P,C,P-Pincer complexes of ruthenium based on ruthenocene and pentamethylruthenocene

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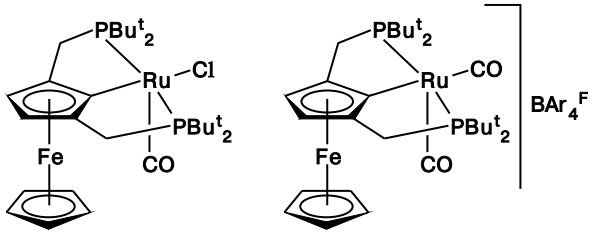
The first ruthenocene- and pentamethylruthenocene-based ruthenium pincer complexes, RuCl(CO)[{2,5-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5H_5)] and RuCl(CO)[{2,5-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5Me_5)], were synthesized by cyclometallation of {1,3-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5H_5) and {1,3-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5Me_5), respectively, with $RuCl_2(DMSO)_4$ in 2-methoxyethanol and characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and X-ray diffraction.

Key words: ruthenium, pincer complexes, ruthenocenes, pentamethylruthenocenes, diphosphines, carbonyls, X-ray diffraction analysis.

The interest in organometallic complexes bearing a tridentate anionic aryl ligand (the so-called pincer complexes) is due to their high thermal stability and their high potential as catalysts in a wide variety of organic reactions.[1,2] Recently we have synthesized the novel pincer complexes based on metallocenes. Cyclometallation of 1,3-bis[(dialkylphosphino)methyl]-ferrocene and bis[(dialkylphosphino)methyl]ruthenocene was used to prepare the first rhodium[3], iridium,[4,5] and palladium[6—9] complexes with metallocene-based pincer ligands. Later the first ruthenium complexes **1** and **2** with ferrocene-based pincer ligands have been synthesized.[10]



1 **2**

Ar^F = 3,5-(CF_3)$_2C_6H_3$

In this work we report the synthesis of novel ruthenium pincer complexes based on ruthenocene and pentamethylruthenocene.

Results and Discussion

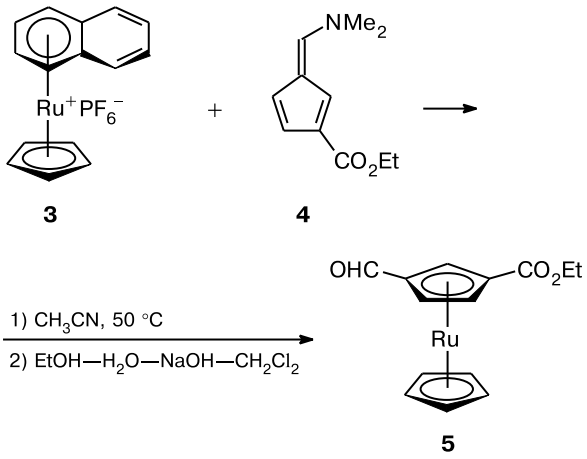
To synthesize a precursor for the pincer ligands with ruthenocene backbone, we have previously employed the multi-step procedure[11,12] incorporating slow photochemical reaction characterized by a relatively low product yield. Now we have developed an alternative route without photochemical reaction that affords the desired 1,3-functionally disubstituted metallocene in a high yield. As a starting material we have used η^6-naphthalene-η^5-cyclopentadienylruthenium hexafluorophosphate **3**; its preparation is described earlier.[13] We found that the thermal reaction of complex **3** with 3-ethoxycarbonyl-6-dimethylaminopentafulvene **4** in acetonitrile solution at 50 °C for 8 h followed by hydrolysis gives 1-ethoxycarbonyl-3-formylruthenocene **5** in 82% yield (Scheme 1).

The further synthesis of *bis*-(di-*tert*-butylphosphinomethyl)ruthenocene **6** from **5** we have described earlier.[4,8] The synthesis of diphosphine precursor **7** (Scheme 2) of the pincer complex based on pentamethylruthenocene is also described in Ref. 8.

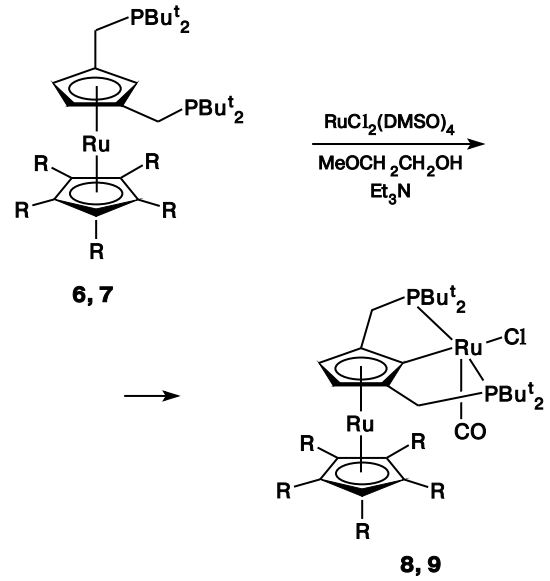
The key factor in successful preparation of metal pincer complexes is the choice of a cyclometallating agent. As in the previous work,[10] we used $RuCl_2(DMSO)_4$ as a ruthenium source. Its reaction with compounds **6** and **7** occurs readily in refluxing 2-methoxyethanol in the presence of triethylamine, leading to chlorocarbonyl complexes RuCl(CO)[{2,5-($Bu^t_2PCH_2$)$_2C_5H_2$}Ru(C_5R_5)] (**8**, R = H; **9**, R = Me) (see Scheme 2).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1694—1698, September, 2010.

Scheme 1



Scheme 2



R = H (**6**, **8**), Me (**7**, **9**)

Complexes **8** and **9** were characterized by NMR and IR spectra, elemental analysis and X-ray diffraction data. $^{31}P\{^1H\}$ NMR spectra of complexes **8** and **9** contain the singlet from two equivalent phosphorus nuclei at δ 83.1 and 79.3, respectively. In the ^1H NMR spectrum of complex **8**, the signals for cyclopentadienyl-ring protons appear as two singlets at δ 4.44 (5 H) and 4.73 (2 H), in agreement with the expected structure, and in the spectrum of complex **9**, the protons of the metallated cyclopentadienyl ring give a singlet at δ 4.11; the signals from fifteen methyl protons appear as a singlet at δ 1.79. The signals from CH_2 groups at $CH_2PBu^t_2$ in complex **8** are nonequivalent and appear as a doublet of triplets at δ 2.86 ($C\underline{H}_AH_B$, $J_{H,H}$ = 16.7 Hz, $J_{H,P}$ = 4.6 Hz) and δ 2.98 ($CH_A\underline{H}_B$, $J_{H,H}$ = 16.7 Hz, $J_{H,P}$ = 3.3 Hz). At the same time, the difference in chemical shifts of these protons in complex **9** (δ 2.73 $C\underline{H}_AH_B$, $J_{H,H}$ = 16.3 Hz, $J_{H,P}$ = 4.4 Hz; δ 2.76 $CH_A\underline{H}_B$, $J_{H,H}$ = 16.3 Hz, $J_{H,P}$ = 3.6 Hz) is rather small compared to complex **8**, which causes partial overlapping of methylene proton signals. *tert*-Butyl groups of both complexes appear as two virtual triplets at δ 1.19 (18 H, $J_{H,P}$ = 6.4 Hz), δ 1.44 (18 H, $J_{H,P}$ = 7.0 Hz) for **8**, and at δ 1.15 (18 H, $J_{H,P}$ = 6.2 Hz), δ 1.44 (18 H, $J_{H,P}$ = = 6.9 Hz) for **9**, respectively.

The IR spectra ($CDCl_3$) of complexes **8** and **9** show intense ν(CO) bands at 1923 cm^{-1} and 1921 cm^{-1}, respectively, indicative of the carbonyl ligand. The CO source should be the solvent since the platinum metals complexes are well known for their ability to eliminate CO from primary carbinols.[14,15] According to X-ray diffraction data, CO ligand in complexes **8** and **9**, as well as in ferrocene complex **1**, is in *endo*-position with respect to the central atom of metallocene.

Crystals of complex **8** are isostructural with those of complex **1** prepared previously, with most of atoms being disordered over two positions with equal occupancy. This disorder is due to superposition in a crystal of the two symmetrically nonequivalent forms of complex **8** (whose asymmetry results from different displacement of phosphorus atoms out of the Cp-ring plane) and was described in detail earlier.[10] Figure 1 shows one of the forms of complex **8**. Selected bond lengths and angles in complex **8** are collected in Table 1.

As shown by X-ray diffraction analysis, the chelated ruthenium atom Ru(1) in complex **8** has a distorted tetragonal pyramid configuration with basal Cl(1) atom oriented *trans* to C(1) carbon and apical CO ligand in *endo*-position to Ru(2). Because of disorder, it would hardly be reasonable to discuss the structure of **8** in greater detail.

Since the crystal structures of ferrocene complex **1** and ruthenocene counterpart **8** show equal disorder, it was of

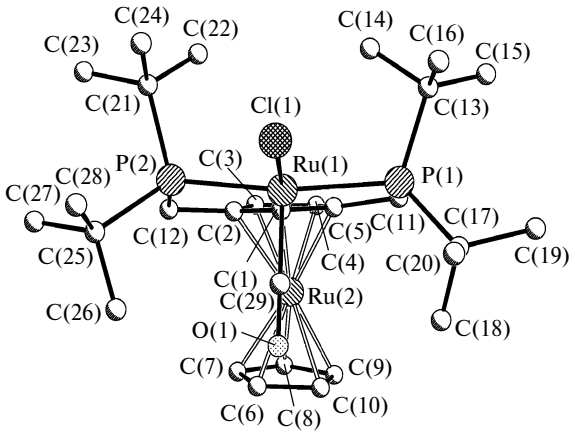


Fig. 1. Molecular structure of complex **8** (shown is one form of **8**, hydrogen atoms are omitted for clarity).

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **8**

Bond	*d*/Å	Angle	ω/deg
Ru(1)—C(29)	1.770(3)	C(29)—Ru(1)—C(1)	89.8(5)
Ru(1)—C(1)	1.99(2)	C(29)—Ru(1)—P(2)	95.96(8)
Ru(1)—P(2)	2.404(1)	C(29)—Ru(1)—P(1)	96.39(8)
Ru(1)—P(1)	2.416(1)	P(2)—Ru(1)—P(1)	156.67(2)
Ru(1)—Cl(1)	2.462(1)	C(29)—Ru(1)—Cl(1)	98.71(8)

interest to perform X-ray diffraction study for the similar complex with a pentasubstituited non-metallated Cp ring. The presence of bulky substituents could facilitate the formation of the ordered structure.

Indeed, X-ray diffraction analysis of complex **9** demonstrated the lack of the aforesaid disorder. The molecular structure of **9** is shown in Fig. 2, and selected geometric parameters are summarized in Tables 2 and 3.

Because of the steric strain, the metallated cyclopentadienyl ring in complex **9** is nonplanar, folding across C(2)...C(5) being 5.2°, C(1) atom is shifted 0.076 Å out of the plane defined by four other Cp-ring atoms (away from Ru(2) atom). Two cyclopentadienyl rings are nonparallel with the dihedral angle between the middle planes of pentamethylated and metallated rings of 13.4°. For comparison, in the related palladium complex based on pentamethylruthenocene, PdCl[{2,5-$(Bu^t_2PCH_2)_2C_5H_2$}Ru-(C_5Me_5)], an angle between the ring planes is 10.3° (see Ref. 8). Ruthenium atom Ru(1) is displaced from the middle plane of the metallated Cp-ring by 0.575 Å. Phosphorus atoms P(1) and P(2) deviate from this plane differently (displacement 0.455 Å for P(1) and 1.028 Å for P(2)). At the same time, C(11) and C(12) carbons linked to P(1) and P(2), respectively, are displaced from this plane only slightly, by 0.078 and 0.088 Å, respectively. This results in the distortion of the molecule´s general symmetry with respect to the *pseudo*-plane of symmetry passing through Ru(1), C(1), Ru(2). It is noteworthy that weak agostic interaction between the chelated ruthenium atom and a C—H bond of one of the *tert*-butyl groups at the P atom has recently been found[10] for the ferrocene analog

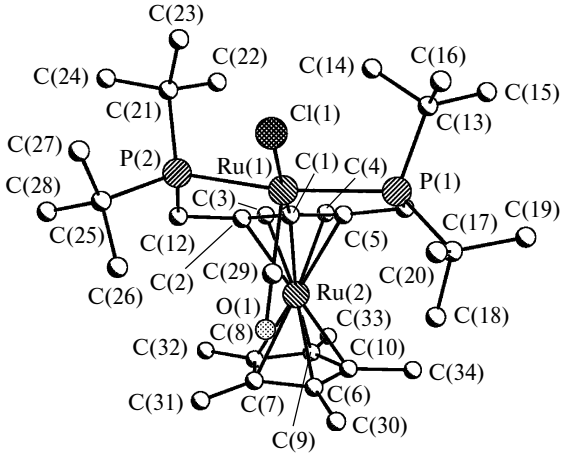


Fig. 2. Structure of complex **9** (hydrogen atoms are omitted for clarity).

RuCl(CO)[{2,5-$(Bu^t_2PCH_2)_2C_5H_2$}Fe(C_5H_5)] (**1**) and the cationic complex $Ru(CO)_2$[{2,5-$(Bu^t_2PCH_2)_2C_5H_2$}Ru-(C_5H_5)]BAr_4^F (**2**); in cationic complex **2**, this results in the broadening of the methylene proton signal in ^{1}H NMR spectrum recorded at room temperature. The ^{1}H NMR spectra of complexes **8** and **9** recorded under similar conditions show no evidence for significant agostic interaction. Anyway, if present in complexes **8** and **9**, it should be weaker than that observed in complex **2**. Indeed, in complex **9**, the interatomic distance between Ru(1) atom and the proximal axial *tert*-butyl hydrogen H(14B) is 2.68 Å, whereas between Ru(1) and *tert*-butyl carbon C(14) it is equal to 3.268(4) Å, which is substantially larger than the values characteristic of ferrocene complex **2** (with the shortest separation of ruthenium from *tert*-butyl hydrogen and carbon of 2.34 and 3.01 Å, respectively). For comparison, the very similar relevant distances have been found in the ruthenium complexes postulated as having an agostic bond between *tert*-butyl group and Ru atom, *e.g.*, in complex [Ru{CH=C$(SiMe_3)$(Ph)}(CO)-(PBu^t_2Me)]$^+$ (Ru···C_{agost} = 3.049 Å)[16] and in complex $RuCl_2$[$(Bu^t_2PCH_2CH_2)_2O$] (Ru···C_{agost} = 2.845 Å).[17]

In such comparing it should be taken into account that the chelated ruthenium atom in cationic ferrocene com-

Table 2. Selected bond lengths (*d*) in complex **9**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Ru(1)—C(1)	2.026(4)	Ru(2)—C(4)	2.157(4)	P(1)—C(11)	1.873(4)	C(1)—C(2)	1.421(5)
Ru(1)—C(29)	1.773(4)	Ru(2)—C(5)	2.222(4)	P(1)—C(17)	1.879(4)	C(1)—C(5)	1.429(5)
Ru(1)—P(1)	2.385(1)	Ru(2)—C(6)	2.222(4)	P(1)—C(13)	1.890(4)	C(2)—C(3)	1.440(5)
Ru(1)—P(2)	2.395(1)	Ru(2)—C(7)	2.203(4)	P(2)—C(12)	1.871(4)	C(2)—C(12)	1.506(6)
Ru(1)—Cl(1)	2.470(1)	Ru(2)—C(8)	2.169(4)	P(2)—C(25)	1.883(4)	C(3)—C(4)	1.421(6)
Ru(2)—C(1)	2.306(4)	Ru(2)—C(9)	2.155(4)	P(2)—C(21)	1.900(4)	C(4)—C(5)	1.444(5)
Ru(2)—C(2)	2.200(4)	Ru(2)—C(10)	2.182(4)	O(1)—C(29)	1.162(5)	C(5)—C(11)	1.506(6)
Ru(2)—C(3)	2.149(4)						

Table 3. Selected bond angles (ω) in complex **9**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(29)—Ru(1)—C(1)	89.2(2)	C(12)—P(2)—C(25)	105.0(2)	C(4)—C(5)—C(11)	131.0(4)
C(29)—Ru(1)—P(1)	97.7(1)	C(12)—P(2)—C(21)	102.6(2)	C(5)—C(11)—P(1)	107.5(3)
C(1)—Ru(1)—P(1)	80.5(1)	C(25)—P(2)—C(21)	111.1(2)	C(2)—C(12)—P(2)	105.7(3)
C(29)—Ru(1)—P(2)	95.9(1)	C(12)—P(2)—Ru(1)	103.3(1)	C(16)—C(13)—P(1)	110.8(3)
C(1)—Ru(1)—P(2)	79.8(1)	C(25)—P(2)—Ru(1)	122.3(1)	C(15)—C(13)—P(1)	116.7(3)
P(1)—Ru(1)—P(2)	155.75(4)	C(21)—P(2)—Ru(1)	110.2(1)	C(14)—C(13)—P(1)	103.0(3)
C(29)—Ru(1)—Cl(1)	101.3(1)	C(2)—C(1)—C(5)	108.3(3)	C(18)—C(17)—P(1)	107.3(3)
C(1)—Ru(1)—Cl(1)	169.3(1)	C(2)—C(1)—Ru(1)	125.0(3)	C(19)—C(17)—P(1)	113.2(3)
P(1)—Ru(1)—Cl(1)	100.17(4)	C(5)—C(1)—Ru(1)	125.0(3)	C(20)—C(17)—P(1)	108.0(3)
P(2)—Ru(1)—Cl(1)	96.70(4)	C(1)—C(2)—C(3)	108.1(3)	C(23)—C(21)—P(2)	110.6(3)
C(11)—P(1)—C(17)	106.5(2)	C(1)—C(2)—C(12)	119.7(3)	C(24)—C(21)—P(2)	113.2(3)
C(11)—P(1)—C(13)	102.5(2)	C(3)—C(2)—C(12)	131.5(3)	C(22)—C(21)—P(2)	107.5(3)
C(17)—P(1)—C(13)	111.7(2)	C(4)—C(3)—C(2)	107.8(3)	C(28)—C(25)—P(2)	114.0(3)
C(11)—P(1)—Ru(1)	105.3(1)	C(1)—C(5)—C(4)	107.5(3)	C(26)—C(25)—P(2)	106.7(3)
C(17)—P(1)—Ru(1)	121.0(1)	C(3)—C(4)—C(5)	108.1(3)	C(27)—C(25)—P(2)	109.8(3)
C(13)—P(1)—Ru(1)	108.1(1)	C(1)—C(5)—C(11)	120.9(3)	O(1)—C(29)—Ru(1)	179.7(4)

plex **2** carries a positive charge, while in complex **9** this atom is electroneutral. Nonetheless, the obvious asymmetry of the positions of the two axial *tert*-butyl groups with respect ro Ru(1) atom can hardly be explained as an effect of crystal packing.

Experimental

All experiments were run under dry argon using an argon chamber or Schlenk techniques. All solvents were dried by refluxing over appropriate drying agents followed by distillation in a stream of argon. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance-400 spectrometer; the chemical shifts are given on the δ scale and were measured at 400.13 and 161.98 MHz, respectively. ^{31}P NMR spectra are measured using 85% H_3PO_4 as the external standard. IR spectra were recorded on a Magna-IR 750 (Nicolet) FT-IR spectrometer.

Preparation of 1-ethoxycarbonyl-3-formylruthenocene (5). To a solution of 3-ethoxycarbonyl-6-dimethylaminofulvene (1.0 g, 5.18 mmol) in acetonitrile (120 mL) was added $[C_{10}H_8Ru(C_5H_5)]PF_6$ (2.27 g, 5.18 mmol) and hexane (60 mL). The reaction mixture was stirred at 50—60 °C for 8 h. After the mixture was cooled, the acetonitrile layer was separated from hexane, and acetonitrile was removed *in vacuo*. The residue was dissolved in methylene chloride (50 mL) and treated with an aqueous NaOH (2 *M*, 25 mL)—methanol (20 mL) mixture. The mixture was stirred at a high rate at room temperature for 45 min, then the layers were separated, the aqueous fraction was extracted with CH_2Cl_2 (3×40 mL), and the combined extracts were dried *in vacuo*. The residue was dissolved in a small amount of CH_2Cl_2, evaporated with silica gel, and chromatographed on silica eluting with hexane—benzene (1 : 1), then with benzene. Pale yellow eluate was concentrated *in vacuo*. Yield 1.42 g (82%). ^{1}H NMR ($(CD_3)_2CO$, δ): 1.26 (t, 3 H, CH_3, $J_{H,H}$ = 7.1 Hz); 4.19 (q, 2 H, CH_2, $J_{H,H}$ = 7.1 Hz); 4.74 (s, 5 H, C_5H_5); 5.28 (m, 1 H, C_5H_3); 5.38 (m, 1 H, C_5H_3), 5.60 (m, 1 H, C_5H_3); 9.72 (s, 1 H, CHO). Found (%): C, 50.37; H, 4.33. $C_{14}H_{14}O_3Ru$. Calculated (%): C, 50.74; H, 4.27.

Preparation of {2,5-bis[(di(*tert*-butyl)phosphino)methyl]-ruthenocen-1-yl}chlorocarbonylruthenium (8). A solution of $\{1,3\text{-}(CH_2P^tBu_2)_2C_5H_3\}Ru(C_5H_5)$ (0.61 g, 1.113 mmol) in 2-methoxyethanol (50 mL) (distilled over sodium under argon) was treated with $RuCl_2(DMSO)_4$ (0.56 g, 1.156 mmol), triethylamine (0.23 g, 2.277 mmol) and stirred at 115 °C for 4 h. The solvent was removed *in vacuo*, and a crimson-red precipitate was chromatographed on a short neutral alumina column. A crimson-red fraction was eluted with hexane—ethyl acetate (7 : 1), the solvent was removed *in vacuo*, and the precipitate was recrystallized from CH_2Cl_2—hexane to yield crimson-red crystalline powder (0.57 g (72%)). ^{1}H NMR ((CDCl$_3$, δ): 1.19 (virt. t, 18 H, CH_3, $J_{H,P}$ = 6.4 Hz); 1.44 (virt. t, 18 H, CH_3, $J_{H,P}$ = 7.0 Hz); 2.86 (dt, 2 H, $C\underline{H}_AH_BP$, $J_{H,H}$ = 16.7 Hz, $J_{H,P}$ = 4.6 Hz); 2.98 (dt, 2 H, $CH_A\underline{H}_BP$, $J_{H,H}$ = 16.7 Hz, $J_{H,P}$ = 3.3 Hz); 4.44 (s, 5 H, C_5H_5); 4.73 (s, 2 H, C_5H_2). ^{31}P{^{1}H} NMR (CDCl$_3$, δ): 83.14 (s, 2 P). IR (CDCl$_3$), ν/cm^{-1}: 1923 (C=O). Found (%): C, 48.82; H, 6.39. $C_{29}H_{47}ClOP_2Ru_2$. Calculated (%): C, 48.97; H, 6.67.

Preparation of {2,5-bis[(di(*tert*-butyl)phosphino)methyl]-pentamethylruthenocen-1-yl}chlorocarbonylruthenium (9). Complex **9** was synthesized analogously to complex **8** starting from diphosphine **5** (0.45 g, 0.73 mmol), $RuCl_2(DMSO)_4$ (0.36 g, 0.74 mmol), and triethylamine (0.15 g, 1.48 mmol) in 2-methoxyethanol (40 mL). The product is a violet-red powder. Yield 0.35 g (61%). ^{1}H NMR ((CDCl$_3$, δ): 1.15 (virt. t, 18 H, CH_3, $J_{H,P}$ = 6.2 Hz), 1.44 (virt. t, 18 H, CH_3, $J_{H,P}$ = 6.9 Hz); 1.79 (s, 15 H, 5 CH_3); 2.73 (dt, 2 H, $C\underline{H}_AH_BP$, $J_{H,H}$ = 16.3 Hz, $J_{H,P}$ = 4.4 Hz); 2.76 (dt, 2 H, $CH_A\underline{H}_BP$, $J_{H,H}$ = 16.3 Hz, $J_{H,P}$ = = 3.6 Hz); 4.11 (s, 2 H, C_5H_2). ^{31}P{^{1}H} NMR (CDCl$_3$, δ): 79.4 (s, 2 P). IR (CDCl$_3$), ν/cm^{-1}: 1921 (C=O). Found (%): C, 52.19; H, 7.31; P, 8.02. $C_{34}H_{57}ClOP_2Ru_2$. Calculated (%): C, 52.25; H, 7.37; P, 7.93.

X-ray diffraction analysis of complexes 8 and 9. The single crystals of complexes **8** and **9** for X-ray examination were grown from the methylene chloride—hexane mixture.

The crystallographic parameters, and the X-ray data collection and structure refinement statistics for complexes **8** and **9** are listed in Table 4. The data were collected on SMART APEX II (for complex **8**)[18] and SMART 1000 CCD (for complex **9**)[19]

Table 4. Crystallographic data and X-ray diffraction data collection and refinement statistics for structures **8** and **9**

Compound	**8**	**9**
Molecular weight	711.20	781.33
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
T/K	298(2)	120(2)
a/Å	18.1546(6)	8.2335(6)
b/Å	8.3626(3)	11.4527(8)
c/Å	20.4777(7)	18.779(1)
α/deg	90	91.561(1)
β/deg	95.745(1)	93.739(2)
γ/deg	90	101.080(1)
V/Å^3	3093.3(2)	1732.6(2)
Z	4	2
d_{calc}/g cm^{-3}	1.527	1.498
$2\theta_{max}$/deg	58	56
μ/cm^{-1}	11.86	10.66
Number of independent reflections (R_{int})	8210 (0.0360)	8305 (0.0317)
$R_1(F)$ ($I > 2\sigma(I)$) with $I > 2\sigma(I)$)	0.0278 (6417)	0.0475 (6252)
$wR_2(F^2)$ (all reflections)	0.0640	0.1177
Number of refined parameters	529	378
GOOF	1.029	1.076
Δρ (max/min)/e Å^{-3}	0.45/−0.37	1.41/−0.76
Index ranges	$-24 \le h \le 24$ $-11 \le k \le 11$ $-27 \le l \le 27$	$-10 \le h \le 10$ $-14 \le k \le 15$ $-24 \le l \le 24$

diffractometers (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω scans). The absorption corrections were applied using the semiempirical procedure (SADABS software).[20] The structures were solved by direct methods and refined by the full-matrix least-squares on F^2_{hkl} with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were positioned geometrically and refined using a riding model. All calculations were performed on a PC using the SHELXTL program package.[21] The complete structural (atomic coordinates, bond lengths and bond angles, anisotropic displacement parameters) and crystallographic data were deposited with the Cambridge Structural Database.

The work was supported by the International Science and Technology Center (Grants 3082 and G1361), Program of the Presidium of the Russian Academy of Sciences P-18, and the Russian Foundation for Basic Research (Project No. 08-03-01020).

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Received December 13, 2009;
in revised form May 25, 2010