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Journal of Organometallic Chemistry 689 (2004) 1930–1943
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Cationic methyl complexes of rhodium(III): synthesis, structure, and some reactions

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Received 30 November 2003; accepted 23 February 2004

Abstract

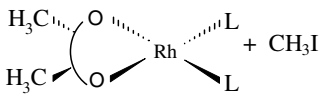
Cationic methyl complex of rhodium(III), *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**1**) is prepared by interaction of *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] with $AgBPh_4$ in acetonitrile. Cationic methyl complexes of rhodium(III), *cis*-[Rh(Acac)(PPh_3)$_2$-(CH_3)(CH_3CN)][BPh_4] (**2**) and *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**3**) (Acac, BA are acetylacetonate and benzoylacetonate, respectively), are obtained by CH_3I oxidative addition to rhodium(I) complexes [Rh(Acac)(PPh_3)$_2$] and [Rh(BA)(PPh_3)$_2$] in acetonitrile in the presence of $NaBPh_4$. Complexes **2** and **3** react readily with NH_3 at room temperature to form *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**4**) and *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**5**), respectively. Complexes **1**–**5** were characterized by elemental analysis, ^1H and $^{31}P\{^1H\}$ NMR spectra. Complexes **1**, **2**, **3** and **4** were characterized by X-ray diffraction analysis. Complexes **2** and **3** in solutions (CH_2Cl_2, $CHCl_3$) are presented as mixtures of *cis*-(PPh_3)$_2$ isomers involved into a fluxional process. Complex **2** on heating in acetonitrile is converted into *trans*-isomer **1**. In parallel with that isomerization, reductive elimination of methyl group with formation of [CH_3PPh_3][BPh_4] takes place. Replacement of CH_3CN in complexes **1** and **2** by anion I^- yields in both cases the neutral complex *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I]. Strong *trans* influence of CH_3 ligand manifests itself in the elongation (in solid) and labilization (in solution) of rhodium–acetonitrile nitrogen bond.

Keywords: Rhodium methyl complexes; Oxidative addition; X-ray; NMR

1. Introduction

The interaction of planar rhodium(I) complexes with methyl iodide keeps drawing attention as a simple and convenient model of the reaction of oxidative addition, one of the key stages of important catalytic processes. Mechanistic concepts suggest in many cases the methyl iodide oxidative addition to proceed through intermediates with separated charges, $[L_nM(CH_3)]^+I^-$ [1, 2]. The existence of such intermediates is not yet clearly documented, and their structure remains so far a subject of speculation [3].

In the cases which are not complicated by subsequent reactions, such as elimination or insertion of ligands, the final products of methyl iodide oxidative addition to planar rhodium(I) complexes are octahedral complexes of rhodium(III). For instance, in reactions



$$\longrightarrow [Rh(Acac)L_2(CH_3)]^+I^- \longrightarrow [Rh(Acac)L_2(CH_3)I]$$

$$[Rh(Acac)L_2],\ L = P(OPh)_3, PPh_3$$

the final products are octahedral complexes with different mutual disposition of ligands [2b, 4, 5]:

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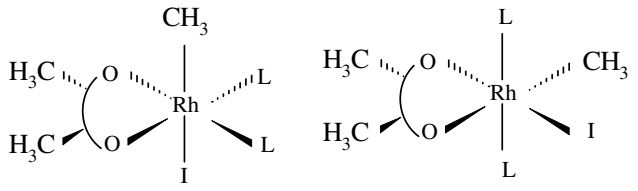
doi:10.1016/j.jorganchem.2004.02.041



In both examples above, methyl iodide adheres to planar rhodium(I) complexes with the initial *cis*-disposition of P-donor ligands. In the case of triphenylphosphite, the P-ligands retain their initial disposition (*trans*-addition of methyl iodide), whereas in the case of triphenylphosphine, P-ligands migrate to the mutual *trans*-positions (*cis*-addition of methyl iodide). It can be supposed that the mutual disposition of ligands in the final product is determined by an intramolecular rearrangement of the intermediate pentacoordinate cationic methyl complex before the iodide anion enters the coordination sphere, and the complex attains its final octahedral configuration.

Study of structure, isomerization, and reactivity of cationic methyl intermediates might shed more light on the mechanism of oxidative addition, but high reactivity of these intermediates prevents their study directly in the reaction mixtures. For instance, the intermediates formed in the course of the reactions [Rh(β-diket)$(PPh_3)_2$] + CH_3I in benzene solutions (NMR at a temperature just above the melting point of benzene) instantly convert into the final octahedral complexes on heating the reaction mixture to room temperature [6]. However, in some cases, in the course of oxidative addition reactions, it was possible to isolate cationic methyl complexes as sufficiently stable salts with bulk anions, for instance, $[CpIr(CO)_2(CH_3)]^+[BPh_4]^-$ [7] and $[CpRh(CO)(PPhMe_2)(CH_3)]^+[BPh_4]^-$ [8]. Some stable cationic complexes were also obtained on interaction of the halogen containing neutral complexes with silver salts, for instance, $AgBF_4$ or $AgPF_6$ [9,10]:

$$[L_nMCl] + AgX \rightarrow [L_nM]^+X^- + AgCl$$

We describe here synthesis of isomers of cationic methyl rhodium(III) complexes, [Rh(β-diket)$(PPh_3)_2$-$(CH_3)(CH_3CN)]^+[BPh_4]^-$, where β-diket is acetylacetonate or benzoylacetonate ligand, report structures of these complexes in the crystalline state and in solutions, and present data on some of their reactions. We believe that data on structure and reactivity of cationic methyl complexes isolated in the form of stable salts may give an insight into chemistry of their unstable analogs. Data presented in this paper have been partially published in our communications [11,12].

2. Results and discussion

2.1. Synthesis and characterization of trans-[Rh(Acac)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ (1)

Stirring of suspension of orange crystals of *trans*-[Rh(Acac)$(PPh_3)_2(CH_3)$I] and white solid $AgBPh_4$ in acetonitrile or acetone/acetonitrile mixture at room temperature results in formation of a yellow solution and a pale yellow precipitate. The reaction mixture was filtered, and solvent was removed from yellow filtrate. The yellow solid obtained by evaporation of the solvent was dissolved in chloroform, filtered, and then, on removal of chloroform, dissolved in acetonitrile. A very fine precipitate contained in the solution was removed by thorough filtration. The product was isolated by evaporation of acetonitrile solution and then recrystallized from acetonitrile. An elemental analysis of the yellow crystalline product and X-ray study of the crystal grown from acetonitrile showed the substance obtained to be a salt of cationic rhodium(III) complex containing $[BPh_4]^-$ as an anion and solvated with acetonitrile (1:1), *trans*-[Rh(Acac)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]\cdot CH_3CN$. A view of the molecular geometry is shown in Fig. 1. The positions of the cations *trans*-[Rh(Acac)$(PPh_3)_2$-$(CH_3)(CH_3CN)]^+$, anions $[BPh_4]^-$, and molecules CH_3CN in the unit cell are presented in Fig. 2.

The cation *trans*-$[Rh(Acac)(PPh_3)_2(CH_3)(CH_3CN)]^+$ retains the octahedral structure of the parent neutral complex with the only difference that the ligand I^- in the rhodium-(β-diketonate) plane (the equatorial plane in

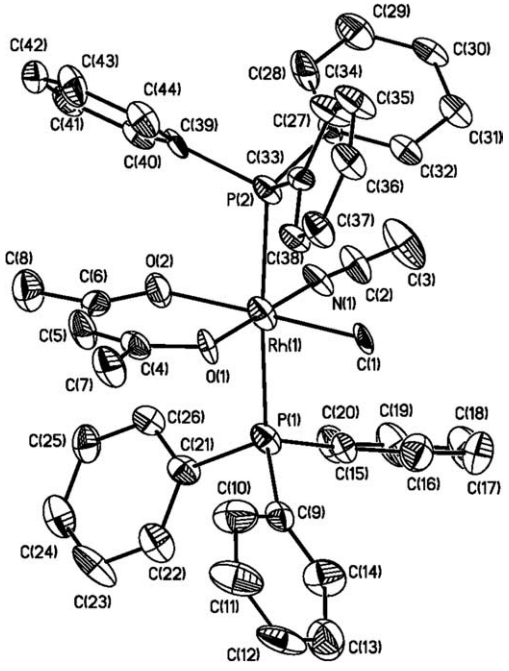


Fig. 1. The structure of the cation of compound *trans*-[Rh(Acac)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ (**1**) (50% probability ellipsoids).

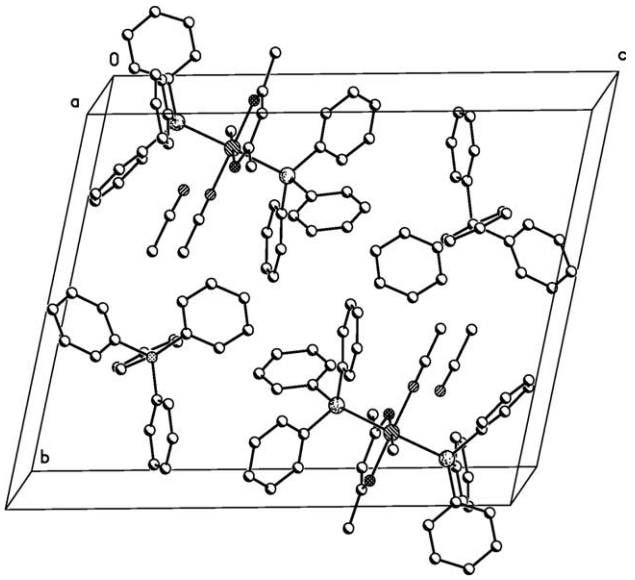


Fig. 2. The crystal structure of *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**1**).

our further discussion) is replaced by the CH_3CN molecule coordinated via the nitrogen atom. Table 1 presents values of the important bond lengths and angles in the cation *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)]$^+$. For comparison, the corresponding values are given for the parent neutral complex *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] [5] and for the closely related complex *trans*-[Rh(Acac)(PPh_3)$_2$$I_2$] [13].

Two phosphine ligands in all these structures occupy axial positions *trans* to each other. The P(1)–Rh–P(2) angle (176.07(9)°) in complex **1** is statistically identical with the P(1)–Rh–P(2) angles of the related complexes, [Rh(Acac)(PPh_3)$_2$(CH_3)I] (177.34(11)°) [5] and [Rh(Acac)(PPh_3)$_2$$I_2$] (177.5(3)°) [13]. The averaged (2.390 Å) Rh–P bond length in **1** compares well with the average of 2.385 and 2.391 Å found in [Rh(Acac)-(PPh_3)$_2$(CH_3)I] [5] and [Rh(Acac)(PPh_3)$_2$$I_2$] [13], respectively. The two Rh–O bonds in complex **1** differ significantly, by 0.116 Å, due to the difference in the *trans*-influence of the methyl and acetonitrile ligands. The longer Rh–O(2) bond, *trans* to methyl ligand, is of the same length, 2.141(5) Å, as in the parent neutral complex. The Rh–CH_3 bond length in **1** is slightly shorter than that in [Rh(Acac)(PPh_3)$_2$(CH_3)I].

Table 1
Selected bond lengths (Å) and angles (°) for complexes *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**1**) (this work), *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] [5], and *trans*-[Rh(Acac)(PPh_3)$_2$$I_2$] [13] with estimated standard deviations in parentheses

	Complex **1**	*Trans*-[Rh(Acac)-(PPh_3)$_2$(CH_3)I]	*Trans*-[Rh(Acac)-(PPh_3)$_2$$I_2$]
Rh–C(1)	2.085(7)	2.11(2)	–
Rh–O(1)	2.025(5)	2.073(7)	2.07(2)
Rh–O(2)	2.141(5)	2.141(7)	2.07(2)
Rh–P(1)	2.405(2)	2.394(3)	2.395(8)
Rh–P(2)	2.376(2)	2.377(3)	2.388(8)
Rh–N(1)	1.988(7)	–	–
Rh–I(1)	–	2.611(2)	2.606(3)
Rh-I(2)	–	–	2.637(4)
P(1)–Rh–P(2)	176.07(9)	177.34(11)	177.5(3)
O(1)–Rh–O(2)	91.9(2)	89.7(3)	90.2(8)
P(1)–Rh–O(1)	93.45(15)	92.3(2)	89.3(6)
P(1)–Rh–O(2)	91.47(15)	92.6(2)	92.0(6)
P(2)–Rh–O(1)	88.71(15)	90.0(2)	92.1(6)
P(2)–Rh–O(2)	91.74(15)	92.6(2)	90.0(6)
P(1)–Rh–C(1)	87.1(2)	91.3(11)	–
P(2)–Rh–C(1)	89.6(2)	87.5(11)	–
P(1)–Rh–N(1)	87.32(19)	–	–
P(2)–Rh–N(1)	90.43(19)	–	–

The $^{31}P\{^1H\}$ NMR spectrum of **1** ($CDCl_3$ solvent, Table 2) shows a doublet at δ 21.2 ppm with coupling constant ^1J(Rh–P) 99.6 Hz, which indicates the phosphine ligands to be equivalent. The parent neutral complex *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] with axial positions of triphenylphosphine ligands has close ^{31}P NMR spectroscopic parameters, a doublet at δ 20.0 ppm with coupling constant ^1J(Rh–P) 106.1 Hz ($CDCl_3$ solvent) [4].

The *trans*-position of phosphine ligands in complex **1** in solution is confirmed by ^1H NMR spectral data.

The ^1H NMR spectrum of complex **1** ($CDCl_3$, Table 3) contains three groups of signals. In the region 6.8–7.5 ppm there are signals of phenyl protons of ligands PPh_3 and anion $[BPh_4]^-$. A singlet at δ 4.22 ppm (1H) belongs to the methine proton of the acetylacetonate ligand [4]. Present in the region 0–2 ppm are four singlets, at δ 2.00 (3H), 1.43, and 1.40 (two latter are partially superimposed, 9H in the total), and 0.68 (3H) ppm. The first of them, the signal at δ 2.00 ppm, is to be assigned to acetonitrile, which passes into solution on dissolving the solvated complex in chloroform. This assignment is founded on the following considerations: (i) the ^1H chemical shift of free acetonitrile in chloroform solution is δ 1.98 ppm [14]; (ii) the signal disappeared on recrystallization of the complex from methylene chloride; (iii) this signal is absent in the spectrum of the complex **1′**, *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CD_3CN)][BPh_4]·CD_3-CN, synthesized in deuterated solvent, CD_3CN, and recrystallized from CD_3CN. In order to analyze the two close signals at δ 1.43 and 1.40 ppm (the total of 9H; the first signal is more intense), we synthesized a complex containing the deuterated methyl ligand, *trans*-[Rh(Acac)(PPh_3)$_2$(CD_3)(CH_3CN)][BPh_4]·CH_3CN (**1″**). Intensity of signals at δ 1.43 and 1.40 ppm in the spectrum of **1″** turned out equal (3H and 3H). Thus, we may conclude that these signals in the spectra of both **1** and **1″** belong to two non-equivalent methyl groups of the acetylacetonate ligand, and in the spectrum of **1**, one of these signals (δ 1.43 ppm) coincides with the signal from methyl ligand, CH_3(–Rh). This overlapping makes the splitting of CH_3(–Rh) signal almost unobservable. The

Table 2
$^{31}P\{^{1}H\}$ NMR spectral parameters of cationic methyl complexes of rhodium(III) **1**–**5** (solvent $CDCl_3$)

Compound	Cation		20 °C		−50 °C	
			δ, ppm/^{1}J(RhP), Hz	^{2}J(PP), Hz	δ, ppm/^{1}J(RhP), Hz	^{2}J(PP), Hz
1	*Trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)CH_3CN]$^+$	Single isomer	21.2/99.6	–	21.2/99.4	–
2	*Cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)CH_3CN]$^+$	Major isomer **2a**	29.8/137.8[a]	–	29.7 /136.0	–
		Minor isomer **2b**			27.3/143.1	36.9
					23.6 /128.4	
3	*Cis*-[Rh(BA)(PPh_3)$_2$(CH_3)CH_3CN]$^+$	Major isomer **3a**	29.6/138.1[a]	–	31.1/135.1	38.5
					28.8/138.0	
		Minor isomers (**3b**, **3b′**)[b]			27.4/142.9	36.0
					24.4/128.7	
4	*Cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)NH_3]$^+$	Single isomer	26.7/133.8	35.2	27.0/134.2	35.5
			24.0/128.6		23.0/127.2	
5	*Cis*-[Rh(BA)(PPh_3)$_2$(CH_3)NH_3]$^+$	Isomer′	27.3/134.1	34.8	27.5/134.6	35.2
			24.0/128.3		23.3/126.7	
		Isomer″	26.9/134.8	35.4	27.2/134.8	35.6
			23.4/128.2		22.8/127.0	

[a] Spectral parameters of averaged spectrum.
[b] We failed to measure spectral parameters for one of the minor isomers of **3** (**3b** or **3b′**) due to partial overlapping of their signals (Fig. 6).

Table 3
^{1}H chemical shifts of methyl, β-diketonate, CH_3CN, and NH_3 ligands in complexes **1**–**5** (solvent $CDCl_3$)

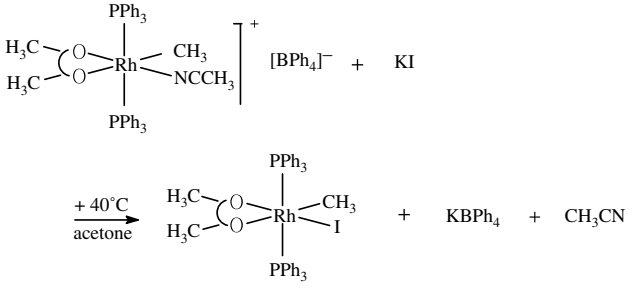
Compound	Cation		T (°C)	CH_3–Rh	CH_3(β-diketonate)	CH (β-diketonate)	CH_3CN–Rh	NH_3–Rh
1	*Trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)CH_3CN]$^+$	Single isomer	~20	~1.43	1.43; 1.40	4.22	0.68	–
			−50	~1.37	1.38, 1.37	4.22	0.51	–
2	*Cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)CH_3CN]$^+$	[a]	~20	1.90	1.70	5.40	1.40	–
		Major isomer **2a**[b]	−50	1.46	1.80	5.35	1.65	–
3	*Cis*-[Rh(BA)(PPh_3)$_2$(CH_3)CH_3CN]$^+$	[a]	~20	2.04	1.84	6.10	1.30	–
		Major isomer **3a**[b]	−50	–[b]	1.95	6.00	1.65	–
4	*Cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)NH_3]$^+$	Single isomer	~20	1.33	1.92; 1.64	4.72	–	0.20
			−50	1.24	1.92; 1.65	4.70	–	−0.30
5	*Cis*-[Rh(BA)(PPh_3)$_2$(CH_3)NH_3]$^+$	Isomer′	~20	1.42	1.82	5.45	–	0.32
		Isomer″		1.47	2.06	5.40	–	0.32
		Isomer′	−50	1.36	1.82	5.45	–	−0.19
		Isomer″		1.39	2.06	5.40	–	−0.19

[a] Spectral parameters of averaged spectrum.
[b] We failed to make a reliable assignment of ^{1}H resonances for the minor isomers (**2b**, **3b** and **3b′**) and for the methyl ligand in the major isomer **3a** due to partial overlapping or/and low intensities of signals.

splitting of this signal is more pronounced in the spectrum of **1** recorded in the CD_3CN solution, triplet of doublets at δ 1.42 ppm with ^2J(RhH) 1.8 Hz; ^3J(PH) 5.4 Hz. These parameters are close to those of the CH_3 (–Rh) group in the spectrum of the parent neutral complex, [Rh(Acac)(PPh_3)$_2$(CH_3)I], triplet of doublets at δ 1.39 ppm with ^2J(RhH) 2.1 Hz; ^3J(PH) 5.7 Hz (in $CDCl_3$ solution) [4]. Finally, the signal at δ 0.68 ppm is to be assigned to methyl group of coordinated acetonitrile, as this signal is absent in the spectrum of the complex **1′** containing deuterated acetonitrile. The non-equivalence of methyl groups of the acetylacetonate ligand in **1** is due to the different nature of the ligands, CH_3 and CH_3CN, lying in the equatorial plane in *trans*-positions to acetylacetonate oxygens. This proves that when in solution complex **1** retains its solid-state octahedral geometry.

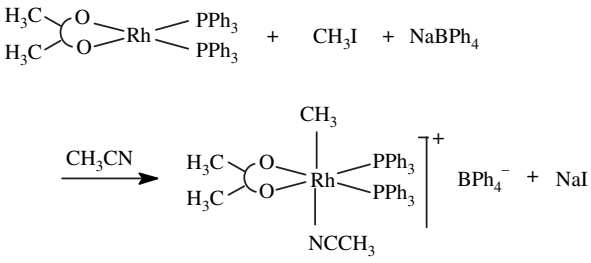
The $^{31}P\{^1H\}$ NMR spectrum of **1** is temperature invariant down to −50 °C. In the ^1H NMR spectrum, only minor changes in the positions of signals were observed with a decrease of temperature (Tables 2 and 3).

Acetonitrile ligand in complex **1** could be replaced by anion I^- on heating with potassium iodide in the acetone solution. As a result, **1** is quantitatively transformed into the parent neutral complex [Rh(Acac)-(PPh_3)$_2$(CH_3)I] [4] that was isolated from the reaction mixture and characterized by elemental analysis, $^{31}P\{^1H\}$, and ^1H NMR spectra.



2.2. Synthesis and characterization of *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**) and *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**3**)

We have also prepared cationic methyl complexes of rhodium(III) by action of methyl iodide on rhodium(I) complexes, [Rh(β-diket)(PPh_3)$_2$], in the presence of sodium tetraphenylborate in acetonitrile. In the case of β-diket = Acac, a light-yellow crystalline product was formed. Crystal for the structure investigation was obtained by recrystallization from methylene chloride/diethyl ether solution. According to the results of elemental analysis and X-ray study, the product is cationic complex *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4]·0.5CH_2Cl_2. Thus, the formation of *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] may be represented by following scheme:



The structure of the cation is shown in Fig. 3. The positions of the cations *cis*-[Rh(Acac)(PPh_3)$_2$-(CH_3)(CH_3CN)]$^+$, anions [BPh_4]$^-$, and molecules CH_2Cl_2 in the unit cell are presented in Fig. 4. Selected bond lengths and angles are given in Table 4.

According to the X-ray diffraction data, the cation has geometry of distorted octahedron with phosphines in the equatorial plane and the CH_3 and CH_3CN ligands in axial positions. The C(1)–Rh–N(1) angle, 167.59(11)°, differs markedly from the ideal value of 180°, the acetonitrile molecule being deflected towards the acetylacetonate ligand. The angle P(1)–Rh–P(2) amounts to 99.14(3)°, which markedly exceeds the value of the corresponding angle in the bisphosphite complex *cis*-[Rh($CH_3COCHCOCF_3$)(P(OPh)$_3$)$_2$$I_2$] (91.3(3)°) [15]. This difference can result from a larger cone angle for triphenylphosphine [16]. It is to be noted that the Rh–N(1) bond *trans* to the methyl ligand (complex **2**) is

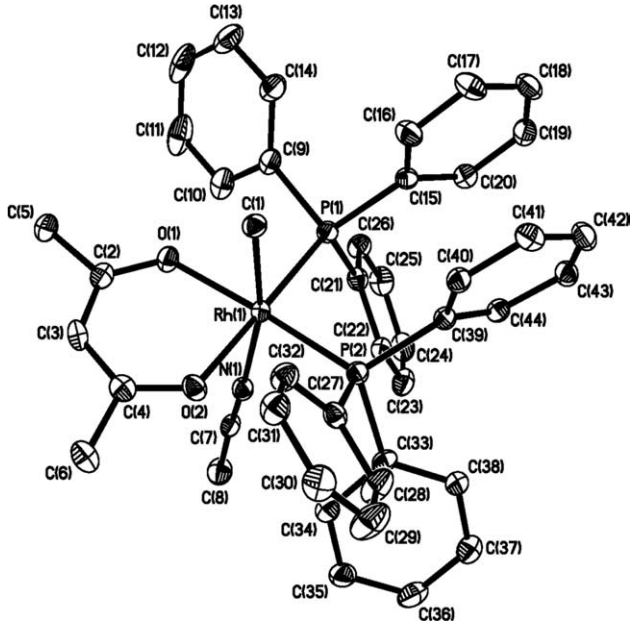


Fig. 3. The structure of the cation of compound *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**) (50% probability ellipsoids).

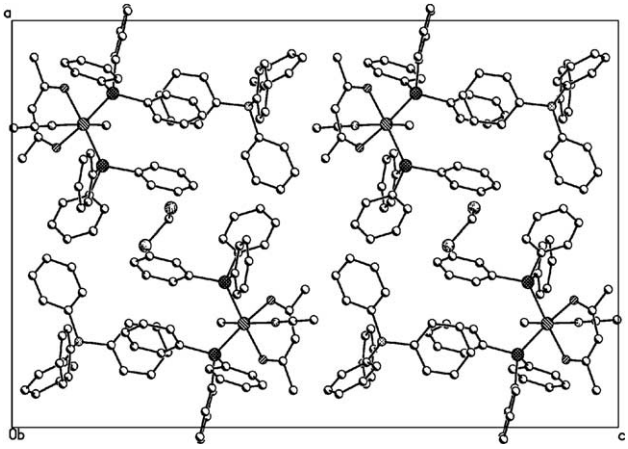


Fig. 4. The crystal structure of *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**), projection along the *Y*-axis.

Table 4
Selected bond lengths (Å) and angles (°) for complexes *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**), *cis*-[Rh(BA)(PPh_3)$_2$-(CH_3)(CH_3CN)][BPh_4] (**3**), and *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)]-[BPh_4] (**4**) with estimated standard deviations in parentheses

	2	3	4
Rh–C(1)	2.059(3)	2.062(3)	2.075(3)
Rh–O(1)	2.0829(18)	2.068(2)	2.152(2)
Rh–O(2)	2.0653(18)	2.0775(19)	2.071(2)
Rh–P(1)	2.3262(8)	2.3078(8)	2.3111(7)
Rh–P(2)	2.3032(7)	2.3383(9)	2.3291(7)
Rh–N(1)	2.190(2)	2.192(3)	2.118(2)
P(1)–Rh–P(2)	99.14(3)	98.81(3)	99.86(3)
O(1)–Rh–O(2)	90.01(7)	89.75(8)	89.21(8)
P(1)–Rh–O(1)	88.31(6)	84.43(6)	98.13(6)
P(1)–Rh–O(2)	177.28(6)	171.22(6)	169.00(6)
P(2)–Rh–O(1)	170.77(6)	175.55(6)	89.77(5)
P(2)–Rh–O(2)	82.74(6)	87.37(6)	88.30(6)
P(1)–Rh–C(1)	90.21(9)	89.31(9)	89.88(9)
P(2)–Rh–C(1)	90.50(9)	93.39(9)	94.43(8)
P(1)–Rh–N(1)	93.16(6)	101.40(7)	90.81(7)
P(2)–Rh–N(1)	100.73(6)	90.70(7)	168.33(7)
C(1)–Rh–N(1)	167.59(11)	167.82(10)	90.27(11)

significantly (0.202 Å) longer than Rh–N(1) bond *trans* to acetylacetonate oxygen (complex **1**). This fact, as well as the above-mentioned asymmetry in the rhodium–oxygen bonds in complex **1**, displays a strong *trans*-influence of the methyl ligand.

The $^{31}P\{^1H\}$ and ^1H NMR spectra of **2** are temperature dependent. At room temperature, its $^{31}P\{^1H\}$ spectrum in $CDCl_3$ (Table 2) is averaged and shows a single doublet of broadened lines at δ 29.8 ppm with apparent ^1J(RhP) value of 137.8 Hz, while at −50 °C two sets of signals are observed, a doublet at δ 29.7 ppm with high intensity and two doublets of doublets (δ 27.3 and 23.6 ppm) with very low intensity. This indicates that two related forms of **2** are present in the solution. In one of them the phosphine ligands occupy equivalent positions, while in the other their positions are non-equivalent. It is evident that at room temperature these complexes are involved into a fast interconversion, while at −50° these dynamic processes slow down and do not affect the ^{31}P NMR spectrum. The intense doublet at δ 29.7 ppm corresponds to the complex containing two equivalent phosphines, and should be ascribed to the major form **2a**, that retains in solution the solid-state geometry of **2** with both PPh_3 ligands in the equatorial plane (Fig. 3). Structure of the minor form, **2b**, present in the solution and containing non-equivalent phosphines will be discussed in Section 2.4.

Cationic complex with the benzoylacetonate ligand *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**3**) was prepared similarly to the complex **2** by action of methyl iodide on [Rh(BA)(PPh_3)$_2$] in acetonitrile in the presence of $NaBPh_4$. After recrystallization from methylene chloride/diethyl ether solution, complex **3** was characterized by elemental analysis, and its solid-state structure was established by X-ray crystallography (Fig. 5).

The complex is solvated with diethyl ether (1:1). Selected bond lengths and angles are given in Table 4. As can be seen, in solid state, cation **3**, *cis*-[Rh(BA)-(PPh_3)$_2$(CH_3)(CH_3CN)]$^+$, like cation **2**, has a distorted octahedral geometry with two *cis*-triphenylphosphine ligands in the equatorial plane and the methyl and CH_3CN ligands in axial positions, *trans* to each other. The structural parameters of complex **3** are very close to those of complex **2**.

The $^{31}P\{^1H\}$ and ^1H NMR spectra of **3**, like those of **2**, are temperature dependent (Tables 2 and 3, Fig. 6).

The $^{31}P\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ at room temperature is averaged and shows a single doublet of broadened lines, δ 29.6 ppm with apparent ^1J(RhP) 138.1 Hz. In the spectrum recorded at −20 °C, the

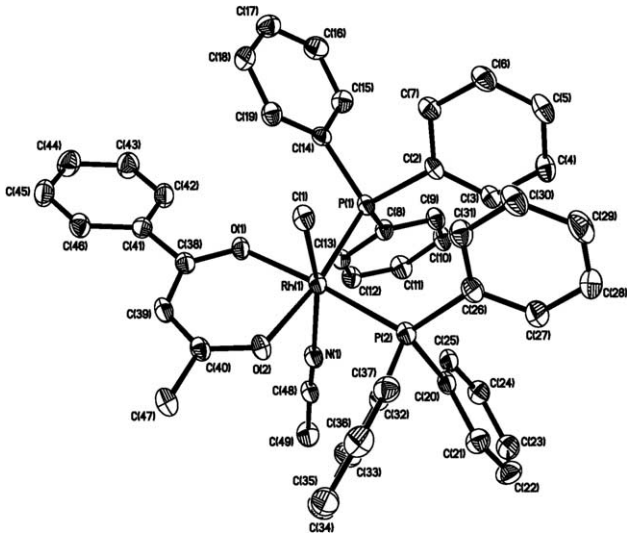


Fig. 5. The structure of the cation of compound *cis*-[Rh(BA)(PPh_3)$_2$-(CH_3)(CH_3CN)][BPh_4] (**3**) (50% probability ellipsoids).

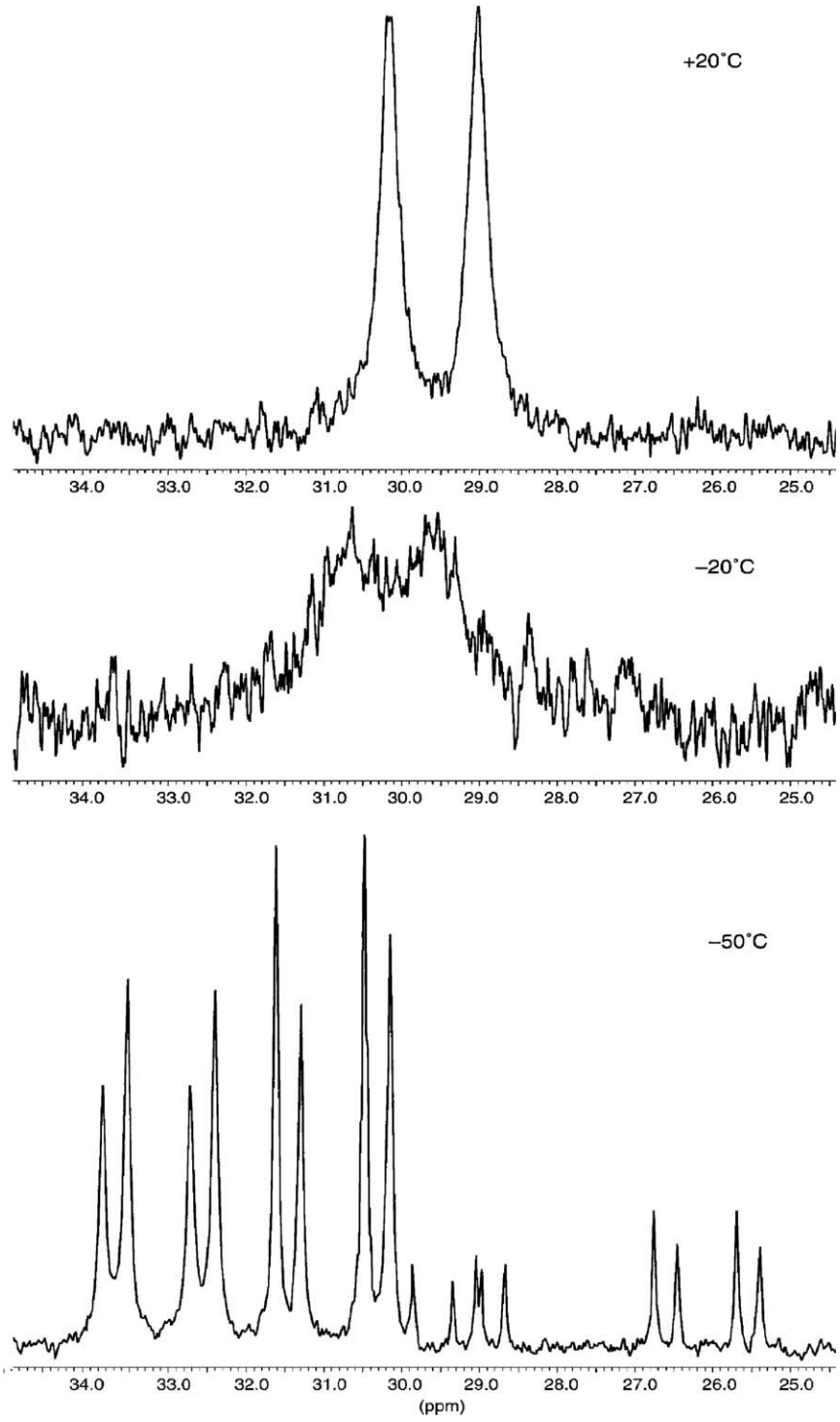


Fig. 6. The $^{31}P\{^{1}H\}$ NMR spectra of *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**3**) in $CDCl_3$ at various temperatures.

corresponding resonance appears as a combination of two very broad, poorly resolved bands. The spectrum measured at −50 °C contains two groups of signals differing by intensity. The group of signals with a high intensity consists of two doublets of doublets and belongs to a complex with two non-equivalent phosphines (δ 31.1 and 28.8 ppm). We believe this group of signals to belong to cation **3a** that retains in solution the solid-state structure of **3** with two equatorial phosphines in the *cis*-position to each other (Fig. 5). This complex is a structural analog of **2a**, and the non-equivalence of the phosphine ligands in its structure is a consequence of the asymmetry of the benzoylacetonate ligand. The second group of signals has a lower intensity and seems to be the superimposed spectra of two other cations that contain phosphines in non-equivalent positions (Fig. 6,

Table 2). The structure of these minor forms will be discussed in Section 2.4.

The ^{1}H NMR spectra of complexes **2** and **3** recorded at room temperature consist of three groups of signals. In the region 6.8–7.8 ppm there are signals of phenyl protons of PPh_3, BPh_4^-, and benzoylacetonate. Signals of methine protons for complexes **2** and **3** are located at δ 5.40 ppm (1H) and δ 6.10 ppm (1H), respectively. Signals of methyl protons represent the third group lying in the region δ 0–2.1 ppm. In the spectrum of **2** the signal at δ 1.90 ppm (3H) should be assigned to the methyl ligand, CH_3(–Rh), as this signal is absent in the spectrum of the complex with deuterated methyl ligand, *cis*-[Rh(Acac)$(PPh_3)_2(CD_3)(CH_3CN)$][BPh_4] (**2′**). Two equivalent methyl groups of the acetylacetonate ligand give a singlet at δ 1.70 ppm with intensity corresponding to 6H. Finally, we assign a singlet at δ 1.40 ppm to methyl group of coordinated acetonitrile. In the ^{1}H NMR spectrum of complex **3** the signal at δ 2.04 ppm should be assigned to the methyl ligand, CH_3(–Rh), as this signal is absent in the spectrum of the complex with deuterated methyl ligand, *cis*-[Rh(BA)$(PPh_3)_2(CD_3)$-(CH_3CN)][BPh_4] (**3′**). By analogy with complex **2**, the signals at δ 1.84 and 1.30 ppm should be assigned to the methyl groups of the benzoyl acetonate and coordinated acetonitrile, respectively. In the ^{1}H NMR spectra of complexes **2** and **3** are also present signals from protons of the solvent molecules contained in the solvated crystals, a singlet at δ 5.30 ppm from CH_2Cl_2 (complex **2**) and two multiplets, quartet at δ 3.50 ppm and triplet at δ 1.25 ppm, from diethyl ether (complex **3**). The ^{1}H NMR spectra of complexes **2** and **3** at room temperature evidently are averaged. At −50 °C the ^{1}H NMR spectra of both complexes contain a number of overlapping signals, as spectra of major and minor forms are separated due to deceleration of dynamic exchange processes. By comparing the ^{1}H NMR spectra of complexes **2** and **2′**, we succeeded in assigning the signals belonging to the major form, **2a**, with equatorial phosphine ligands (Table 3). For **2b** and **3b**, and for the methyl ligand CH_3(–Rh) in **3a**, we failed to make a reliable assignment of signals due to their overlapping or low intensity. It is to be noted that in the spectra of **2** we did not observe splitting of signal from protons of the CH_3(–Rh) ligand at room temperature as well as at −50 °C.

2.3. Reactions of complexes 2 and 3 with ammonia: characterization of cis-[Rh(Acac)$(PPh_3)_2(CH_3)$-(NH_3)][BPh_4] (4) and cis-[Rh(BA)$(PPh_3)_2(CH_3)$-(NH_3)][BPh_4] (5)

Complex *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)(NH_3)$][BPh_4] (**4**) is easily formed by passing a stream of NH_3 through the methylene chloride solution of **2** or the suspension of **2** in acetonitrile at room temperature. Complex **4** was characterized by elemental analysis, crystal X-ray diffraction study, and $^{31}P\{^1H\}$ and ^{1}H NMR spectra. Crystal for the X-ray diffraction analysis was grown from the methylene chloride/diethyl ether solution. The structure of the cation is shown in Fig. 7.

Selected bond lengths and angles are given in Table 4. The equatorial plane of cation **4** contains triphenylphosphine and methyl ligands. The second triphenylphosphine ligand and the ammonia molecule occupy axial positions, *trans* to each other. The angle P(1)–Rh–P(2) amounts to 99.86(3)°, which is very close to the angle P(1)–Rh–P(2) in structures **2** and **3** (Table 4). Lengths of two Rh–O bonds differ significantly (0.081 Å), the bond *trans* to the CH_3 ligand being longer. The values of angles P(1)–Rh–O(1) (98.13(6)°), P(1)–Rh–O(2) (169.00(6)°), and P(2)–Rh–N(1) (168.33(7)°) indicate the structure of complex **4** to be a markedly distorted octahedron, with the NH_3 ligand deviating towards the acetylacetonate ligand.

The $^{31}P\{^1H\}$ NMR spectrum of complex **4** in chloroform solution (Table 2) at room temperature represents two doublets of doublets (δ 26.7 and 24.0 ppm) and corresponds to the complex with two non-equivalent phosphine ligands, which is present in solution in one isomer form. Thus, complex **4** in solution retains its solid-state geometry (Fig. 7). The ^{1}H NMR spectrum of complex **4** (Table 3) consists of a group of phenyl proton signals (δ 6.8–7.5 ppm), a signal of methine proton of acetylacetonate ligand at δ 4.72 ppm (1H), and a set of signals of methyl groups and coordinated ammonia in the region 0–2 ppm. Within this region, signals at δ 1.92 (3H) and 1.64 (3H) ppm belong to protons of two non-equivalent methyl groups of the acetylacetonate ligand. The signal with poorly resolved splitting at δ 1.33 ppm (3H) should be assigned to the methyl ligand, CH_3-(–Rh). Splitting of this signal is caused by spin–spin

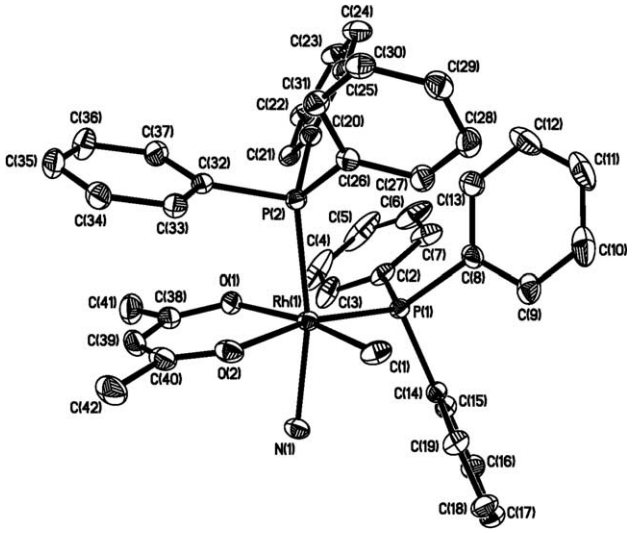
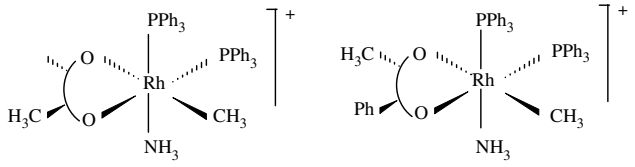


Fig. 7. The structure of the cation of compound *cis*-[Rh(Acac)-$(PPh_3)_2(CH_3)(NH_3)$][BPh_4] (**4**) (50% probability ellipsoids).

interaction of methyl ligand protons with ^{103}Rh and two non-equivalent ^{31}P nuclei. We assign signal at δ 0.20 ppm (3H) to the protons of coordinated ammonia, as this signal is absent in the spectrum of the deuterated complex, *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(ND_3)][BPh_4] (**4′**), prepared by action of ND_3 gas on **2**.

Complex **3** also reacts readily with ammonia gas at room temperature to form *cis*-[Rh(BA)(PPh_3)$_2$-(CH_3)(NH_3)][BPh_4] (**5**). The obtained compound was characterized by elemental analysis, $^{31}P\{^1H\}$ and ^1H NMR spectra. In its $^{31}P\{^1H\}$ NMR spectrum two sets of signals differing by intensity could be detected. Each of these sets represents two doublets of doublets (Table 2), which indicates that complex **5** is formed from **3** in two isomeric forms with non-equivalent phosphine ligands. Taking into account close values of $^{31}P\{^1H\}$ NMR spectroscopic parameters of the acetylacetonate and benzoylacetonate derivatives (Table 2) and the X-ray diffraction data for **4**, the acetylacetonate analog, we assign to these isomeric cations the following structures:



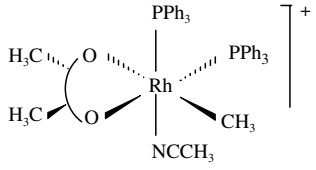
The ^1H NMR spectrum of complex **5** consists of three groups of signals. The region 6.8–7.8 ppm contains signals of phenyl protons. In the region of methine protons two singlets differing by intensity are present at δ 5.40 and 5.45 ppm, which correspond to two isomers of **5**. In the region 0–2.1 ppm, signals of methyl groups and coordinated ammonia are present. Signals at δ 1.42 and 1.47 ppm are broadened and exhibit a complex splitting. Therefore, we assign them to methyl ligands, CH_3(–Rh), in two isomers of **5**. Signals at δ 1.82 and 2.06 ppm belong to methyl groups of benzoylacetonate ligands in these two isomers. Signal at δ 0.32 ppm should be assigned to ligand NH_3, as this signal is absent in the complex containing deuterated ammonia. It is to be noted that the position of this signal is identical for both isomers of the complex **5**. A reduction of temperature to −50 °C produces no essential changes in the $^{31}P\{^1H\}$ and ^1H NMR spectra of complexes **4** and **5**, except for some shifts of the ^1H signals of the methyl ligand, CH_3(–Rh), and of the coordinated ammonia (Tables 2 and 3).

*2.4. Discussion of structure of minor forms of complexes cis-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**) and cis-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**3**)*

As mentioned above, at −50 °C the $^{31}P\{^1H\}$ NMR spectrum of complex **2** in $CDCl_3$, alongside with the doublet from the octahedral *cis*-(PPh_3)$_2$ complex, **2a**, with equivalent phosphines, contains two doublets of doublets from other *cis*-(PPh_3)$_2$ moiety, **2b**, with non-equivalent phosphines. The coexisting forms of complex **2** at room temperature are in the dynamic exchange:

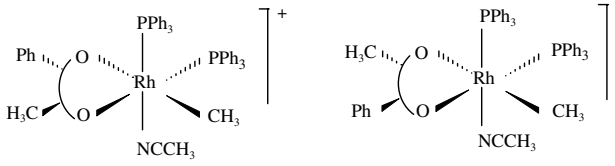
2a ⇄ **2b**

It is reasonable to assume that the dynamic rearrangement of ligands takes place within the fluxional pentacoordinate moiety formed by dissociation of acetonitrile from the cation **2a**, in which acetonitrile is subjected to strong trans effect of methyl ligand. Several geometries are compatible with the low-temperature NMR data for **2b**, namely two octahedral isomers and three pentacoordinate structures formed by acetonitrile dissociation. We suppose that in the reaction with ammonia are involved forms, in which the mutual arrangement of phosphine ligands is fitted well to the final geometry of ammonia complex, and tentatively depict below the structure for **2b** akin to the structure of the ammonia complex **4**, i.e., as an isomer of **2a**:



2b

Likewise, we depict structures of two minor moieties, **3b** and **3b′**, presented in the solutions of **3** as the minor isomers of the octahedral cation **3a**:



3b **3b'**

*2.5. Some reactions of the complex cis-[Rh(Acac)-(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**)*

As seen from above data, complexes **2** and **3** in solutions are present in *cis*-(PPh_3)$_2$ forms, and action of ammonia resulted in the formation of *cis*-(PPh_3)$_2$ complexes with one equatorial and one axial phosphine. Below we will consider two reactions in which complex of the *trans*-(PPh_3)$_2$ type is formed with both phosphines in the axial positions.

*2.5.1. Isomerization of cis-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)(CH$_3$CN)][BPh$_4$] (**2**) into trans-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)(CH$_3$CN)][BPh$_4$] (**1**)*

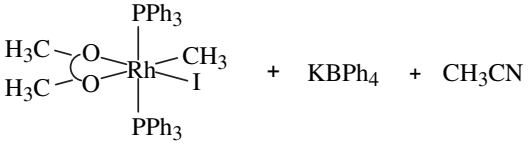
On heating complex **2** in acetonitrile at 75 °C the solution changes its color from light yellow to orange. In the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$ solvent) of the solid isolated from the reaction mixture, the following signals are present: broadened doublet at $\delta \sim 31$ ppm with $^1J(RhP) \sim 140$ Hz, intense sharp doublet at δ 21.2 ppm with $^1J(RhP)$ 99.6 Hz, and intense singlet at δ 22.2 ppm. The obvious assignment of these signals is as follows. The sharp doublet at δ 21.2 ppm, $^1J(RhP)$ 99.6 Hz belongs to the *trans*-bisphosphine complex **1** produced by isomerization of the complex **2**; the doublet with broadened lines centered at $\delta \sim 31$ ppm belongs to the unreacted complex **2**. The unexpectedly appeared singlet at δ 22.2 ppm corresponds to the salt $[CH_3PPh_3][BPh_4]$, which is confirmed by NMR spectra of the authentic sample prepared for this purpose [17]. Formation of the methyltriphenylphosphonium salt is evidence that, in parallel with isomerization of **2** into **1**, cleavage of the Rh–CH_3 bond takes place. This reductive elimination reaction must generate some rhodium(I) complex, but we failed to detect any. Comparison of integral intensities of ^{31}P signals corresponding to the complex **1** and to the salt $[CH_3PPh_3][BPh_4]$ indicated that comparable amounts of the initial complex **2** undergo isomerization and reductive elimination. The following scheme represents tentatively this observation:

$$\{\mathbf{2a} \rightleftarrows \mathbf{2b}\} \xrightarrow[CH_3CN]{+75\,^\circ C} \mathbf{1} + [CH_3PPh_3]^+BPh_4^- + \text{“Rh (I)”}$$

*2.5.2. Interaction of cis-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)(CH$_3$CN)][BPh$_4$] (**2**) with KI*

When stirring complex **2** with KI in acetone at room temperature, formation of an orange crystalline solid is observed. After separation from $KBPh_4$, the orange product was characterized by elemental analysis, $^{31}P\{^1H\}$ and ^1H NMR spectra and thus identified as the neutral octahedral complex *trans*-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)I]. The quantitative conversion of the initial complex takes 30–40 min.

$$\{\ \mathbf{2a} \rightleftharpoons \mathbf{2b}\ \} + KI \xrightarrow[acetone]{+20^\circ C}$$



$+ KBPh_4 + CH_3CN$

The following peculiarities of this reaction draw attention: (i) The product of acetonitrile substitution for anion I^- in the coordination sphere of the *cis*-$(PPh_3)_2$ cation **2** is the neutral *trans*-$(PPh_3)_2$ complex, i.e., the substitution is accompanied by a rearrangement of phosphine ligands. (ii) The *trans*-$(PPh_3)_2$ neutral complex is formed from the *cis*-$(PPh_3)_2$ cation **2** much more readily than from the structurally related *trans*-$(PPh_3)_2$ cation **1** which reacts with KI only at heating. In these facts, like in the dynamic behavior of **2**, the lability of acetonitrile ligand in the *trans*-position to methyl ligand makes itself evident.

3. Concluding remarks

In this work, we have synthesized, isolated as tetraphenylborate salts, and characterized stable methyl cationic rhodium(III) complexes in two isomeric octahedral forms, *trans*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ with β-diket = acetylacetonate and *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ with β-diket = acetylacetonate and benzoylacetonate groups. The *trans*-$(PPh_3)_2$ isomer containing two axial phosphines retains its geometry in solution and is kinetically inert. By contrast, *cis*-$(PPh_3)_2$ isomers containing two equatorial phosphines are remarkably labile. On dissolution, these *cis*-$(PPh_3)_2$ isomers undergo partial transformation with transfer of one PPh_3 ligand from an equatorial to an axial position. That transfer presumably takes place within pentacoordinate species resulting from CH_3CN dissociation. The pentacoordinate species and octahedral minor *cis*-$(PPh_3)_2$ isomers are involved into a dynamic structural exchange with initial major isomers. It seems likely that the main reason of the readiness of the major *cis*-$(PPh_3)_2$ isomers to generate these minor moieties is lability of CH_3CN ligand, which is subjected to the strong *trans* effect of methyl ligand.

CH_3CN ligand in *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)]^+$ cations is readily and quantitatively replaced by NH_3 or I^- even at ambient temperature. It is noticeable that the positions of PPh_3 ligands in the resultant complexes differ from their positions in the starting complexes. The ammonia complexes contain one equatorial and one axial phosphine ligand, whereas the action of I^- yields the neutral complexes *trans*-[Rh(β-diket)$(PPh_3)_2(CH_3)I]$ with two axial *trans* disposed phosphines.

Stable methyl cationic *cis*-$(PPh_3)_2$ complexes with two equatorial phosphines have been synthesized by methyl iodide oxidative addition to rhodium(I) planar complexes [Rh(β-diket)$(PPh_3)_2]$ in acetonitrile solutions in the presence of $NaBPh_4$. The credible speculation is that the unstable cationic intermediates, which retain the initial *cis*-$(PPh_3)_2$ arrangement of phosphine ligands, could be formed at the primary stages of methyl iodide oxidative addition to [Rh(β-diket)$(PPh_3)_2]$ complexes also in less coordinating solvents.

4. Experimental

4.1. Preparation of complexes

All operations were performed under an atmosphere of dry argon. Rhodium complexes $[Rh(Acac)(PPh_3)_2]$, $[Rh(BA)(PPh_3)_2]$, $[Rh(Acac)(PPh_3)_2(CH_3)I]$ were synthesized by published procedures [4,18]. Gaseous NH_3 and ND_3 were prepared by standard methods [19]. Solvents were dried and purified by known procedures [14] and distilled under argon. Methyl iodide was always used as freshly distilled samples. Elemental analyses were performed with Hewlett–Packard 185 microanalyzer. The analytical data for complexes **1**–**5** are presented in Table 5.

4.1.1. Preparation of $[Rh(Acac)(PPh_3)_2(CD_3)I]$

Product was prepared by a modified literature procedure [4]. To a suspension of $[Rh(Acac)(PPh_3)_2]$ (0.30 g, 0.41 mmol) in toluene (10 ml) was added excess of CD_3I (0.20 ml). Reaction mixture was stirred at ambient temperature for 30 min. The solvent was removed in vacuo. Recrystallization from benzene/hexane provided orange fine crystals of $[Rh(Acac)(PPh_3)_2(CD_3)I]$. Yield: 0.34 g (95%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.1 ppm, $^1J(RhP) = 106.1$ Hz. ^1H NMR ($CDCl_3$): δ 7.8–7.2 ppm (m, $2PPh_3$), 4.26 ppm (s, 1H, CH), 1.51 and 0.94 ppm (both s, 6H, CH_3 of Acac).

4.1.2. Preparation of trans-$[Rh(Acac)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ (**1**)

To a suspension of $NaBPh_4$ (0.10 g, 0.29 mmol) and $AgNO_3$ (0.05 g, 0.29 mmol) in acetonitrile (15 ml) was added a suspension of $[Rh(Acac)(PPh_3)_2(CH_3)I]$ (0.22 g, 0.26 mmol) in acetone (10 ml). The reaction mixture was stirred at ambient temperature until complete exhaustion of orange starting rhodium complex ($\sim$2 h). The reaction mixture was filtered, and solvent was removed from yellow filtrate in vacuo. Chloroform (10 ml) was added to yellow solid yielding a yellow solution containing very fine light precipitate. The precipitate was filtered off, and solvent was removed from filtrate under reduced pressure. Acetonitrile (10 ml) was added to yellow solid formed. Solution was filtered, and solvent was removed in vacuo. Recrystallization from acetonitrile provided yellow crystals of **1** as CH_3CN 1:1 solvate. Yield: 0.22 g (74%).

4.1.3. Preparation of trans-$[Rh(Acac)(PPh_3)_2(CH_3)(CD_3CN)][BPh_4]$ (**1′**)

The complex was prepared analogously to **1** from $[Rh(Acac)(PPh_3)_2(CH_3)I]$ (0.30 g, 0.34 mmol) using CD_3CN as solvent. Yield: 0.27 g (69%).

4.1.4. Preparation of trans-$[Rh(Acac)(PPh_3)_2(CD_3)(CH_3CN)][BPh_4]$ (**1″**)

The complex was prepared using the procedure described for **1** starting from $[Rh(Acac)(PPh_3)_2(CD_3)I]$ (0.36 g, 0.41 mmol). Yield: 0.29 g (62%).

4.1.5. Preparation of cis-$[Rh(Acac)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ (**2**)

To a suspension of $[Rh(Acac)(PPh_3)_2]$ (0.49 g, 0.67 mmol) and $NaBPh_4$ (0.47 g, 1.37 mmol) in acetonitrile (15 ml) was added methyl iodide (0.13 ml, 2.09 mmol) at 5 °C. The resulting reaction mixture was stirred for 1 h at 10 °C. A yellow fine crystalline precipitate was isolated by filtration, washed twice with acetonitrile (5 ml) and dried in vacuo. Recrystallization from methylene chloride/diethyl ether provided yellow crystals of **2** as CH_2Cl_2 0.5:1 solvate. Yield: 0.67 g (87%).

4.1.6. Preparation of cis-$[Rh(Acac)(PPh_3)_2(CD_3)(CH_3CN)][BPh_4]$ (**2′**)

The complex was prepared using the procedure described for **2**, starting from $[Rh(Acac)(PPh_3)_2]$ (0.51 g, 0.70 mmol), $NaBPh_4$ (0.47 g, 1.37 mmol) and CD_3I (0.13 ml, 2.09 mmol). Yield: 0.49 g (61%).

4.1.7. Preparation of cis-$[Rh(BA)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ (**3**)

The complex was prepared analogously to **2** from $[Rh(BA)(PPh_3)_2]$ (0.50 g, 0.63 mmol), $NaBPh_4$ (0.76 g, 2.22 mmol) and methyl iodide (0.12 ml, 1.93 mmol) in acetonitrile (15 ml). Recrystallization from methylene chloride/diethyl ether provided yellow crystals of **3** as $(C_2H_5)_2O$ 1:1 solvate. Yield: 0.70 g (90%).

Table 5
Analytical data for complexes **1**, **2**, **3**, **4**, and **5**

Compound	Molecular formula	Color	Analyses, found (%) (calc. (%))	
			C	H
1	$[Rh(Acac)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]\cdot CH_3CN$	Yellow	74.08 (73.58)	6.18 (5.82)
2	$[Rh(Acac)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]\cdot 1/2CH_2Cl_2$	Yellow	71.83 (71.89)	5.53 (5.64)
3	$[Rh(BA)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]\cdot (C_2H_5)_2O$	Yellow	74.70 (74.70)	6.08 (6.10)
4	$[Rh(Acac)(PPh_3)_2(CH_3)(NH_3)][BPh_4]$	Yellow	73.56 (73.54)	5.89 (5.89)
5	$[Rh(BA)(PPh_3)_2(CH_3)(NH_3)][BPh_4]$	Yellow	74.75 (74.80)	5.87 (5.75)

*4.1.8. Preparation of cis-[Rh(BA)(PPh_3)$_2$(CD_3)(CH_3CN)][BPh_4] (**3′**)*

The complex was prepared using the procedure described for **2**, starting from [Rh(BA)(PPh_3)$_2$] (0.50 g, 0.63 mmol), $NaBPh_4$ (0.43 g, 1.26 mmol) and CD_3I (0.13 ml) in acetonitrile (20 ml). Yield: 0.60 g (77%).

*4.1.9. Preparation of cis-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**4**)*

A stream of gaseous NH_3 was passed through a suspension of complex **2** (0.81 g, 0.71 mmol) in acetonitrile (10 ml) for 30 min at room temperature. Within 10 min the initial complex was completely dissolved to yield pale yellow solution. Then yellow crystals began to precipitate. Crystalline precipitate was isolated by filtration, washed with acetonitrile and dried in vacuo. Recrystallization from methylene chloride/diethyl ether provided yellow crystals of **4**. Yield: 0.51 g (67%).

*4.1.10. Preparation of cis-[Rh(Acac)(PPh_3)$_2$(CH_3)(ND_3)][BPh_4] (**4′**)*

The complex **4′** was prepared using the procedure described for **4**, starting from complex **2** (0.31 g, 0.27 mmol) and ND_3. Yield: 0.20 g (69%).

*4.1.11. Preparation of cis-[Rh(BA)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**5**)*

A stream of gaseous NH_3 was passed through a suspension of complex **3** (0.075 g, 0.060 mmol) in acetonitrile (2 ml) for 15 min at room temperature. The initial complex was completely dissolved to yield pale yellow solution. The reaction mixture was filtered, and acetonitrile was removed in vacuo. The oily residue turned into crystalline product on cooling in refrigerator. Yield: 0.065 g (95%).

*4.1.12. Preparation of cis-[Rh(BA)(PPh_3)$_2$(CH_3)(ND_3)][BPh_4] (**5′**)*

The complex was prepared analogously to **5** from complex **3** (0.33 g, 0.27 mmol) and ND_3. Yield: 0.29 g (97%).

4.1.13. Preparation of [CH_3PPh_3][BPh_4]

Product was prepared by modifying a literature procedure [17]. To a solution of triphenylphosphine (1.0 g, 3.80 mmol) in methylene chloride (5 ml) was added methyl iodide (0.5 ml, 7.6 mmol). Reaction mixture was stirred at ambient temperature for 10 min. A solvent was removed in vacuo. The white solid thus obtained was mixed with $NaBPh_4$ (1.41 g, 4.10 mmol) and methanol (20 ml) yielding a white fine crystalline product. The precipitate was isolated by filtration, washed twice with methanol (5 ml) and dried in vacuo. Yield: 1.86 g (82%). Found: C = 86.58, H = 6.48%. $C_{43}H_{38}PB$ requires C = 86.57, H = 6.42%. Melting point (m.p.) 197.0 °C (197.0 °C [17]). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.2 ppm. ^1H NMR ($CDCl_3$): δ 7.8–6.7 ppm (m, PPh_3, BPh_4), 1.37 ppm (d, 3H, CH_3), ^2J(H–P) 12.8 Hz.

*4.1.14. The reaction of trans-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**1**) with KI in acetone*

Mixture of **1** (0.04 g, 0.03 mmol), KI (0.02 g, 0.11 mmol) and acetone (1 ml) was stirred for 1.5 h at 40 °C. The initial yellow suspension turned orange. Then acetone was removed in vacuo. Toluene (10 ml) was added to dry orange solid. Solution was filtered, and the filtrate was concentrated to ca. 0.5 ml in vacuo; addition of hexane (5 ml) led to the precipitation of orange solid. The solvent was decanted, and the residue was washed with hexane (2 ml) and dried in vacuo. Yield: 0.026 g (96%). Found: C = 57.98, H = 4.73%. $RhC_{42}H_{40}P_2O_2I$ requires C = 58.08, H = 4.64%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.1 ppm, ^1J(RhP) = 106.1 Hz. ^1H NMR ($CDCl_3$): δ 7.8–7.2 ppm (m, 2PPh_3), 4.26 ppm (s, 1H, CH), 1.51 and 0.94 ppm (both s, 6H, CH_3 of Acac), 1.40 ppm (td, 3H, Rh–CH_3), ^2J(H–Rh) = 2.1 Hz, ^3J(H–P) = 5.7 Hz. $^{31}P\{^1H\}$ and ^1H NMR spectral characteristics of the resulted product agree well with those of *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] [4].

*4.1.15. The reaction of cis-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**) with KI in acetone*

Mixture of complex **2** (0.09 g, 0.08 mmol), KI (0.02 g, 0.11 mmol) and acetone (1 ml) was stirred at ambient temperature for 40 min. The initial yellow suspension turned orange. Acetone was removed in vacuo. Methylene chloride (5 ml) was added to dry orange solid. Solution was filtered, and solvent was removed from filtrate in vacuo. Yield: 0.06 g (90%). Found: C = 58.31, H = 4.88%. $RhC_{42}H_{40}P_2O_2I$ requires C = 58.08, H = 4.64%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.1 ppm, ^1J(RhP) = 106.1 Hz. ^1H NMR ($CDCl_3$): δ 7.8–7.2 ppm (m, 2PPh_3), 4.26 ppm (s, 1H, CH), 1.51 and 0.94 ppm (both s, 6H, CH_3 of Acac), 1.41 ppm (td, 3H, Rh–CH_3), ^2J(H–Rh) = 2.1 Hz, ^3J(H–P) = 5.7 Hz. $^{31}P\{^1H\}$ and ^1H NMR spectral characteristics of the resulted product agree well with those of [Rh(Acac)*trans*-(PPh_3)$_2$(CH_3)I] [4].

*4.1.16. Heating of cis-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**2**) in acetonitrile*

Complex **2** (0.2 g, 0.17 mmol) in acetonitrile (4 ml) was heated up to 75 °C for 30 min. Complex **2** was fully dissolved at 60 °C. Then the pale yellow solution turned orange. Acetonitrile was removed in vacuo. The orange solid thus obtained was characterized by $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): broadened doublet at $\delta \sim 31$ ppm with ^1J(RhP) $\sim$ 140 Hz from unreacted complex **2**, singlet at 22.2 ppm from [CH_3PPh_3][BPh_4], doublet at 21.2 ppm, ^1J(Rh–P) 99.6 Hz, from complex **1**.

Table 6
Crystallographic data for complexes **1**, **2**, **3**, and **4**

	1·CH_3CN	**2**·$1/2CH_2Cl_2$	**3**·$C_4H_{10}O$	**4**
Molecular formula	$C_{70}H_{66}BN_2O_2P_2Rh$	$C_{68}H_{63}BNO_2P_2Rh \cdot 1/2CH_2Cl_2$	$C_{77}H_{75}BNO_3P_2Rh$	$RhC_{66}H_{63}BNO_2P_2$
Formula weight	1142.91	1144.32	1238.04	1077.83
T (K)	110(2)	110(2)	120(2)	115(2)
Radiation, λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*Pbcn*	$C2/c$	$P2_1/c$
Color, shape	Colorless, plate	Yellow, prism	Yellow, prism	Yellow, prism
a (Å)	9.780(2)	19.522(4)	51.481(5)	16.6550(18)
b (Å)	15.919(3)	19.313(3)	9.8086(16)	16.8739(18)
c (Å)	19.496(5)	30.305(4)	30.539(5)	20.568(2)
α (°)	101.899(7)	90	90	90
β (°)	96.078(5)	90	121.861(3)	109.934(2)
γ (°)	99.853(6)	90	90	90
V (Å^3)	2894.8(11)	11426(3)	13097(3)	5434.1(10)
Z	2	8	8	4
γ_{calc} (g cm^{-3})	1.311	1.330	1.256	1.317
Linear absorption, μ (cm^{-1})	3.98	4.49	3.58	4.20
$F(000)$	1192	4760	5184	2248
Dimension (mm×mm×mm)	0.20×0.10×0.03	0.30×0.20×0.10	0.30×0.10×0.10	0.30×0.20×0.10
Diffractometer	SMART CCD 1000	SMART CCD 1000	SMART CCD 1000	SMART CCD 1000
Scan type	φ and ω	φ and ω	φ and ω	φ and ω
θ range (°)	1.90–27.60	1.70–29.30	1.69–28.02	1.82–30.04
Measured reflections (R_{int})	17 852 (0.1224)	117 258 (0.0759)	59 344 (0.0526)	64 493 (0.0458)
Unique reflections	12 609	15 093	15 705	15 844
Reflections with $I > 2\sigma(I)$	3075	9378	9735	11 400
Parameters	588	944	784	658
Final $R(F_{hkl})$: R_1 [$I > 2\sigma(I)$]	0.07520	0.0516	0.0540	0.0588
Final $R_w(F^2_{hkl})$: wR_2 [all data]	0.1810	0.1194	0.1247	0.1358
Goodness-of-fit	0.64	1.061	1.000	1.003
ρ_{max}/ρ_{min} (e Å^{-3})	1.476/−1.061	1.335/−0.593	1.678/−0.533	2.341/−1.001

4.2. X-ray analysis

The X-ray diffraction data were collected on Bruker SMART CCD 1000 diffractometer (λ(Mo Kα)-radiation, graphite monochromator, φ and θ scan mode) and corrected for Lorentz and polarization effects and for absorption [20]; details are given in Table 6.

The structure were solved by direct methods and refined by full-matrix least-squares in the anisotropic–isotropic approximation. The crystal of complex **3** contains a solvate diethyl ether molecules which are disordered over two sites with occupancies 0.6 and 0.4, respectively. The hydrogen atoms of all compounds were placed in calculated positions and refined in riding model with fixed thermal parameters ($U_{iso}(H) = 1.5U_{eq}(C)$ for the CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other groups). All calculations were carried out by use of the SHELXTL (PC Version 5.10) program package [21].

4.3. NMR measurements

NMR spectra were measured in deuterochloroform solutions on Bruker AM-300 spectrometer operating in the Fourier-transform mode with noise proton decoupling for ^{31}P. The ^1H chemical shifts were measured with solvent residual proton as internal standard, δ $^1H = 7.25$ ppm. The ^{31}P chemical shifts were measured with 85% phosphoric acid as external standard, δ ^{31}P 0.0 ppm.

5. Supporting information available

Tables of atom coordinates, bond lengths and angles, torsion angles and anisotropic displacement parameters for **1**, **2**, **3** and **4**: CCDC Nos. 225212, 225213, 225214, 225215, respectively. Ordering information is given on any current masthead page.

Acknowledgements

We thank Prof. Brian T. Heaton for valuable discussion that stimulated us to carry out this study. X-ray studies (A.A.K., K.A.L., and V.N.Kh.) were financially supported by the Russian Foundation for Basic Research (Projects Nos. 00-03-32807a and 00-15-97359). We also thank Dr. N.G. Antonov and Dr. S.N. Smirnov for NMR measurements. Financial support from the Russian Federation Ministry of Education (''Universi-

ties of Russia'' Program, UR.05.01.032) is gratefully acknowledged.

References

[1] A.J. Hart-Davis, W.A.G. Graham, Inorg. Chem. 9 (1970) 2658.
[2] (a) S.S. Basson, J.G. Leipoldt, A. Roodt, J.A. Venter, T.J. Van Der Walt, Inorg. Chim. Acta 119 (1986) 35;
(b) G.J. Van Zyl, G.J. Lamprecht, J.G. Leipoldt, Inorg. Chim. Acta 43 (1988) 223;
(c) J.G. Leipoldt, S.S. Basson, L.J. Botha, Inorg. Chim. Acta 168 (1990) 215;
(d) J.A. Venter, J.G. Leipoldt, R. Van Eldik, Inorg. Chem. 30 (1991) 2207.
[3] (a) T. Kinnunen, K. Laasonen, J. Organomet. Chem. 542 (2001) 273;
(b) T. Kinnunen, K. Laasonen, J. Organomet. Chem. 665 (2003) 150.
[4] E.P. Shestakova, T.G. Cherkasova, L.V. Osetrova, Yu.S. Varshavsky, J.G. Leipoldt, A. Roodt, Rhodium Express 7–8 (1994) 24.
[5] A. Roodt, J.M. Botha, S. Otto, E.P. Shestakova, Yu.S. Varshavsky, Rhodium Express 17 (1994) 4.
[6] E.P. Shestakova, T.G. Cherkasova, L.V. Osetrova, Yu.S. Varshavsky, J.G. Leipoldt, A. Roodt, Rhodium Express 7–8 (1994) 30.
[7] J.W. Kang, P.M. Maitlis, J. Organomet. Chem. 26 (1971) 393.
[8] A.J. Oliver, W.A.G. Graham, Inorg. Chem. 9 (1970) 243.
[9] J.W. Suggs, J. Am. Chem. Soc. 100 (1978) 640.
[10] R.F. Jordan, W.E. Dasher, S.F. Echols, J. Am. Chem. Soc. 108 (1986) 1718.
[11] E.P. Shestakova, Yu.S. Varshavsky, A.A. Korlyukov, N.G. Antonov, A.B. Nikol'skii, Abstr. 20th International Chugaev Conference on Co-ordination Chemistry, Rostov-on-Don, 2001, p. 507.
[12] E.P. Shestakova, Yu.S. Varshavsky, V.N. Khrustalev, K.A. Lyssenko, M.V. Andreeva, A.B. Nikol'skii, 21th International Chugaev Conference on Co-ordination Chemistry, Kiev, 2003, p. 150.
[13] S.S. Basson, J.G. Leipoldt, I.M. Potgieter, A. Roodt, T.J. Van Der Walt, Inorg. Chim. Acta 119 (1986) L9.
[14] A.J. Gordon, R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, Wiley, New York, 1972.
[15] G.J. Van Zyl, G.J. Lamprecht, J.G. Leipoldt, Inorg. Chim. Acta 122 (1986) 75.
[16] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[17] L. Naldini, Gazz. Chim. Ital. 90 (1960) 1231.
[18] E.P. Shestakova, T.G. Cherkasova, I.S. Podkorytov, Yu.S. Varshavsky, Rhodium Express 7–8 (1994) 17.
[19] Yu.V. Karjakin, I.I. Angelov, Chistie Khimicheskie Veshchestva (Pure Chemical Substances), Khimija, Moscow, 1974.
[20] SMART and SAINT: Release 5.0. Area detector control and integration software. Bruker AXS, Analytical X-Ray Instruments, Madison, Wisconsin, USA, 1998.
[21] G.M. Sheldrick, SHELXTL: V5.10, Bruker AXS Inc., Madison, WI-53719, USA, 1997.