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Ruthenium complexes with ferrocene-based P,C,P pincer ligand*

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First ruthenium complexes with a ferrocene-based pincer ligand were synthesized. The cyclometallation of 1,3-bis[(di-*tert*-butylphosphino)methyl]ferrocene with $RuCl_2(DMSO)_4$ in 2-methoxyethanol afforded the $RuCl(CO)[\{2,5\text{-}(Bu^t{}_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ ($RuCl(CO)[^{Bu^t}P,C,P^{Fe}]$) complex (**5**). Complex **5** reversibly binds CO to form the $RuCl(CO)_2[^{Bu^t}P,C,P^{Fe}]$ complex (**6**). The analogous reaction in the presence of $NaBAr'_4$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$) produced the cationic complex $\{Ru(CO)_2[^{Bu^t}P,C,P^{Fe}]\}BAr'_4$ (**7**). The structures of complexes **5** and **7** were established by single-crystal X-ray diffraction. The X-ray diffraction study revealed an agostic interaction between one of the C—H bonds of the axial (*exo*-oriented with respect to the ferrocene iron atom) *tert*-butyl group and the Ru atom in complexes **5** and **7**.

Key words: ruthenium, pincer complexes, ferrocenes, diphosphines, carbonyls, agostic bonding, X-ray diffraction study.

Organometallic complexes with tridentate monoanionic aryl ligands, so-called pincer complexes, have been extensively studied in recent years.[1,2] These complexes have attracted interest due to their high stability and ability of catalyzing various organic reactions.

Recently, we have studied a new type of pincer complexes, *viz.*, metallocene-based bimetallic pincer complexes.[3] The availability of these complexes was exemplified by the cyclometallation of 1,3-bis[(dialkylphosphino)methyl]ferrocene[3,4] and bis[(dialkylphosphino)methyl]ruthenocene.[4] Platinum metal complexes with metallocene-based pincer ligands[2—7] proved to be as stable as their benzene analogs. Recently, we have demonstrated[8] that the iridium complexes $IrH_2[\{2,5\text{-}(Bu^t{}_2PCH_2)_2C_5H_2\}M(C_5H_5)]$ (M = Fe or Ru) are the most active of all the known homogeneous catalysts for alkane dehydrogenation.

The sandwich nature of metallocene pincer ligands provides new possibilities for fine controlling the steric and electronic effects of chelated metal atoms serving as the catalytic centers, for example, by introducing substituents into the unmetallated cyclopentadienyl ring[9] (not only the electron density on the chelated metal atom but also the steric accessibility of this atom for the substrate can be controlled), varying the nature of the central atom of the metallocene moiety[8] and its redox state,[7,8] and constructing planar chiral structures. The synthesis of metallocene-based rhodium,[3,10] iridium,[4,8] and palladium[5—7,9] pincer complexes was documented. However, related ruthenium complexes have not been described in the literature. The properties of ruthenium complexes as excellent catalysts for the hydrogenation of carbonyl compounds[11] and olefin metathesis[12] are well known.

In the present study, we report the synthesis and properties of first ferrocene-based ruthenium pincer complexes.

Results and Discussion

Synthesis of ruthenium complexes

As mentioned earlier, the choice of the cyclometallating agent can play a decisive role in the synthesis of metal pincer complexes. Our first attempt, as well as attempts of other researchers,[10] to use the $RuCl_2(PPh_3)_3$ complex as the starting reagent for the cyclometallation of 1,3-bis[(di-*tert*-butylphosphino)methyl]ferrocene (**1**)

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* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

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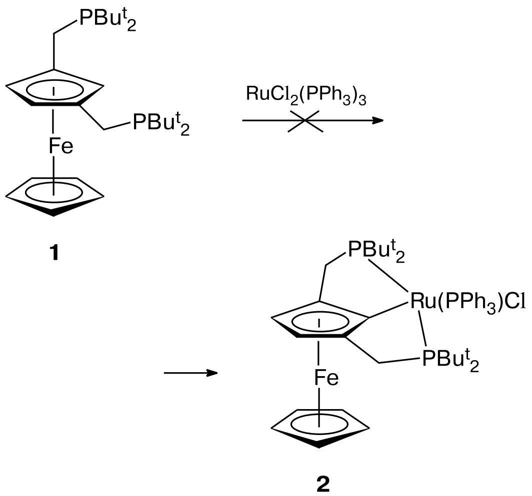
did not allow us to synthesize the desired $RuCl(PPh_3)[\{2,5\text{-}(Bu^t{}_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ complex (hereinafter, $RuCl(PPh_3)[^{Bu^t}P,C,P^{Fe}]$ (**2**) (Scheme 1).

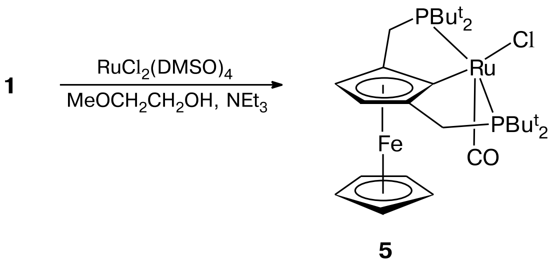
Scheme 1



It should be noted that the related P,C,P pincer complex $RuCl(PPh_3)[\{2,6\text{-}(Ph_2PCH_2)_2C_6H_3]$[13,14] (**3**) and the complex $RuCl(PPh_3)[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3]$[15] (**4**) have been synthesized earlier by the reactions of $RuCl_2(PPh_3)_3$ with the corresponding benzene derivatives. In complexes **3** and **4**, the Ru atom is in a square-pyramidal coordination environment with the PPh_3 ligand in the apical position. It would be expected that the PPh_3 ligand at the ruthenium atom in complex **2** would also occupy the apical position in either an *endo* or *exo* orientation with respect to the iron atom. However, the X-ray diffraction studies of a series of ferrocene-[7,8] and ruthenocene-based[9] pincer complexes showed that both apical positions in these complexes are more shielded compared to those in the benzene analogs by two axial alkyl groups at the P atoms (in metallocene-based pincer complexes, two alkyl groups at the P atoms *exo*-oriented with respect to the central atom of the metallocene moiety are in approximately axial positions, and two other, *endo*-oriented, alkyl groups are pseudoequatorial (Fig. 1)) in the former complexes and by the unmetallated Cp ring in the latter case. A particularly strong shielding is observed in the presence of two axial *tert*-butyl groups. In this case, such bulky ligands as tertiary phosphines cannot be coordinated to the ruthenium atom in *exo* positions with respect to the central atom of the metallocene moiety.

We succeeded in synthesizing the first ferrocene-based ruthenium pincer complex using the $RuCl_2(DMSO)_4$ compound as a source of Ru^{II}.[16,17] The reaction proceeds smoothly in refluxing 2-methoxyethanol in the presence of triethylamine to give the dark-green chlorocarbonyl complex $RuCl(CO)[^{Bu^t}P,C,P^{Fe}]$ (**5**) (Scheme 2).

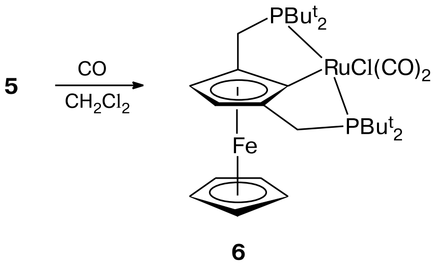
Scheme 2



Complex **5** was characterized by IR and NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum shows one signal for two equivalent phosphorus nuclei at δ 83.1. In the ^1H NMR spectrum, two signals of the protons of the cyclopentadienyl rings are observed as two singlets at δ 4.05 (5 H) and 4.32 (2 H), which is in agreement with the expected structure. The IR spectrum (CH_2Cl_2) shows an intense ν_{CO} band at 1914 cm^{-1} assigned to the carbonyl ligand. The solvent should serve as a source of CO, because it is well known that CO can be eliminated from primary carbinols in the presence of platinum metal complexes.[18,19] According to the X-ray diffraction study, the CO ligand in complex **5** is in the *endo* position with respect to the iron atom. Evidently, the *endo* position is sterically less hindered than the *exo* position.

In complex **5**, the ruthenium atom has a 16-electron configuration and can bind a CO molecule to form the octahedral dicarbonyl complex $RuCl(CO)_2[^{Bu^t}P,C,P^{Fe}]$ (**6**) (Scheme 3). The reaction was carried out by passing a CO flow through a solution of complex **5** in dichloromethane at a low rate and was accompanied by a change in the color of the solution from dark-green to orange-brown. Complex **6** appeared to be rather labile. It easily loses the CO molecule, resulting in the regeneration of the starting complex **5**. Because of this, compound **6** was characterized only by IR and NMR spectra. It is noteworthy that the related benzene pincer complex $RuCl(CO)_2[2,6\text{-}(Cy_2PCH_2)_2C_6H_3]$ (Cy is cyclohexyl) is rather stable, and it has been completely characterized, including by X-ray diffraction.[20]

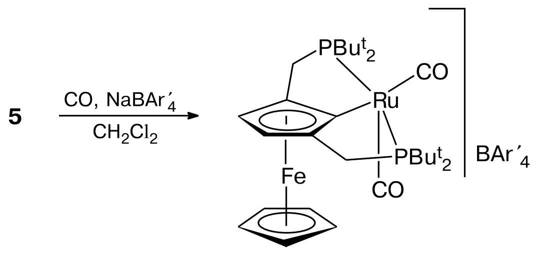
Scheme 3



The $^{31}P\{^1H\}$ NMR spectrum of complex **6** shows one signal at δ 99.9. In the ^1H NMR spectrum, the protons of the cyclopentadienyl rings are observed at δ 3.91 (s, 5 H) and 4.19 (s, 2 H), the methylene protons of the $C\underline{H}_2PCMe_3$ groups are nonequivalent and are observed as a doublet of triplets at δ 2.82 (2 H, $J_{H,H}$ = 16.5 Hz, $J_{H,P}$ = 4.0 Hz) and 2.90 (2 H, $J_{H,H}$ = 16.5 Hz, $J_{H,P}$ = 3.7 Hz), and the *tert*-butyl groups appear as two virtual triplets at δ 1.46 (18 H, $J_{H,P}$ = 6.6 Hz) and 1.63 (18 H, $J_{H,P}$ = 6.5 Hz). The IR spectrum ($CDCl_3$) of complex **6** shows two strong ν_{CO} bands at 1945 and 2024 cm^{-1}. Presumably, two CO groups in complex **6** are in the *cis* positions, as was observed in the related $RuCl(CO)_2[\{2,6\text{-}(R_2PCH_2)_2C_6H_3]$ complexes (R = Ph or Cy).**[14,20]**

The reaction of complex **5** with CO in the presence of $NaBAr'_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) produces the cationic dicarbonyl ruthenium complex $\{Ru(CO)_2[^{Bu^t}P,C,P^{Fe}]\}BAr'_4$ (**7**) (Scheme 4).

Scheme 4



7

Cationic complex **7** was characterized by IR and NMR spectroscopy and X-ray diffraction. The IR spectrum (KBr) shows two intense ν_{CO} bands at 1979 and 2042 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of complex **7** has a signal at δ 98.9, whose position is close to that of uncharged chlorodicarbonyl ruthenium derivative **6**. However, the ^1H NMR spectra ($CDCl_3$) of complexes **6** and **7** are substantially different in the cyclopentadienyl-ring proton region. The signals for the protons of the ferrocene unit in the spectrum of complex **7** experience strong deshielding and are observed at δ 4.32 (s, 5 H) and 4.93 (s, 2 H) in agreement with the presence of the cationic substituent in the cyclopentadienyl ring. The signals for the methyl protons of the *tert*-butyl groups in complex **7** give a typical pattern and appear as two virtual triplets at δ 0.95 (18 H, $J_{H,P}$ = 6.8 Hz) and 1.50 (18 H, $J_{H,P}$ = 7.6 Hz).

An unusual pattern is observed for the methylene protons of the $C\underline{H}_2PBu^t_2$ groups in complex **7**. Thus, two *exo*-oriented (NOE data) methylene protons appear as a typical doublet of triplets at δ 3.15 (2 H, $J_{H,H}$ = 16.6 Hz, $J_{P,H}$ = 4.5 Hz), whereas two other, *endo*-oriented, protons are observed as a very broad signal with a center at δ 3.27.

X-ray diffraction study of complexes 5 and 7

The single-crystal X-ray diffraction study showed that cationic complex **7** (Figs 1 and 2, Table 1) is asymmetric. The *a priori* expected plane of symmetry passing through the Ru(1), C(1), and Fe(1) atoms is absent, two axial *tert*-butyl groups adopting different conformations. One

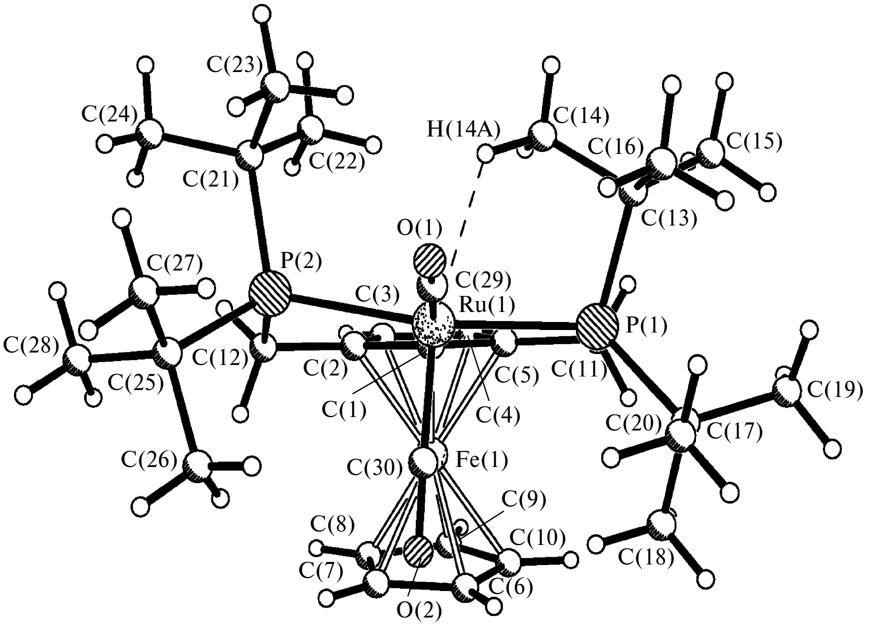


Fig. 1. Molecular structure of complex **7** (only the cationic moiety is shown) viewed along the plane of the metallated cyclopentadienyl ring.

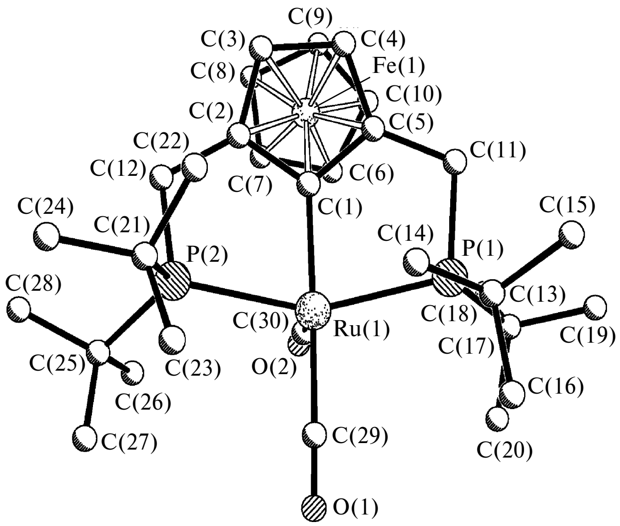


Fig. 2. Projection of cationic complex **7** onto the plane of the metallated cyclopentadienyl ring.

of these groups, the *tert*-butyl group at the P(1) atom, is rotated so that the C(14)H_3 methyl group is in close proximity to the Ru(1) atom.

In addition, the P(1) and P(2) atoms are in nonequivalent positions with respect to the plane of the metallated Cp ring (see Fig. 1) and, correspondingly, the five-membered fused metallacycles have different structures. The chelate ring Ru(1)P(1)C(11)C(5)C(1) is flattened (average deviation from the plane passing through all five atoms is 0.03 Å), whereas the second chelate ring, Ru(1)P(2)C(12)C(2)C(1), adopts an approximate envelope conformation with the P(2) atom deviating from the plane through the other four atoms of the ring (average deviation is 0.03 Å) by 0.50 Å in the direction opposite to the iron atom. The envelope is folded along the Ru(1)···C(12) line by 23.3°.

The X-ray diffraction data unambiguously show that structure of complex **7** is asymmetric due to the presence of the C(14)—H(14A)···Ru(1) agostic interaction. The Ru(1)···C(14) and Ru(1)···H(14A) distances are 3.006(3) and 2.34(3) Å, respectively. The Ru(1)···H(14A)—C(14) angle is 120(2)°. The presence of the agostic bonding in complex **7** is additionally confirmed by distortions of the bond angles and the differences in the bond lengths in the fragments located on the opposite sides with respect to the imaginary plane passing through the Ru(1),C(1),Fe(1) atoms. Thus, the C(13)—P(1)—Ru(1) angle (101.70(10)°) is noticeably smaller than the C(21)—P(2)—Ru(1) angle (110.61(9)°), which is indicative of the tightening effect associated with the presence of the C(14)—H(14A)···Ru(1) agostic bond. The tightening effect resulting from the agostic bond is additionally confirmed by the difference between the P(1)—Ru(1) and P(2)—Ru(1) distances (2.3936(9) and 2.4288(9) Å, respectively).

Therefore, in spite of the rather large Ru(1)···C(14) (3.006(3) Å) and Ru(1)···H(14A) (2.34(3) Å) distances in complex **7**, the X-ray diffraction data provide evidence that the ruthenium atom interacts with the C—H bond of the axial *tert*-butyl group. For comparison, let us note that similar distances were found in ruthenium complexes, for example, in the $[Ru\{CH{=}C(SiMe_3)(Ph)\}(CO)(PBu^t{}_2Me)]^+$ (Ru···C_{agost} =

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **7**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Ru(1)—C(1)	2.047(3)	C(30)—Ru(1)—C(29)	94.06(11)	C(2)—C(1)—Ru(1)	124.8(2)
Ru(1)—C(29)	1.978(3)	C(30)—Ru(1)—C(1)	91.24(11)	C(1)—C(2)—C(3)	107.3(2)
Ru(1)—C(30)	1.816(3)	C(29)—Ru(1)—C(1)	174.31(10)	C(1)—C(2)—C(12)	120.1(2)
Ru(1)—P(1)	2.3936(9)	C(30)—Ru(1)—P(1)	95.63(9)	C(3)—C(2)—C(12)	132.4(2)
Ru(1)—P(2)	2.4288(9)	C(29)—Ru(1)—P(1)	102.16(8)	C(4)—C(3)—C(2)	108.5(2)
Ru(1)...C(14)	3.006(3)	C(1)—Ru(1)—P(1)	79.36(8)	C(3)—C(4)—C(5)	107.8(2)
Ru(1)...H(14A)	2.34(3)	C(30)—Ru(1)—P(2)	96.76(9)	C(1)—C(5)—C(4)	107.8(2)
C(14)—H(14A)	1.05(4)	C(29)—Ru(1)—P(2)	98.43(8)	C(1)—C(5)—C(11)	120.6(2)
P(1)—C(11)	1.862(3)	C(1)—Ru(1)—P(2)	78.84(8)	C(4)—C(5)—C(11)	131.3(2)
P(1)—C(13)	1.875(3)	P(1)—Ru(1)—P(2)	155.08(3)	C(5)—C(11)—P(1)	107.4(2)
P(1)—C(17)	1.865(3)	C(11)—P(1)—Ru(1)	106.21(9)	C(2)—C(12)—P(2)	106.6(2)
P(2)—C(12)	1.847(3)	C(13)—P(1)—Ru(1)	101.70(10)	C(16)—C(13)—P(1)	111.7(2)
P(2)—C(21)	1.892(3)	C(17)—P(1)—Ru(1)	122.74(9)	C(14)—C(13)—P(1)	101.7(2)
P(2)—C(25)	1.888(3)	C(12)—P(2)—Ru(1)	103.71(9)	C(15)—C(13)—P(1)	116.4(2)
C(1)—C(2)	1.433(4)	C(21)—P(2)—Ru(1)	110.61(9)	Ru(1)...H(14A)—C(14)	120.0(2)
C(1)—C(5)	1.424(4)	C(25)—P(2)—Ru(1)	120.21(9)	O(1)—C(29)—Ru(1)	178.9(3)
C(2)—C(3)	1.434(4)	C(5)—C(1)—C(2)	108.5(2)	O(2)—C(30)—Ru(1)	178.7(3)
C(2)—C(12)	1.497(4)	C(5)—C(1)—Ru(1)	125.8(2)		
C(3)—C(4)	1.424(4)				
C(4)—C(5)	1.440(4)				
C(5)—C(11)	1.507(4)				

3.049 Å)[21] and $RuCl_2\{(^tBu_2PCH_2CH_2)_2O\}$ (Ru···C_{agost} = 2.845 Å)[22] complexes, for which the formation of the agostic bond between the *tert*-butyl group and the Ru atom was postulated.

In solution, complex **7** apparently undergoes several exchange processes, resulting in the averaging of the NMR signals of two ^{31}P nuclei and the ^1H nuclei of the *tert*-butyl groups. The reversible cleavage of the C—H···Ru agostic bond involving two axial Bu^t groups (structure of complex **5** is discussed below), the rotation of the *tert*-butyl groups about the Bu^t—P bonds, and the rotation of the methyl groups are such processes. These processes have been identified recently[22] when studying the temperature dependence of the ^1H NMR spectrum of the $RuCl_2\{(Bu^t_2PCH_2CH_2)_2O\}$ complex. Evidently, the agostic interaction in complex **7** is rather weak, because we failed to observe individual signals of the Me group involved in the agostic bond with the Ru atom and the terminal Me groups in the ^1H NMR spectrum measured after cooling of a solution of complex **7** to –60 °C.

Apparently, an even weaker Ru···H—C agostic interaction exists in complex **5**. Thus, although the ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data are consistent with the symmetric structure of molecule **5**, the X-ray diffraction data provide evidence for the presence of a weak Ru···H—C agostic interaction in complex **5** analogous to that found in the crystal structure of cationic dicarbonyl complex **7**.

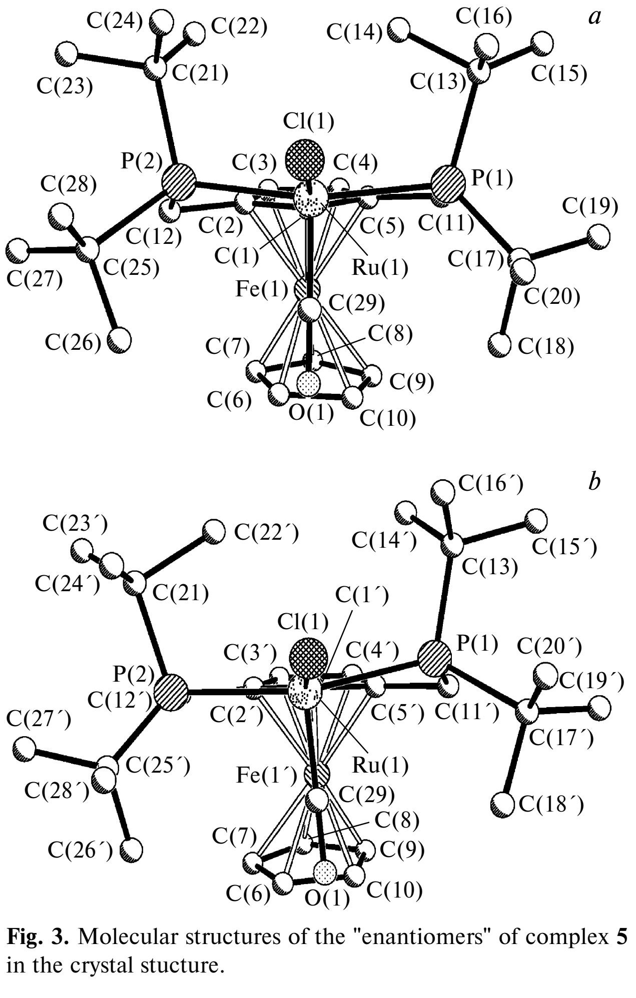


Fig. 3. Molecular structures of the "enantiomers" of complex **5** in the crystal stucture.

The X-ray diffraction study of complex **5** (Fig. 3) showed that the ruthenium atom in this complex is in a distorted tetragonal-pyramidal environment with the Cl atom in the *trans* position with respect to the C(1) atom and the CO ligand in the *endo* position with respect to the iron atom. The orientation of the axial *tert*-butyl groups at the phosphorus atoms in complex **5** is analogous to that found in cationic complex **7**. Unlike the crystal structure of **7**, which contains one "chiral" complex per asymmetric unit, the crystal structure of complex **5** is characterized by a superposition of two "enantiomers" with equal occupancies. These "enantiomers" are shown in Fig. 3. The scheme of their superposition in the crystal structure is presented in Fig. 4.

The "enantiomers" of **5** differ by the formation of an agostic bond between the Ru atom and the methyl group of the axial *tert*-butyl substituent at either the P(1) or P(2) atom (see Fig. 3). A comparison of the structures presented in Figs 1 and 3 shows that two axial *tert*-butyl groups in complexes **7** and **5** have similar orientations with respect to the Ru atom. It is noteworthy that this asymmetry was not found in the crystal structure of the $RuCl(CO)[2,6\text{-}(Bu^t_2PCH_2)_2C_6H_3\}$ complex, which is the benzene analog of complex **5**.[23]

The superposition of two "enantiomers" did not allow the determination of the geometric parameters of molecule **5** with high accuracy, as opposed to complex **7**. Nevertheless, we present selected bond lengths and bond angles of molecule **5** in Table 2.

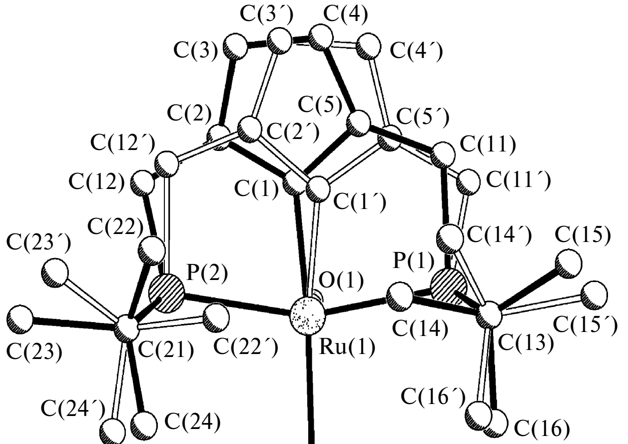


Fig. 4. Scheme of disorder (superposition of two "enantiomers") in the major coordination unit of complex **5** in the crystal structure (*tert*-butyl groups in the *endo* positions, the iron atom, and the unmetallated cyclopentadienyl ring are omitted).

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **5**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Angle	ω/deg
Ru(1)—C(1)	2.08(2)	C(29)—Ru(1)—P(1)	96.66(11)
Ru(1)—C(1′)	1.98(2)	P(2)—Ru(1)—P(1)	155.92(4)
Ru(1)—C(29)	1.769(4)	C(1)—Ru(1)—P(2)	75.3(5)
Ru(1)—P(1)	2.414(1)	C(1′)—Ru(1)—P(2)	85.8(5)
Ru(1)—P(2)	2.397(1)	C(29)—Ru(1)—P(2)	96.49(12)
Ru(1)—Cl(1)	2.477(1)	C(1)—Ru(1)—Cl(1)	171.0(6)
Angle	ω/deg	C(1′)—Ru(1)—Cl(1)	165.8(4)
C(29)—Ru(1)—C(1)	89.7(5)	C(29)—Ru(1)—Cl(1)	98.49(12)
C(29)—Ru(1)—C(1′)	93.8(6)	P(2)—Ru(1)—Cl(1)	99.89(4)
C(1)—Ru(1)—P(1)	84.7(4)	P(1)—Ru(1)—Cl(1)	98.01(4)
C(1′)—Ru(1)—P(1)	73.3(4)	O(1)—C(29)—Ru(1)	178.8(3)

Although the ruthenium atoms in complexes **5** and **7** have a 16-electron configuration and are coordinatively unsaturated, the "pseudooctahedral" coordination environment is formed due to the formation of a weak Ru···H—C agostic bond. This bond in cationic complex **7** should be stronger than that in uncharged complex **5**. This is evidenced by the ^{1}H NMR spectra of complexes **5** and **7** at room temperature. Thus, the averaged spectral pattern is observed for complex **5** (narrow lines due to the fast, on the NMR time scale, "enantiomerization" of the complex), whereas a signal for two methylene protons of the $C\underline{H}_2Bu^t$ groups in **7** are strongly broadened due to the retardation of exchange.

The formation of the Ru···H—C agostic bond between the chelated metal atom and the methyl group of the axial *tert*-butyl substituent at the P atoms in complexes **5** and **7** deserves notice. Presumably, the iridium atom in the 16-electron hydride complexes $IrH_2[^{Bu^t}P,C,P^M]$ and, particularly, in the "14-electron" complexes $Ir[^{Bu^t}P,C,P^M]$ (M = Fe or Ru), which catalyze the alkane dehydrogenation,[8] is involved in analogous agostic interactions. Such interactions can also be present in other electron-deficient and coordinatively unsaturated platinum metal pincer complexes. This provides a possibility for influencing the catalytic activity of metallocene pincer complexes by varying the distance between the axial organyl group and the chelated metal atom (for example, by introducing substituents of different bulkiness into the unmetallated cyclopentadienyl ring of the metallocene moiety[9]). We plan to use this approach for modifying pincer complexes as catalysts for transformations of organic substrates.

Experimental

Principal experimental conditions have been described earlier.[8] The NMR spectra were recorded on a Bruker AMX-400 spectrometer. The ^{1}H and ^{31}P NMR chemical shifts are given on the δ scale and were measured at 400.13 and 161.98 MHz, respectively.

Synthesis of {2,5-bis[(di-*tert*-butylphosphino)methyl]ferrocen-1-yl}chlorocarbonylruthenium(II), $RuCl(CO)[^{Bu^t}P,C,P^{Fe}]$ (5). Triethylamine (84.4 mg, 0.836 mmol) and $RuCl_2(DMSO)_4$ (202 mg, 0.418 mmol) were added to a suspension of 1,3-bis[di-*tert*-butylphosphino)methyl]ferrocene (210 mg, 0.418 mmol) in anhydrous 2-methoxyethanol (50 mL). The reaction mixture was refluxed with stirring for 3 h. The solvent was removed *in vacuo*, and the dark residue was chromatographed on an alumina column. The dark-green fraction was eluted with a 2 : 1 hexane—ethyl acetate mixture, the solvent was removed *in vacuo*, and the residue was recrystallized from an *n*-hexane—CH_2Cl_2 mixture. The product was obtained as a dark-green crystalline powder. The yield was 160 mg (57.5%). ^{1}H NMR ($CDCl_3$), δ: 1.08 (virt.t, 18 H, CH_3, $J_{H,P}$ = 6.4 Hz); 1.53 (virt.t, 18 H, CH_3, $J_{H,P}$ = 7.0 Hz); 2.79 (dt, 2 H, $C\underline{H}_AH_BP$, $J_{H,H}$ = 16.7 Hz, $J_{H,P}$ = 4.8 Hz); 3.22 (dt, 2 H, $CH_A\underline{H}_BP$, $J_{H,H}$ = 16.7 Hz, $J_{H,P}$ = 2.7 Hz); 4.05 (s, 5 H, C_5H_5); 4.32 (s, 2 H, C_5H_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 83.0 (s, 2 P). IR (CH_2Cl_2): ν_{CO} 1914 cm^{-1}. MS, *m/z* (%): 666.1 $[M]^+$ (100). Found (%): C, 52.50; H, 6.89. $C_{29}H_{47}ClFeOP_2Ru$. Calculated: C, 52.30; H, 7.11.

Synthesis of {2,5-bis[(di-*tert*-butylphosphino)methyl]ferrocen-1-yl}chlorodicarbonylruthenium(II), $RuCl(CO)_2[^{Bu^t}P,C,P^{Fe}]$ (6). A solution of complex **5** (60 mg, 0.09 mmol) in $CDCl_3$ was placed in an NMR tube, and carbon monoxide was bubbled through the solution for 0.5 h. The color of the solution changed from dark brown-green to pale yellow-brown. The ^{1}H and $^{31}P\{^1H\}$ NMR and IR spectroscopic data provide evidence for the formation of complex **6**. The evaporation of the solvent or the bubbling of argon through the reaction solution resulted in the backward reaction accompanied by elimination of the CO ligand. The solution contained a mixture of complexes **5** and **6**.

Complex 6. ^{1}H NMR ($CDCl_3$), δ: 1.46 (virt.t, 18 H, CH_3, $J_{H,P}$ = 6.6 Hz); 1.63 (virt.t, 18 H, CH_3, $J_{H,P}$ = 6.5 Hz); 2.82 (dt, 2 H, CH_AH_BP, $J_{H,H}$ = 16.5 Hz, $J_{H,P}$ = 4.0 Hz); 2.90 (dt, 2 H, $CH_A\underline{H}_BP$, $J_{H,H}$ = 16.5 Hz, $J_{H,P}$ = 3.7 Hz); 3.91 (s, 5 H, C_5H_5); 4.19 (s, 2 H, C_5H_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 99.94 (s, 2 P). IR ($CDCl_3$): ν_{CO} 1945, 2024 cm^{-1}.

Synthesis of {2,5-bis[(di-*tert*-butylphosphino)methyl]ferrocen-1-yl}dicarbonylruthenium(II) tetrakis{3,5-bis(trifluoromethyl)phenyl}borate, $\{Ru(CO)_2[^{Bu^t}P,C,P^{Fe}]\}BAr'_4$ (7). Carbon monoxide was bubbled through a solution of complex **5** (66.5 mg, 0.1 mmol) in CH_2Cl_2 (50 mL) for 5 min. The color of the solution changed from brown-green to orange-brown. Then a solution of $NaBAr'_4$ (89 mg, 0.9 mmol) in CH_2Cl_2 was added dropwise to the reaction mixture with continuous bubbling of CO for 15 min. The solution turned dark-green. Then the solution was filtered, the solvent was removed *in vacuo*, and the residue was recrystallized from an *n*-hexane—CH_2Cl_2 mixture. The product was obtained as a dark-green powder. The yield was 130 mg (85%). ^{1}H NMR ($CDCl_3$), δ: 0.95 (virt.t, 18 H, CH_3, $J_{H,P}$ = 6.8 Hz); 1.50 (virt.t, 18 H, CH_3, $J_{H,P}$ = 7.6 Hz); 3.15 (dt, 2 H, $C\underline{H}_AH_BP$, $J_{H,H}$ = 16.6 Hz, $J_{H,P}$ = 4.5 Hz); 3.27 (br, 2 H, $CH_A\underline{H}_BP$); 4.32 (s, 5 H, C_5H_5); 4.93 (s, 2 H, C_5H_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 98.9 (s, 2 P). ^{11}B NMR ($CDCl_3$), δ: −6.70 (s, 1 B). IR (KBr): ν_{CO} 1979, 2042 cm^{-1}. MS, *m/z* (%): 658.9 $[M - BAr'_4]^+$ (100). Found (%): C, 48.17; H, 3.43. $C_{62}H_{59}BF_{24}FeO_2P_2Ru$. Calculated: C, 48.93; H, 3.90.

Table 3. Crystallographic data and the refinement statistics for compounds **5** and **7**

Parameter	**5**	**7**
Molecular formula	$C_{29}H_{47}ClFeOP_2Ru$	$[C_{30}H_{47}FeO_2P_2Ru]^+ \cdot [C_{32}H_{12}F_{24}B]^- \cdot CH_2Cl_2$
Molecular weight	665.98	1606.69
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Temperature/K	120(2)	120(2)
a/Å	17.807(3)	17.684(5)
b/Å	8.321(2)	18.251(5)
c/Å	20.335(4)	20.834(6)
β/deg	94.636(4)	98.001(5)
V/Å^3	3003.2(9)	6659(3)
Z	4	4
d_{calc}/g cm^{-3}	1.473	1.603
μ/cm^{-1}	12.02	6.83
$2\theta_{max}$/deg	58	58
Number of independent reflections (R_{int})	7837 (0.0539)	17580 (0.0356)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0475 (5800)	0.0463 (12661)
wR_2 (based on F^2 for all reflections)	0.1085	0.1087
Number of variables	538	906
GOOF	0.914	1.038

X-ray diffraction study of complexes 5 and 7. Crystallographic data and the refinement statistics for compounds **5** and **7** are given in Table 3. The X-ray diffraction data sets were collected on a 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 based on F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms of the $C(14)H_3$ group involved in the agostic interaction with the ruthenium atom in cationic complex **7** were located in difference electron density maps and refined isotropically. Other hydrogen atoms in complexes **5** and **7** were positioned geometrically and refined using a riding model. All calculations were carried out on a PC with the use of the SHELXTL program package.[24] 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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