bulky axial *tert*-butyl groups at the phosphorus atoms on the chloride ligand.

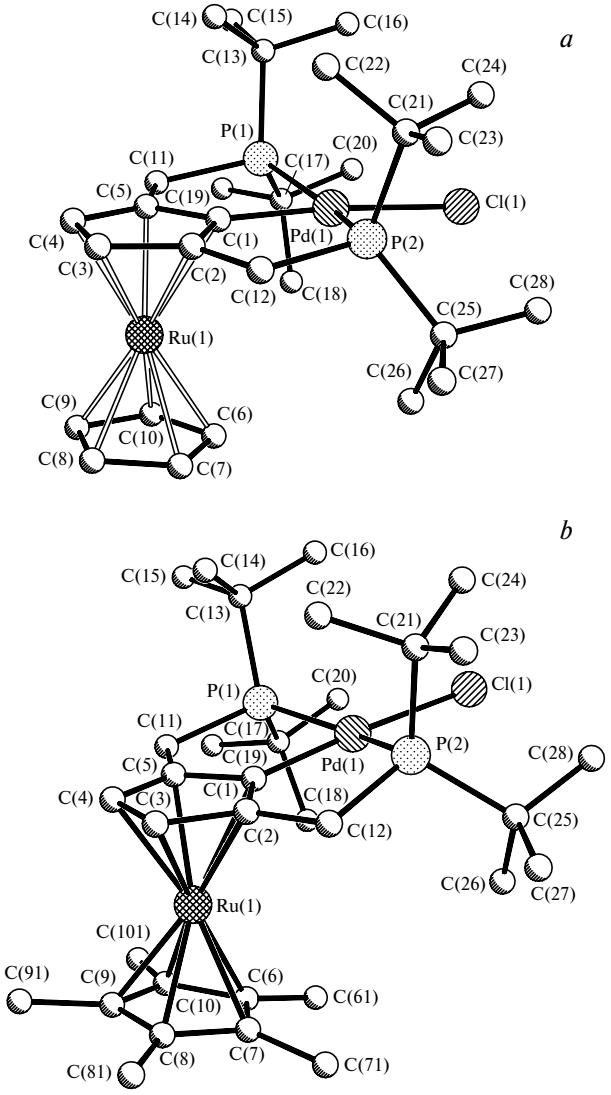


Fig. 1. Molecular structures of the PdCl[{2,5-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5H_5)] (**4**) (*a*) and PdCl[{2,5-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5Me_5)] (**5**) complexes (*b*).

Complexes **4** and **5** differ most substantially in the deviation of the cyclopentadienyl rings from the parallel arrangement (2.6 and 10.1°, respectively), which is undoubtedly due to the contact between the pseudoequatorial *tert*-butyl groups at the P atoms and the unmetallated cyclopentadienyl ring. These distortions of the structure can be seen in Fig. 2. The presence of this contact is also manifested in different shifts of the palladium atom relative to the plane of the metallated cyclopentadienyl ring (0.007 and 0.336 Å in complexes **4** and **5**, respectively).

To conclude, we developed a new procedure for the synthesis of 1,3-disubstituted ruthenocenes derived from (pentamethylcyclopentadienyl)cyclopentadienylruthenium. It was demonstrated that the presence of the bulky

Table 1. Selected bond lengths (d) and bond angles (ω) in complexes **4** and **5**

Bond	d/Å		Angle	ω/deg	
	4	**5**		**4**	**5**
Pd(1)—Cl(1)	2.4054(9)	2.4049(8)	C(1)—Pd(1)—P(1)	80.55(11)	81.31(9)
Pd(1)—P(1)	2.3299(9)	2.3335(8)	C(1)—Pd(1)—P(2)	80.99(11)	80.66(9)
Pd(1)—P(2)	2.3332(9)	2.3221(8)	P(1)—Pd(1)—P(2)	157.94(3)	157.87(3)
Pd(1)—C(1)	1.961(3)	1.972(3)	C(1)—Pd(1)—Cl(1)	175.24(10)	176.84(9)
Ru(1)—C(1)	2.214(3)	2.251(3)	P(1)—Pd(1)—Cl(1)	100.01(3)	99.88(3)
Ru(1)—C(2)	2.183(3)	2.189(3)	P(2)—Pd(1)—Cl(1)	99.39(3)	98.81(3)
Ru(1)—C(3)	2.167(4)	2.150(3)	C(11)—P(1)—C(13)	104.39(17)	104.05(16)
Ru(1)—C(4)	2.165(4)	2.157(3)	C(11)—P(1)—C(17)	104.48(18)	105.45(15)
Ru(1)—C(5)	2.176(3)	2.200(3)	C(13)—P(1)—C(17)	112.08(18)	112.46(15)
Ru(1)—C(6)	2.188(4)	2.207(3)	C(11)—P(1)—Pd(1)	105.76(12)	105.40(10)
Ru(1)—C(7)	2.188(4)	2.185(3)	C(13)—P(1)—Pd(1)	110.67(14)	110.65(10)
Ru(1)—C(8)	2.169(4)	2.168(3)	C(17)—P(1)—Pd(1)	118.11(12)	117.51(10)
Ru(1)—C(9)	2.174(4)	2.157(3)	C(12)—P(2)—C(25)	104.81(18)	105.30(15)
Ru(1)—C(10)	2.179(4)	2.179(3)	C(12)—P(2)—C(21)	104.22(17)	103.48(14)
P(1)—C(11)	1.860(4)	1.848(3)	C(25)—P(2)—C(21)	112.62(18)	117.96(11)
P(1)—C(13)	1.872(4)	1.880(3)	C(12)—P(2)—Pd(1)	106.69(12)	105.80(10)
P(1)—C(17)	1.873(4)	1.873(3)	C(21)—P(2)—Pd(1)	109.23(13)	110.38(10)
P(2)—C(12)	1.867(3)	1.860(3)	C(25)—P(2)—Pd(1)	118.07(13)	112.50(14)
P(2)—C(21)	1.886(4)	1.880(3)	C(2)—C(1)—C(5)	108.0(3)	108.3(3)
P(2)—C(25)	1.877(4)	1.873(3)	C(2)—C(1)—Pd(1)	125.7(3)	125.8(2)
C(1)—C(2)	1.426(5)	1.427(4)	C(5)—C(1)—Pd(1)	126.2(3)	125.3(2)
C(1)—C(5)	1.435(5)	1.432(4)	C(1)—C(2)—C(3)	108.2(3)	108.1(3)
C(2)—C(3)	1.439(5)	1.431(4)	C(1)—C(2)—C(12)	121.4(3)	119.7(3)
C(2)—C(12)	1.530(5)	1.513(4)	C(3)—C(2)—C(12)	130.3(3)	132.1(3)
C(3)—C(4)	1.438(6)	1.429(4)	C(3)—C(4)—C(5)	—	108.6(3)
C(4)—C(5)	1.432(5)	1.429(4)	C(4)—C(3)—C(2)	107.6(3)	107.5(3)
C(5)—C(11)	1.508(5)	1.503(4)	C(4)—C(5)—C(1)	—	107.4(3)
C(6)—C(7)	1.395(7)	—	C(4)—C(5)—C(11)	—	133.0(3)
C(6)—C(10)	1.399(7)	—	C(1)—C(5)—C(11)	—	119.6(3)
C(7)—C(8)	1.400(8)	—	C(5)—C(11)—P(1)	105.6(2)	106.9(2)
C(8)—C(9)	1.441(8)	—	C(2)—C(12)—P(2)	104.3(2)	104.9(2)
C(9)—C(10)	1.397(7)	—			

pentamethylcyclopentadienyl ligand does not exclude the possibility of formation of the corresponding pincer P,C,P complex of ruthenocene. As is evident from the comparative X-ray diffraction study, this leads to a substantial increase in the mutual inclination of the cyclopentadienyl rings. This fact opens new possibilities for the design of metallocene-based pincer complexes with finely controlled steric and electronic properties, which is of particular importance for the use of these complexes in homogeneous catalysis.

In future, we plan to study the influence of this modification of the unmetallated cyclopentadienyl ring on thermal stability and catalytic activity of the iridium complexes $IrH_2[^RP,C,P^M]$ in alkane dehydrogenation.

Experimental

Principal experimental conditions have been described earlier.[3] All NMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature. The ^1H NMR chemical shifts are given on the δ scale and were measured at 400.13 MHz. The ^{31}P NMR chemical shifts were measured at 161.98 MHz relative to 85% H_3PO_4 as the external standard.

1-Ethoxycarbonyl-3-formyl-1′,2′,3′,4′,5′-pentamethylruthenocene (11). Zinc dust (400 mg, 6.15 mmol) was added to a suspension of $[Cp^*RuCl_2]_2$ (1.7 g, 5.5 mmol) in anhydrous THF (30 mL) under a stream of argon at room temperature. The reaction mixture was stirred at room temperature for 30 min, in the course of which the mixture turned blue-green. Then the reaction mixture was heated to 45—50 °C, after which it turned orange-brown. 3-Ethoxycarbonyl-6-dimethylaminopentafulvene (1.062 g, 5.5 mmol) was added to the resulting suspension under a stream of argon. The mixture was refluxed under argon for 6 h, cooled to room temperature, and concentrated. The residue was chromatographed on a silica gel column, and the yellow fraction containing the product was eluted with a hexane—diethyl ether mixture. After removal of the solvent and drying *in vacuo*, the yield was 1.228 g (65%). ^1H NMR ($CDCl_3$), δ: 9.45 (s, 1 H, CHO); 5.32 (br.s, 1 H, $C_5H_2\underline{H}$); 5.03 (br.d, 1 H, $C_5H_2\underline{H}$, J_{H-H} = 2.1 Hz); 4.71 (dd, 1 H, $C_5H_2\underline{H}$, $'J_{H-H}$ = 2.5 Hz,

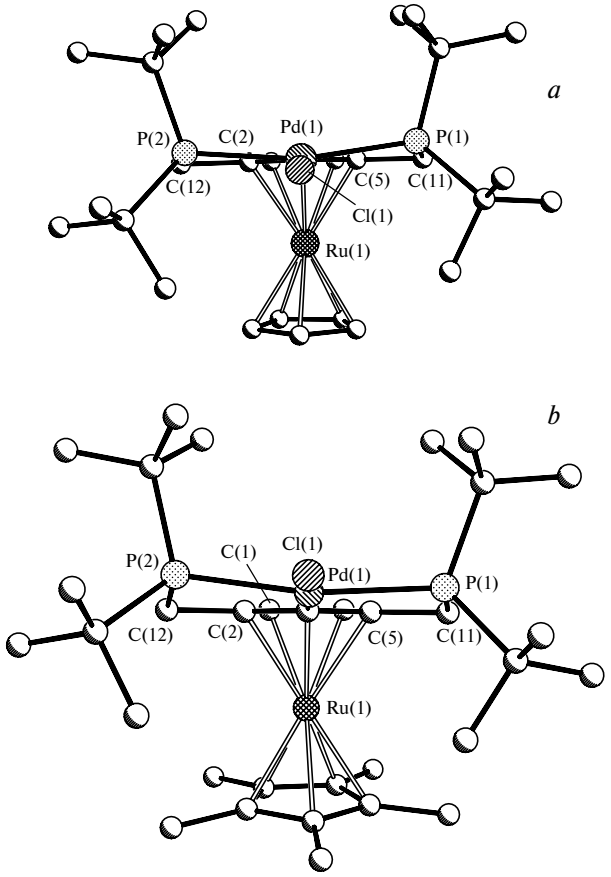


Fig. 2. View of molecules **4** (*a*) and **5** (*b*) along the plane of the metallated cyclopentadienyl ring.

$^{\prime\prime}J_{H-H}$ = 0.9 Hz); 4.12 (q, 1 H, C$\underline{H}_2$CH$_3$, J_{H-H} = 7.1 Hz); 1.71 (s, 15 H, C$_5$(C$\underline{H}_3$)$_5$); 1.50 (t, 3 H, CH$_2$C$\underline{H}_3$, J_{H-H} = 7.1 Hz).

1,3-Bis(hydroxymethyl)-1′,2′,3′,4′,5′-pentamethylruthenocene (12). A solution of aldehyde ester **11** (1.5 g, 3.722 mmol) in anhydrous diethyl ether (30 mL) was added dropwise to a suspension of $LiAlH_4$ (1.9 g, 0.05 mol) in anhydrous diethyl ether (70 mL) at room temperature under argon. Then the reaction mixture was stirred at room temperature for 3 h. An excess of $LiAlH_4$ was decomposed with water, the reaction mixture was repeatedly extracted with diethyl ether (a total of 200 mL), and the solvent was removed *in vacuo*. The residue was recrystallized from a diethyl ether—hexane mixture at low temperature. The yield of compound **12** was 0.87 g (64.4%). ^{1}H NMR ($CDCl_3$), δ: 4.19 (s, 1 H, C$_5$H$_2$$\underline{H}$); 4.14 (d, 2 H, C$_5$$\underline{H}_2$H, J_{H-H} = 1.2 Hz); 3.98 (d, 4 H, C$\underline{H}_2$, J_{H-H} = 5.7 Hz); 3.41 (t, 2 H, OH, J_{H-H} = 5.7 Hz); 1.87 (s, 15 H, C$_5$(C$\underline{H}_3$)$_5$).

1,3-Bis(di-*tert*-butylphosphinomethyl)-1′,2′,3′,4′,5′-pentamethylruthenocene (13). Di-*tert*-butylphosphine (1 mL, 6.16 mmol) was added to a solution of compound **12** (0.87 g, 2.4 mmol) in distilled acetic acid (20 mL) under a stream of argon. The mixture was stirred at 80 °C for 4 h. Then the solvent was distilled off *in vacuo*, and the residue was recrystallized under an inert atmosphere at −20 °C from a CH_2Cl_2—EtOH mixture. The yield was 1.2 g (81.1%). ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 33.22 (s, 2 P). ^{1}H NMR ($CDCl_3$), δ: 4.57 (br.s, 1 H, C$_5$H$_2$$\underline{H}$); 4.41 (d, 2 H, C$_5$$\underline{H}_2$H, J_{H-H} = 1.1 Hz); 2.53 (dd, 2 H, C$\underline{H}_A$H$_B$, J_{H-H} = 14.6 Hz, J_{P-H} = 1.2 Hz); 2.48 (dd, 2 H, CH$_A$$\underline{H}_B$, J_{H-H} = 14.6 Hz, J_{P-H} = 1.2 Hz); 1.99 (s, 15 H, C$_5$(C$\underline{H}_3$)$_5$); 1.25 and 1.23 (both d, 18 H each, C(C$\underline{H}_3$)$_3$, J_{P-H} = 4.2 Hz).

{2,5-Bis(di-*tert*-butylphosphinomethyl)-1′,2′,3′,4′,5′-pentamethylruthenocen-1-yl}palladium chloride (5). A mixture of diphosphine **13** (0.274 g, 0.444 mmol) and $(PhCN)_2PdCl_2$ (0.171 g, 0.444 mmol) in 2-methoxyethanol (45 mL) was refluxed with stirring for 4 h. Then the mixture was filtered through a layer of celite (2 cm), concentrated to 3—4 mL, and cooled to −20 °C, after which a crystalline yellowish compound precipitated. The mother liquor was decanted, and the crystals were washed with diethyl ether and dried *in vacuo*. The yield was 101 mg (30%). ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 81.96 (s, 2 P). ^{1}H NMR ($CDCl_3$), δ: 3.89 (s, 2 H, C$_5$$\underline{H}_2$); 2.49 (dt, 2 H, C$\underline{H}_AH_B$, J_{H-H} = 16.3 Hz, J_{P-H} = 4.2 Hz); 2.43 (dt, 2 H, CH$_A$$\underline{H}_B$, J_{H-H} = 16.3 Hz, J_{P-H} = 3.2 Hz); 1.77 (s, 15 H, C$_5$(C$\underline{H}_3$)$_5$); 1.46 and 1.32 (both t, 18 H each, C(C$\underline{H}_3$)$_3$, J_{P-H} = 7.2 Hz). Found (%): C, 52.37; H, 7.60. $C_{33}H_{57}ClP_2PdRu$. Calculated (%): C, 52.24; H, 7.52.

{2,5-Bis(di-*tert*-butylphosphinomethyl)ruthenocen-1-yl}palladium chloride (4) was synthesized analogously to complex **5** from diphosphine **8** (0.13 g, 0.237 mmol) and $(PhCN)_2PdCl_2$ (0.091 g, 0.237 mmol) in 2-methoxyethanol (20 mL). The yield was 120 mg (72.6%). ^{31}P{^{1}H} NMR ($CDCl_3$), δ: 84.52 (s, 2 P). ^{1}H NMR ($CDCl_3$), δ: 4.62 (s, 2 H, C$_5$$\underline{H}_2$); 4.33 (s, 5 H, C$_5$$\underline{H}_5$); 2.74 (dt, 2 H, C$\underline{H}_AH_B$, J_{H-H} = 16.4 Hz, J_{P-H} = 3.0 Hz); 2.60 (dt, 2 H, CH$_A$$\underline{H}_B$, J_{H-H} = 16.4 Hz, J_{P-H} = 4.3 Hz); 1.45 and 1.33 (both t, 18 H each, C(C$\underline{H}_3$)$_3$, J_{P-H} = 7.2 Hz). Found (%): C, 49.01; H, 6.68. $C_{28}H_{47}ClP_2PdRu$. Calculated (%): C, 48.97; H, 6.85.

X-ray diffraction study of complexes 4 and 5. Crystallographic data and refinement statistics for compounds **4** and **5** are given in Table 2. The X-ray diffraction data sets were collected on a

Table 2. Crystallographic data and refinement statistics for compounds **4** and **5**

Parameter	**4**	**5**
Molecular formula	$C_{28}H_{47}ClP_2PdRu$	$C_{33}H_{57}ClP_2PdRu$
Molecular weight	688.52	758.65
Space group	*Pbca*	$P2_12_12_1$
Temperature/K	120(2)	100(2)
a/Å	17.1065(8)	11.3128(6)
b/Å	16.4807(8)	14.7759(8)
c/Å	21.188(1)	20.978(1)
V/Å^3	5973.5(5)	3506.6(3)
Z	8	4
d_{calc}/g cm^{-3}	1.531	1.437
μ/cm^{-1}	13.19	11.31
$2\theta_{max}$/deg	58	60
Number of independent reflections (R_{int})	7911 (0.0429)	10172 (0.0610)
R_1 (based on *F* for reflections with $I > 2\sigma(I)$)	0.0436 (6285)	0.0350 (8869)
wR_2 ((based on F^2 for all reflections)	0.1020	0.0572
Number of parameters in refinement	310	361
GOOF	1.044	1.003

Bruker SMART 1000 diffractometer equipped with an area detector (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω-scanning technique). The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms in both complexes were placed in geometrically calculated positions and refined using a riding model. All calculations were carried out on a PC with the use of the SHELXTL program package.[13] The absolute configuration of complex **2** was determined by refining the Flack parameter ($x = 0.01(2)$).[14] The complete tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters were deposited with the Cambridge Structural Database.

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