Journal of Organometallic Chemistry 696 (2011) 3214–3222

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Trifluoroacetylacetonate rhodium(III) methyl complexes, *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(L)][BPh_4] and *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(I)] (L = CH_3CN, NH_3, pyridine), in comparison with their acetylacetonate analogs

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ARTICLE INFO

Article history:
Received 18 May 2011
Received in revised form
21 June 2011
Accepted 28 June 2011

Keywords:
Rhodium(III) methyl complexes
β-Diketonates
Oxidative addition
NMR
X-ray

ABSTRACT

The oxidative addition of CH_3I to planar rhodium(I) complex [Rh(TFA)(PPh_3)$_2$] in acetonitrile (TFA is trifluoroacetylacetonate) leads to the formation of cationic, *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**1**), or neutral, *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(I)] (**4**), rhodium(III) methyl complexes depending on the reaction conditions. **1** reacts readily with NH_3 and pyridine to form cationic complexes, *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**2**) and *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(Py)][BPh_4] (**3**), respectively. Acetylacetonate methyl complex of rhodium(III), *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(I)] (**5**), was obtained by the action of NaI on *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] in acetone at −15 °C. Complexes **1**–**5** were characterized by elemental analysis, $^{31}P\{^1H\}$, ^1H and ^{19}F NMR. For complexes **2**, **3**, **4** conductivity data in acetone solutions are reported. The crystal structures of **2** and **3** were determined. NMR parameters of **1**–**5** and related complexes are discussed from the viewpoint of their isomerism.

1. Introduction

The oxidative addition of methyl iodide to planar rhodium(I) complexes attracts wide and persistent attention ([1–10] and references therein), being a simple and adequate model of one of the key stages of important catalytic processes. Published works are concerned mainly with rhodium(I) complexes containing carbonyl ligand. In our research, we focused on reactions of the methyl iodide oxidative additions to the non-carbonyl complexes of general formula [Rh(β-diket)(PPh_3)$_2$]. These reactions are not complicated by subsequent conversions, such as elimination or migratory insertion of ligands. We have studied earlier some of these reactions in acetonitrile [11] and in an aromatic solvent (benzene) [12]. In acetonitrile, the reactions of [Rh(Acac)(PPh_3)$_2$] or [Rh(BA)(PPh_3)$_2$] in the presence of anion $[BPh_4]^-$ yielded salts of cationic rhodium(III) methyl complexes, *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] and *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (Acac and BA are acetylacetonate and benzoylacetonate ligands, respectively). These well-defined complexes may be considered stable analogs to unstable ionic intermediates $[L_nRh(CH_3)]^+[I]^-$, which are generally observed or assumed as products of the initial step of the CH_3I oxidative addition to rhodium(I) complexes [1,8,13–17]. In benzene at room temperature, the final products are octahedral neutral rhodium(III) methyl complexes with mutual *trans* arrangement of two phosphine ligands, *trans*-[Rh(β-diket)(PPh_3)$_2$(CH_3)(I)] (β-diket is acetylacetonate, trifluoroacetylacetonate, hexafluoroacetylacetonate) [12]. We have detected the formation of intermediates in the course of these reactions by ^{31}P NMR [18]. Though we did not isolate these intermediates, our ^{31}P NMR data showed distinctly that electronegativity of substituents in the β-diketonate ligand influences the structure of intermediates in solutions. It is known also that electronegativity of the β-diketonate ligand in rhodium(I) complexes affects the reaction rate of the methyl iodide oxidative addition [16,19]. These facts motivated us to scrutinize the differences between species formed in the course of interaction of two complexes, [Rh(Acac)(PPh_3)$_2$] and [Rh(TFA)(PPh_3)$_2$], with methyl iodide. In the present paper we report on the preparation and structural characterization of

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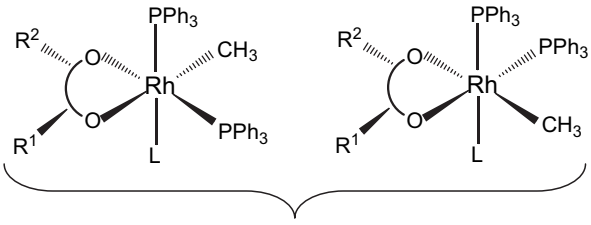
doi:10.1016/j.jorganchem.2011.06.035

rhodium(III) cationic complexes, *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(L)][BPh_4] (L is CH_3CN, NH_3, pyridine), and neutral complexes, *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)I] and *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)I], and consider these data against the background of our previous results.

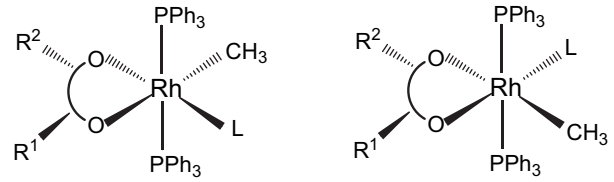
2. Results and discussion

2.1. Precursory remarks

Because a variety of geometrical isomers of the octahedral bisphosphine complexes will appear in the consideration below, we think it expedient to introduce short notations for the specific positions of ligands in the complexes under discussion. For this purpose we conventionally adopt the RhOO plane as equatorial one, and thus denote two ligands coplanar with the β-diketonate ligand as equatorial ones, L_{eq}, whereas two ligands lying on the axis perpendicular to this plane as axial ones, L_{ax}. Thus, in the case of symmetrical β-diketonate ligand ($R^1 = R^2$), four isomers of [Rh(β-diket)(PPh_3)$_2$(CH_3)(L)] are conceivable (cationic if L is a neutral ligand or neutral if it is an anionic ligand):

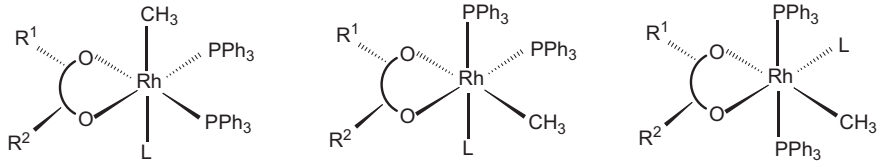


cis isomers (P_{eq} P_{ax})

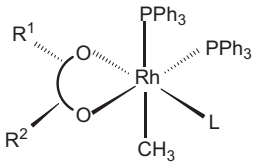


trans-isomers (P_{ax} P_{ax})

cis-isomers *trans*-isomer



(P_{eq} P_{eq}) (P_{eq} P_{ax}) (P_{ax} P_{ax})

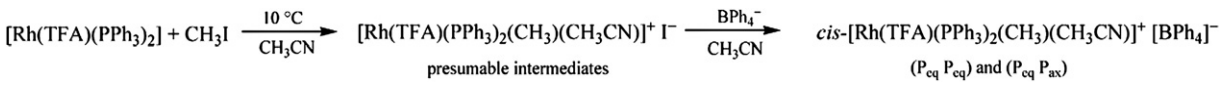


(P_{eq} P_{ax})'

To our knowledge isomers of octahedral Rh(III) complexes containing phosphine in *trans*-position to methyl ligand, i.e. those of (P_{eq} P_{ax})′ type, have not been described except a rather peculiar example [8]. In our previous studies only one type of (P_{eq} P_{ax}) isomers was observed [11,20], namely isomers with two triphenylphosphines and CH_3 ligands lying in mutual *cis* position. In the case of unsymmetrically substituted β-diketonate ligand ($R^1 \neq R^2$), along with this kind of isomerism based on the mutual arrangement of two phosphine ligands, one more kind of isomerism appears. Due to the inequivalence of two equatorial positions, each of the isomers, except the (P_{eq} P_{eq}) isomer, can exist in two isomeric forms, which differ from each other by mutual disposition of the equatorial ligands with respect to the substituents R^1 and R^2 in the β-diketonate ligand:

2.2. Synthesis and characterization of *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**1**)

Previously [11] we have prepared cationic β-diketonate rhodium(III) methyl complexes, *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] and *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (Acac, BA are acetylacetonate and benzoylacetonate ligands), by the CH_3I oxidative addition to the respective rhodium(I) complexes, [Rh(β-diket)(PPh_3)$_2$], in the presence of $NaBPh_4$ in acetonitrile as a solvent. However in attempting to prepare the TFA complex of this type by a similar procedure, we encountered the unexpected fact that [Rh(TFA)(PPh_3)$_2$] immediately reacted with $NaBPh_4$ to produce the known rhodium(I) complex containing the coordinated phenyl ring of anion $[BPh_4]^-$, [Rh(PPh_3)$_2$(π-*Ph*BPh_3)]. We



Scheme 1.

have described this new reaction, i.e. the replacement of the β-diketonate ligand by the $[BPh_4]^-$ anion, in [21]. In the present work, we succeeded in preparation of cationic methyl complex *cis*-$[Rh(TFA)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ (**1**) by partitioning the procedure into two consecutive stages. In the first stage, the oxidative addition of CH_3I to $[Rh(TFA)(PPh_3)_2]$ in acetonitrile at +10 °C was carried out in the absence of $NaBPh_4$. During the course of the reaction we observed the conversion of the initial suspension into a clear yellow-orange solution. There is a reason to believe that cationic methyl complex with iodide counter-ion, $[Rh(TFA)(PPh_3)_2(CH_3)(CH_3CN)]^+$ $[I]^-$, was formed in this stage. Then, in the second stage, an excess of $NaBPh_4$ was added to the solution. Complex **1,** in contrast to the related Acac complex *cis*-$[Rh(Acac)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$, is highly soluble in acetonitrile, and thus its isolation required rather complicated manipulations (see Section 4; Scheme 1).

Complex **1** was characterized by elemental analysis and $^{31}P\{^1H\}$, ^1H and ^{19}F NMR spectra. The NMR spectra of **1** are temperature-dependent. At room temperature, the ^{31}P NMR spectrum of **1** in $CDCl_3$ solution shows a very broad unresolved signal centered at ~28 ppm, while at −50 °C two sets of well-resolved intense signals are observed: two doublets of doublets centered at 30.7 and 29.6 ppm and two doublets of doublets centered at 27.0 and 24.7 ppm, the latter being partially overlapped with two low-intensity doublets of doublets centered at 27.3 and 25.0 ppm (Table 1).

This spectral pattern is rather close to that we observed earlier for *cis*-$[Rh(BA)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ under comparable conditions [11], and we interpret it in the same way. The first group of signals (32–29 ppm) in the spectrum of **1**, like the group of two doublets of doublets (32–28 ppm) in the spectrum of BA complex, belongs to the *cis*-isomer of (P_{eq} P_{eq}) structure. Phosphine ligands in these complexes are inequivalent due to asymmetry of the β-diketonate ligands, TFA or BA. The second intense doublet of doublets, together with the group of concomitant weak signals, seems to be the superimposed spectra of two *cis*-isomers of the other structural type, (P_{eq} P_{ax}), one of which is significantly predominant, whereas the second is present in small proportion.

It should be remarked that in the case of **1**, both spin-spin coupling constants, $^1J(PRh)$ and $^2J(PP)$, are higher for both (P_{eq} P_{ax}) isomers as compared to (P_{eq} P_{eq}) isomer (Table 1).

The ^1H NMR (−50 °C) spectrum of the mixture of three isomers of **1** is complicated due to superposition of signals, thus we succeeded in complete assignment of the proton signals only for the predominant (P_{eq} P_{ax}) isomer (Table 2).

The ^{19}F NMR spectrum of **1** at −50 °C exhibits three singlets which we assigned on the basis of their relative intensities to the three isomers: −71.76 ppm, major (P_{eq} P_{ax},); −70.25 ppm, minor (P_{eq} P_{ax},); −70.09 ppm, (P_{eq} P_{eq}) (Table 3).

2.3. Synthesis and characterization of cis-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)(NH$_3$)][BPh$_4$] (**2**) and cis-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)(Py)][BPh$_4$] (**3**)

Cationic methyl complexes, *cis*-$[Rh(TFA)(PPh_3)_2(CH_3)(NH_3)][BPh_4]$ (**2**) and *cis*-$[Rh(TFA)(PPh_3)_2(CH_3)(Py)][BPh_4]$ (**3**), have been prepared by the treatment of **1** in a methylene chloride solution at room temperature with ammonia gas or with excess pyridine,

Table 1
$^{31}P\{^1H\}$ NMR spectral parameters of methyl rhodium(III) complexes (solvent $CDCl_3$).

Complex	Isomer	T (°C)	δ, ppm/$^1J(PRh)$, Hz	$^2J(PP)$, Hz
cis-$[Rh(TFA)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$(**1**)	(P_{eq} P_{eq})	−50	30.7/128.9 29.6/125.3	28.8
	(P_{eq} P_{ax}) major		27.0/141.0 24.7/132.8	36.7
	(P_{eq} P_{ax}) minor		27.3/141.5 25.0/133.3	~40
cis-$[Rh(TFA)(PPh_3)_2(CH_3)(NH_3)][BPh_4]$ (**2**)	(P_{eq} P_{ax})[a] major	+20	27.5/138.3 23.0/126.7	35.2
cis-$[Rh(TFA)(PPh_3)_2(CH_3)Py][BPh_4]$ (**3**)	(P_{eq} P_{ax}) major	+20	24.4/139.2 20.5/127.1	35.7
	(P_{eq} P_{ax}) minor		24.4/139.0 20.8/127.4	35.8
cis-$[Rh(TFA)(PPh_3)_2(CH_3)I]$ (**4**)	(P_{eq} P_{eq}) (traces)	+20	36.0/150 30.7/139	28.0
	(P_{eq} P_{ax}) major		26.2/139.6 19.5/130.7	22.3
	(P_{eq} P_{ax}) minor		27.0/141 19.5/131	~20
trans-$[Rh(TFA)(PPh_3)_2(CH_3)I]$ [12]	(P_{ax} P_{ax}) major	+20	19.3/104.7	–
	(P_{ax} P_{ax}) minor		19.4/103.9	–
cis-$[Rh(Acac)(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ [11]	(P_{eq} P_{eq}) dominant (P_{eq} P_{ax})	−50	29.7/136 27.3/143.1 23.6/128.4	36.9
cis-$[Rh(Acac)(PPh_3)_2(CH_3)(NH_3)][BPh_4]$ [11]	(P_{eq} P_{ax})	+20	26.7/133.8 24.0/128.6	35.2
cis-$[Rh(Acac)(PPh_3)_2(CH_3)Py][BPh_4]$ [20]	(P_{eq} P_{ax})	+20	23.1/134.5 21.5/129.3	35.2
cis-$[Rh(Acac)(PPh_3)_2(CH_3)I]$ (**5**)	(P_{eq} P_{eq}) (P_{eq} P_{ax}) dominant	−30	30.2/137.7 25.8/134.7 20.7/134.8	– 23.0
trans-$[Rh(Acac)(PPh_3)_2(CH_3)I]$ [12]	(P_{ax} P_{ax})	+20	20.0/106.1	–

[a] ^{31}P signals of the minor isomer were not observed.

Table 2
Selected ^{1}H NMR spectral parameters of methyl rhodium(III) complexes (solvent $CDCl_3$).

Complex	Isomer	T (°C)	CH_3–Rh	CH_3 (β-diketonate)	CH (β-diketonate)
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4](**1**)[a]	(P_{eq} P_{ax}) major	−50	2.02	1.76	5.06
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**2**)[b]	(P_{eq} P_{ax}) major	+20	1.54	1.80	5.05
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)Py][BPh_4] (**3**)	(P_{eq} P_{ax}) major	+20	2.03	1.63	4.73
	(P_{eq} P_{ax}) minor		1.90	2.0	~4.73
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)I] (**4**)	(P_{eq} P_{ax}) major	+20	1.96	1.74	5.27
	(P_{eq} P_{ax}) minor		2.03	1.88	5.25
trans-[Rh(TFA)(PPh_3)$_2$(CH_3)I] [12]	(P_{ax} P_{ax}) major	+20	1.48	0.97	4.37
	(P_{ax} P_{ax}) minor		1.68	1.39	4.37
cis-[Rh(Acac)(PPh_3)$_2$(CH_3)I] (**5**)	(P_{eq} P_{eq})	−30	1.54	1.76	5.40
	(P_{eq} P_{ax})		1.73	1.93	4.96
				1.62	
trans-[Rh(Acac)(PPh_3)$_2$(CH_3)I] [12]	(P_{ax} P_{ax}) single	+20	1.39	1.49	4.25
				0.92	

[a] It was impossible to give a reliable assignment of ^{1}H resonances for (P_{eq} P_{eq}) and minor (P_{eq} P_{ax}) isomers of **1**, as well as for the (P_{eq} P_{eq}) isomer of **4** due to low intensity and/or overlapping of signals; δ^1H (CH_3CN) for **1** 0.02 ppm.
[b] δ^1H (NH_3) 0.1 ppm.

respectively. As isolation of pure **1** is very laborious, we used it without isolation from the above reaction mixture (see Section 2.2). Volatiles were removed from the reaction mixture, methylene chloride was added to the residue, and then the reaction with ammonia or pyridine was carried out (see Section 4). Pale-yellow crystals of **2** (yield 50%) and **3** (yield 76%) were crystallized in solvated forms, **2**·$(C_2H_5)_2O$ and **3**·0.75CH_2Cl_2, from the methylene chloride/diethyl ether solutions. Complexes **2** and **3** were characterized by elemental analysis, $^{31}P\{^1H\}$, ^{1}H and ^{19}F NMR spectra, conductivity of their acetone solutions, and X-ray diffraction data for their crystalline solvates.

The structures of complexes **2** and **3** are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Table 4. For comparison, the corresponding values for *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] from our previous work [11] are included.

The equatorial plane in every structure contains triphenylphosphine and methyl ligands, the latter occupying in **2** and **3** *trans* position to the CF_3 substituent. The second triphenylphosphine and N-donor ligand occupy axial positions, *trans* to each other. As may be seen from Table 4, complexes **2** and **3** are closely similar in their structure parameters to each other and also to the related Acac complex. The values of angles P(1)–Rh–O(1), P(1)–Rh–O(2), P(2)–Rh–N(1), O(1)–Rh–N(1), and O(2)–Rh–N(1) indicate that the structures of **2**, **3**, and *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] correspond to the same geometry of markedly distorted octahedron with the N-ligand deviating toward the β-diketonate ligand. An insignificant difference in the Rh–O(1) bond lengths in **2** and in the related Acac complex (2.172(4) Å and 2.152(2) Å, respectively) indicates that the CF_3-group affects the adjacent Rh–O(1) bond only slightly. The lengths of two Rh–O bonds in **2** and **3**, as well as in Acac complex, differ significantly due to the considerable difference in the *trans*-influence of the methyl and triphenylphosphine ligands.

Table 3
^{19}F NMR spectral parameters of methyl rhodium(III) complexes (solvent $CDCl_3$).

Complex	Isomer	T (°C)	δ, ppm
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4](**1**)	(P_{eq} P_{eq})	−50	−70.09
	(P_{eq} P_{ax}) major		−71.76
	(P_{eq} P_{ax}) minor		−70.25
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**2**)	(P_{eq} P_{ax}) major	+20	−71.64
	(P_{eq} P_{ax}) traces		−69.45
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)Py][BPh_4] (**3**)	(P_{eq} P_{ax}) major	+20	−72.24
	(P_{eq} P_{ax}) minor		−70.87
cis-[Rh(TFA)(PPh_3)$_2$(CH_3)I] (**4**)	(P_{eq} P_{eq}) (traces)	−30	−70.70
	(P_{eq} P_{ax}) major		−72.01
	(P_{eq} P_{ax}) minor		−70.47
trans-[Rh(TFA)(PPh_3)$_2$(CH_3)I] [12]	(P_{ax} P_{ax}) major	+20	−71.67
	(P_{ax} P_{ax}) minor		−68.04
trans-[Rh(HFA)(PPh_3)$_2$(CH_3)I] [12]	(P_{ax} P_{ax}) single	+20	−71.9
			−69.0

The ^{31}P NMR spectrum of **2** in chloroform at room temperature represents two doublets of doublets (Table 1) and corresponds to the complex with two inequivalent phosphine ligands which is detected almost exclusively in one isomeric form of the (P_{eq} P_{ax}) structure. We believe that complex **2** in solution retains solid-state geometry with CH_3(-Rh) ligand *trans* to the CF_3 substituent. The ^{1}H NMR spectrum of **2** consists of a group of phenyl proton signals (6.8–7.6 ppm), a signal of methine proton of TFA ligand at 5.05 ppm, and a group of signals in the region 0–2 ppm: a singlet from TFA methyl group at 1.80 ppm, a broadened singlet from methyl ligand, CH_3(−Rh), at 1.54 ppm, and a singlet from coordinated ammonia at 0.1 ppm (Table 2). The ^{19}F NMR spectrum of **2** shows a singlet at −71.64 ppm from the major isomer and a very weak singlet at −69.45 ppm from traces of the minor isomer containing CH_3(−Rh) ligand *trans* to the CH_3 substituent of TFA (Table 3).

In the ^{31}P NMR spectrum of **3**, two sets of signals differing by intensity are present, and each of them represents two doublets of doublets (Table 1). We believe that complex **3** is formed as two isomers of the (P_{eq} P_{ax}) structure, and the predominant form retains in solution the solid-state geometry with CH_3(−Rh) ligand *trans* to the CF_3 substituent. The ^{1}H NMR spectrum of **3** consists of signals from coordinated pyridine and phenyl protons in the region 6.8–7.8 ppm, a singlet from methine proton of TFA ligand for the major isomer at 4.73 ppm (apparently the corresponding signal from the minor isomer is covered with this signal), and methyl signals for both isomers in the region 1.5–2.1 ppm (Table 2). The singlets at δ 1.63 and 2.00 ppm differing by intensity belong to methyl groups of TFA ligands in these two isomers. Signals at 2.03 and 1.90 ppm should be assigned to methyl ligands, CH_3(−Rh), of two isomers as these signals are split into doublets with ^{2}J(HRh) ≅ 2 Hz [11,12,20].

The ^{19}F NMR spectrum of **3** shows two singlets, −72.24 ppm from the major isomer and −70.87 ppm from the minor one (Table 3). It should be noted that in the spectra of both complexes, **2** and **3**, the more negative value of δ^{19}F corresponds to the major (P_{eq} P_{ax}) isomer of the complexes, with the CF_3 substituent *trans* to CH_3(−Rh) ligand.

Conductivity data for complexes **2** and **3** in acetone solution are given in Table 5. Conductivity measurements for $NaBPh_4$ and for *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] [11] and *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)Py][BPh_4] [20] were performed too, and these data were

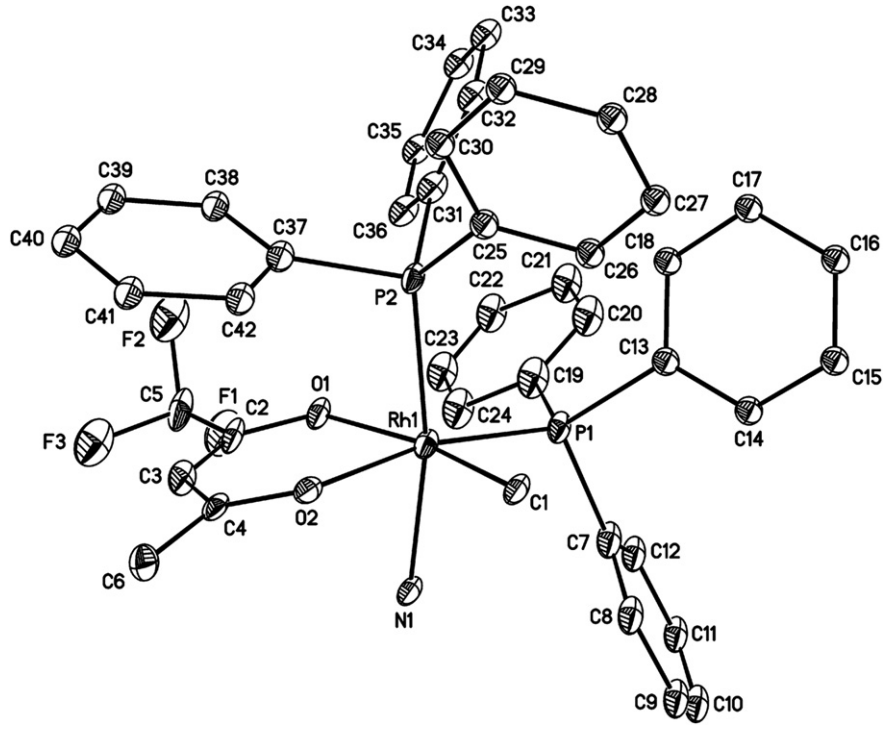


Fig. 1. X-ray structure of *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(NH_3)]$^+$ (**2**) (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

added for comparison. The values of conductivity show that these complexes behave as 1:1electrolytes [22].

2.4. Synthesis and characterization of cis-[Rh(TFA)(PPh_3)$_2$(CH_3)I] (**4**)

Complex *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)I] (**4**) has been obtained when we carried out the oxidative addition of CH_3I in acetonitrile in conditions differing from those outlined above for preparation of **1**. Namely, the higher concentrations of reactants were used, and the reaction mixture was kept at a reduced temperature during the reaction period (see Section 4). It seems reasonable to suppose that, as well as in the above synthesis of **1**, the cationic methyl complex *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(CH_3CN)]$^+$[I]$^-$ is formed in the first stage of the reaction. These conditions of reaction apparently are favorable for the replacement of acetonitrile with anion I^- in the second stage. The resulting complex **4** poorly soluble in acetonitrile at 0 °C, precipitates from the reaction mixture as a bright-yellow bulk solid (75% yield).

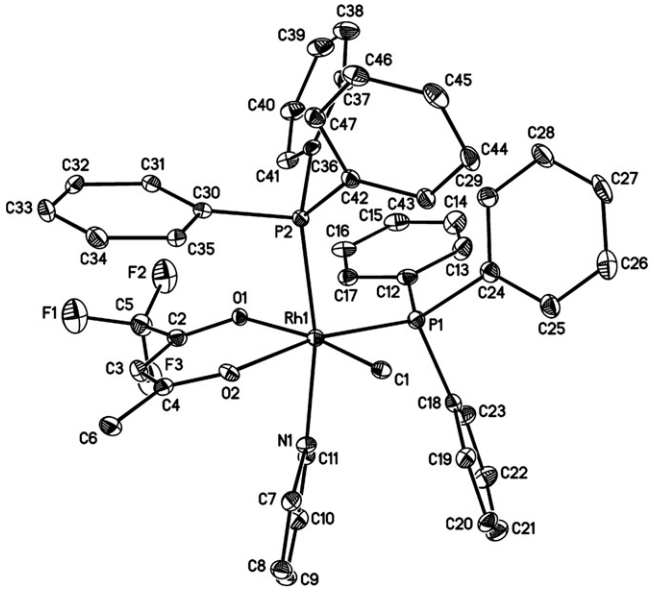


Fig. 2. X-ray structure of *cis*-[Rh(TFA)(PPh_3)$_2$(CH_3)(Py)]$^+$ (**3**) (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) for complexes 2, 3, and *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] [11] with the estimated standard deviations in parentheses.

	2	**3**	*cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4]
Rh–C(1)	2.068(5)	2.075(4)	2.075(3)
Rh–O(1)	2.172(4)	2.155(3)	2.152(2)
Rh–O(2)	2.075(4)	2.080(3)	2.071(2)
Rh–P(1)	2.297(2)	2.317(1)	2.311(7)
Rh–P(2)	2.332(2)	2.350(1)	2.3291(7)
Rh–N(1)	2.122(4)	2.158(3)	2.118(2)
P(1)–Rh–P(2)	98.83(6)	98.92(4)	99.86(3)
O(1)–Rh–O(2)	87.0(1)	88.6(1)	89.21(8)
P(1)–Rh–O(1)	98.7(1)	98.92(8)	98.13(6)
P(1)–Rh–O(2)	167.9(1)	169.38(9)	169.00(6)
P(2)–Rh–O(1)	88.6(1)	90.46(8)	89.77(5)
P(2)–Rh–O(2)	91.9(1)	88.42(8)	88.30(6)
P(1)–Rh–C(1)	90.7(2)	89.6(1)	89.88(9)
P(2)–Rh–C(1)	93.3(2)	91.9(1)	94.43(8)
C(1)–Rh–N(1)	89.9(2)	93.0(2)	90.27(11)
P(1)–Rh–N(1)	91.4(1)	91.5(1)	90.81(7)
P(2)–Rh–N(1)	169.2(1)	168.6(1)	168.33(7)
C(1)–Rh–N(1)	89.9(2)	92.9(2)	90.27(11)
O(1)–Rh–N(1)	86.5(2)	83.2(1)	84.01(9)
O(2)–Rh–N(1)	78.3(2)	81.9(1)	81.76(9)

Table 5
Molar conductivity in acetone of selected methyl rhodium (III) complexes ($T = 25\ ^\circ C$).

Compound	Λ (ohm^{-1} cm^2 mol^{-1})	C (mol/l)
cis-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)(NH$_3$)][BPh$_4$] (**2**)	80.3	0.95×10^{-3}
cis-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)(Py)][BPh$_4$] (**3**)	100.0	1.07×10^{-3}
cis-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)I] (**4**)	1.33	0.98×10^{-3}
trans-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)I] [12]	0.81	1.0×10^{-3}
cis-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)(NH$_3$)][BPh$_4$] [11]	72.8	0.90×10^{-3}
cis-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)(Py)][BPh$_4$] [20]	82.4	0.99×10^{-3}
NaBPh$_4$	124	1.00×10^{-3}

Complex **4** was characterized by elemental analysis, $^{31}P\{^1H\}$, ^1H and ^{19}F NMR spectra, and by conductivity in acetone solution (Scheme 2).

In chloroform solution, the ^{31}P NMR spectrum of 4 exhibits two sets of signals differing by intensity (regions 27.0 and 19.5 ppm). Each of these sets represents two doublets of doublets (Table 1), which indicates that **4** is formed predominantly as two isomers containing inequivalent phosphine ligands. Additionally, in the region 37–30 ppm two doublets of doublets of very low intensity can be detected (Table 1). Most likely the intense signals belong to two (P_{eq} P_{ax}) isomers of **4**, whereas the very weak signals correspond to the inequivalent phosphorous nuclei in the (P_{eq} P_{eq}) isomer of **4** which is present in trace amount. Along with the signals considered above, in the ^{31}P NMR spectrum of a freshly prepared solution of **4** in chloroform measured at room temperature, a very weak doublet at δ 19.3 ppm, $^1J(PRh) \sim 105$ Hz, can be detected. Within two hours this doublet gains high intensity, and a complete set of signals from two isomers of *trans*-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)I] [12] appears (Table 1). Concurrently, the signals of all *cis* forms of **4** become very weak. Obviously these observations point to the fact that **4** undergoes *cis* to *trans* isomerization in solution at room temperature. At reduced temperature (−20/−30 °C) the isomerization does not occur or proceeds rather slowly (no signals of *trans* complex after 2 h solution storage at −30 °C). Our attention was arrested by the fact that the values of the ^{31}P NMR parameters of **4** in toluene-d_8 solution are very close to the values found earlier for the reaction mixture {[Rh(TFA)(PPh$_3$)$_2$] + CH$_3$I} in benzene [18] (Table 6). It is likely that isomers of **4** are intermediates formed in the course of the CH$_3$I oxidative addition to [Rh(TFA)(PPh$_3$)$_2$] in aromatic solvents.

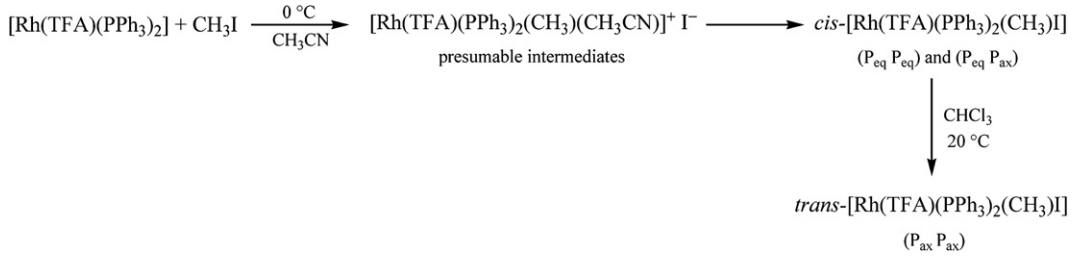
The ^1H NMR spectrum of **4** consists of three groups of signals. The region 6.8–7.8 ppm contains signals of phenyl protons. In the region of methine protons two singlets differing by intensity are present, at δ 5.27 and 5.25 ppm, which correspond to two (P_{eq} P_{ax}) isomers of **4**. In the region 1.6–2.1 ppm, signals of methyl groups are present. The singlets at δ 1.74 and 1.88 ppm differing by intensity belong to methyl groups of TFA ligands in these two (P_{eq} P_{ax}) isomers. The broadened singlets at δ 1.96 and 2.03 ppm were assigned to methyl ligands, CH$_3$(−Rh), in these two isomers (Table 2). This assignment is confirmed by the absence of these signals in the spectrum of the complex with deuterated methyl ligand, *cis*-[Rh(TFA)(PPh$_3$)$_2$(CD$_3$)I]. The proton signals of the (P_{eq} P_{eq}) isomer in the spectrum of **4** are very weak, and we do not discuss them.

The ^{19}F NMR spectrum of **4** (−30 °C) shows two singlets: δ −72.01 ppm from the major (P_{eq} P_{ax}) isomer, and δ −70.47 ppm from the corresponding minor isomer. A very weak singlet at δ −70.70 ppm probably corresponds to traces of (P_{eq} P_{eq}) isomer. The ^{19}F NMR spectrum of *trans*-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)I] shows two singlets differing by intensity: δ −71.67 ppm from the major (P_{ax} P_{ax}) isomer, and δ −68.04 ppm from the corresponding minor isomer (Table 3). Conductivity data for **4** and for *trans*-[Rh(TFA)(PPh$_3$)$_2$(CH$_3$)I] in acetone solutions (Table 5) confirm the non-electrolyte nature of these complexes [22].

2.5. Synthesis and characterization of *cis*-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)I] (**5**)

As previously noted [11], cationic methyl complex *cis*-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)(CH$_3$CN)][BPh$_4$] reacts with KI in acetone solution at room temperature to form neutral methyl complex *trans*-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)I]. We revealed however that treatment of *cis*-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)(CH$_3$CN)][BPh$_4$] in acetone with NaI at −15 °C yielded bright-yellow bulk precipitate. This product **5** was isolated, characterized by elemental analysis and by $^{31}P\{^1H\}$ and ^1H NMR spectra. In the ^{31}P NMR spectrum of **5** ($CDCl_3$, −30 °C) two sets of signals differing by intensity could be detected. The first set represents a doublet centered at 30.2 ppm, which corresponds to the complex with two equivalent phosphine ligands. The second set represents two doublets of doublets centered at 25.8 ppm and at 20.7 ppm, which correspond to the complex with two inequivalent phosphine ligands (Table 1). Thus product **5** is formed as a mixture of two *cis*-(PPh$_3$)$_2$ isomers belonging to the structural types (P_{eq} P_{eq}) and (P_{eq} P_{ax}). A comparison of intensities of these signals points to the isomer ratio (P_{eq} P_{eq}):(P_{eq} P_{ax}) of *ca.* 1:3. Furthermore, the ^{31}P NMR room-temperature spectrum of freshly prepared chloroform solution of **5** contains a doublet at δ 20 ppm ($^1J(RhP) \sim 106$ Hz), its intensity increasing markedly in time at the expense of the signals of the *cis* isomers. This signal apparently belongs to *trans*-[Rh(Acac)(PPh$_3$)$_2$(CH$_3$)I] [12]. Evidently **5** undergoes *cis* to *trans* isomerization in solution at room temperature. Therefore, to prevent isomerization of the primarily formed *cis*-(PPh$_3$)$_2$ isomers to *trans*-(PPh$_3$)$_2$ complex, reduced temperature during formation of **5** is of crucial importance.

As in the case of **4**, the ^{31}P NMR spectral parameters of **5** in toluene-d_8 solution are close to those of the reaction mixture {[Rh(Acac)(PPh$_3$)$_2$] + CH$_3$I} in benzene [18] (Table 6). Thus it appears that isomers of **5** are intermediates forming in the process of the CH$_3$I oxidative addition to [Rh(Acac)(PPh$_3$)$_2$] in aromatic solvents. The ^1H NMR spectrum (−30 °C) of **5** consists of three groups of signals. The region 6.9–7.6 ppm contains signals of phenyl protons. In the region of methine protons, two singlets differing by intensity are present, at δ 5.40 and 4.96 ppm with intensity ratio 1:3, which corresponds to two isomers of **5**, (P_{eq} P_{eq})



Scheme 2.

Table 6
$^{31}P\{^1H\}$ NMR spectral parameters of rhodium(III) methyl complexes, *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)I$], and reaction mixtures {[Rh(β-diket)$(PPh_3)_2$] + CH_3I]} in C_6D_6 [18] (β-diket = TFA, Acac).

Complex/reaction mixture	Isomer	T (°C)	Solvent	δ, ppm/^{1}J(RhP),Hz	^{2}J(PP), Hz
cis-[Rh(TFA)$(PPh_3)_2(CH_3)I$] (**4**)	(P_{eq} P_{ax}) major	−30	Toluene-d_8	27.4/140.3 18.4/127.1	21.7
	(P_{eq} P_{ax}) minor			28/141 19/128	21
{[Rh(TFA)$(PPh_3)_2$] + CH_3I]} [18]	(P_{eq} P_{ax}) major	~+6	C_6D_6	26.4/140.5 17.0/127.3	20.6
	(P_{eq} P_{ax}) minor			27.4/142.4 17.1/128.4	19.4
cis-[Rh(Acac)$(PPh_3)_2(CH_3)I$] (**5**)	(P_{eq} P_{eq}) (P_{eq} P_{ax})	−20	Toluene-d_8	32.1/137.8 27.8/136.0 18.5/130.4	– 20.8
{[Rh(Acac)$(PPh_3)_2$] + CH_3I} [18]	(P_{eq} P_{eq}) (P_{eq} P_{ax})	~+6	C_6D_6	30.5/138.1 26.9/136.1 17.6/130.8	– 20.2

and (P_{eq} P_{ax}). In the region 1.6–2.0 ppm, signals of methyl groups are present. Two singlets, at δ 1.93 and 1.62 ppm belong to the inequivalent methyl groups of acetylacetonate ligand in the (P_{eq} P_{ax}) isomer. The singlet at δ 1.76 ppm belongs to two equivalent acetylacetonate methyl groups in the (P_{eq} P_{eq}) isomer. The singlets at δ 1.54 and 1.73 ppm are broadened (Table 2). Based on their relative intensities (1:3 ratio) and their absence in the spectrum of the deuterated product, *cis*-[Rh(Acac)$(PPh_3)_2(CD_3)I$], we assign them to methyl ligands, CH_3(−Rh), in the isomers of **5**, (P_{eq} P_{eq}) and (P_{eq} P_{ax}).

3. Concluding remarks. Some tentative assignments

As stated above, cation complexes *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)$ (CH_3CN)][BPh_4], and *cis*-[Rh(BA)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4] [11], and their TFA analog **1**, as well as neutral complexes **4** and **5** are present in solutions as mixtures of *cis*-isomers of two different types, (P_{eq} P_{eq}) and (P_{eq} P_{ax}). In the case of *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4] and *cis*-[Rh(BA)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4], (P_{eq} P_{eq}) isomers are dominant in $CDCl_3$ solutions at −50 °C [11], whereas in the case of the corresponding TFA complex **1**, (P_{eq} P_{ax}) isomers are dominant under the same conditions. The neutral Acac complex **5** in $CDCl_3$ solution is present as a mixture of *cis*-isomers, (P_{eq} P_{eq}) and (P_{eq} P_{ax}), with ratio of *ca.* 1:3, but neutral TFA complex **4** is present almost entirely as (P_{eq} P_{ax}) isomers with only traces of (P_{eq} P_{eq}) isomer. Thus it is evident, that the presence of electronegative β-diketonate ligand, TFA, in these complexes favors the formation of (P_{eq} P_{ax}) isomers.

As already noted, (P_{eq} P_{eq}) and (P_{eq} P_{ax}) isomers of cationic complexes *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4] at ambient temperature are involved into mutual dynamic interconversion, and at −50 °C these dynamic processes slow down. As for neutral complexes, we have no evidence for interconversion of (P_{eq} P_{eq}) and (P_{eq} P_{ax}) isomers. However, in solution, both neutral complexes, **4** and **5**, transform into respective *trans*, i.e. (P_{ax} P_{ax}) isomers, which are known to be the final products of the CH_3I oxidative addition to [Rh(β-diket)$(PPh_3)_2$] complexes [12]. We believe that isomers of complexes **4** and **5** are intermediates formed in the course of the CH_3I oxidative addition to [Rh(β-diket)$(PPh_3)_2$] in aromatic solvents. As mentioned above, we detected these intermediates and made some speculations about their structures long ago [18]. However, our preliminary assumptions on the structures of these intermediates are not supported with the data of this paper.

Complexes **2** and **3**, as well as the previously described *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)(NH_3)$][BPh_4] [11], *cis*-[Rh(BA)$(PPh_3)_2(CH_3)$ (NH_3)][BPh_4] [11], and *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)$Py][BPh_4] [20], have been isolated with good yields as (P_{eq} P_{ax}) isomers. It is easy to see that the structure of these complexes does not depend on the nature of β-diketonate ligand, in particular, its electronegativity. It should be noted however, that in the case of TFA complexes, **2** and **3**, one of two (P_{eq} P_{ax}) isomers dominates. In the dominant isomer, CH_3(−Rh) ligand is located *trans* to the CF_3 substituent, i.e. methyl ligand in these complexes appreciably prefers the position *trans* to the CF_3 substituent. As already noted, in each isomeric pair the $\delta^{19}F$ value of CF_3 substituent for the major isomer, CF_3 *trans* to CH_3(−Rh), is more negative as compared to the minor isomer (Table 3). Data in Table 3 also indicates that the more negative $\delta^{19}F$ value of the CF_3 substituent belongs to the major (P_{eq} P_{ax}) isomers of complexes **1** and **4**. So, we can assume that this geometrical preference (CH_3(−Rh) ligand *trans* to the CF_3 substituent) is common for all isomeric pairs of the TFA complexes of this structural type, including complexes **1** and **4**. Furthermore, the more positive δ^1H value of the CH_3 substituent (Table 2) belongs to the minor (P_{eq} P_{ax}) isomers of complexes **3** and **4**, where, evidently, the CH_3 substituent is *trans* to CH_3(−Rh) ligand. Moreover, this regularity makes it

Table 7
Crystallographic data for **2** and **3**.

	2·$(C_2H_5)_2O$	**3**·0.75 CH_2Cl_2
Empirical formula	$C_{74}H_{80}BNO_4F_3P_2Rh$	$C_{71.75}H_{63.5}BNO_2F_3P_2Cl_{1.5}Rh$
fw	1205.93	1257.57
T, K	100(2)	120(2)
Crystal size, mm	0.06 × 0.15 × 0.18	0.10 × 0.12 × 0.18
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a, Å	13.900(4)	12.1838(10)
b, Å	14.802(4)	14.0810(11)
c, Å	29.308(8)	19.1853(15)
α, deg.	90	74.348(2)
β, deg.	95.080(5)	79.491(2)
γ, deg.	90	80.242(2)
V, Å^3	6006(3)	3091.0(4)
Z	4	2
d_c, g cm^{-3}	1.334	1.351
F(000)	2512	1299
μ, mm^{-1}	0.395	0.449
$2\theta_{max}$, deg.	50	56
Index range	$-16 \le h \le 16$ $-17 \le k \le 17$ $-34 \le l \le 34$	$-16 \le h \le 16$ $-18 \le k \le 18$ $-25 \le l \le 25$
No. of rflns collected	50,929	31,739
No. of unique rflns	10,495	14,821
No. of rflns with $I > 2\sigma(I)$	3739	8408
Data/restraints/parameters	10495/0/358	14821/21/762
$R1$; $wR2$ ($I > 2\sigma(I)$)	0.0899; 0.1053	0.0693; 0.1508
$R1$; $wR2$ (all data)	0.1324; 0.1299	0.1375; 0.1734
GOF on F^2	0.956	1.009
T_{min}; T_{max}	0.932; 0.977	0.924; 0.957

possible to propose a tentative assignment of δ^1H and δ^{19}F values for the inequivalent methyl and trifluoromethyl substituents in the complexes with symmetric β-diketonate ligands, *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] (**5**), *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] [12], and *trans*-[Rh(HFA)(PPh_3)$_2$(CH_3)I] (HFA is hexafluorocetylacetonate) [12]. According to this criterion, in the ^{1}H spectra of the (P_{eq} P_{ax}) isomer of **5** and of *trans*-[Rh(Acac)(PPh_3)$_2$(CH_3)I] chemical shifts 1.93 and 1.49 ppm, respectively (Table 2), correspond to the CH_3 substituent *trans* to CH_3(−Rh) ligand; in the ^{19}F spectrum of *trans*-[Rh(HFA)(PPh_3)$_2$(CH_3)I] chemical shift −71.9 ppm (Table 3) corresponds to the CF_3 substituent *trans* to CH_3(−Rh) ligand.

For every (P_{eq} P_{ax}) isomer of the complexes under discussion there are two well separated ^{31}P resonances with distinct coupling constants, ^{1}J(PRh), (Table 1). We attempted to assign these resonances specifically to P_{ax} and P_{eq} nuclei. Our consideration is based on a noticeable difference in the sensitivity of the ^{1}J(PRh) values, presented in Table 1, toward specific changes in the ligand surrounding of the metallocenter. We tentatively ascribe to equatorial phosphines the signals which ^{1}J(PRh) values are more sensitive to the nature of β-diketonate ligand. These are signals at 23.6; 26.7; 23.1; 25.8 ppm for L = MeCN, NH_3, Py, I, respectively, in the β-diket = Acac series and 24.7; 27.5; 24.4; 26.2 ppm for the same sequence of ligands L in the β-diket = TFA series (major isomers). The remaining signals in these spectra which ^{1}J(PRh) values are more sensitive to variation in the axial ligands, we assign to axial phosphines.

It is interesting to note that cations with the (P_{eq} P_{ax}) structure of complexes under discussion have very close values of constants ^{2}J(PP) (35–37 Hz) without regard to the nature of β-diketonate and L-ligands (Table 1). The (P_{eq} P_{ax}) isomers of neutral complexes **4** and **5** also have very close values of constants ^{2}J(PP) (22–23 Hz), but these values differ markedly from the values for (P_{eq} P_{ax}) isomers of cation complexes (L = NH_3, Py, MeCN).

4. Experimental

4.1. Preparation of complexes

All operations were performed under a dry argon atmosphere. The rhodium complexes [Rh(Acac)(PPh_3)$_2$], [Rh(TFA)(PPh_3)$_2$], *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] were synthesized by the published procedures [11,23]. Gaseous NH_3 was prepared by standard methods [24]. Solvents were dried and purified by known procedures [25] and distilled under argon. Methyl iodide was used as freshly distilled samples. Elemental analyses were performed on a Hewlett–Packard 185 microanalyzer. Conductivity measurements were carried out on an E 7–11 universal CRL instrument at 25 °C for 10^{-3} M solutions in acetone.

4.1.1. Preparation of cis-[Rh(TFA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (**1**)

Methyl iodide (0.1 ml, 1.6 mmol) was added to a suspension of [Rh(TFA)(PPh_3)$_2$] (0.201 g, 0.26 mmol) in acetonitrile (15 ml) at −20 °C with stirring. The reaction mixture was allowed to warm to +10 °C. After 1 h the starting complex was entirely dissolved, then the yellow-orange solution was mixed with solution of $NaBPh_4$ (0.43 g, 1.26 mmol) in acetonitrile (10 ml) at +10 °C. The resulting reaction mixture was stirred for 10 min at +10 °C, filtered, and then volatiles were removed in vacuo without heating. Then acetonitrile (15 ml) was added to the resulting oil, the solution was filtered, and solvent was removed from filtrate in vacuo. Methylene chloride (15 ml) was added to the oily residue, and the white precipitate was filtered off. Then solvent was removed from filtrate yielding a yellow-orange solid. This solid was dissolved in acetonitrile (10 ml), a very fine light precipitate was filtered off, and solvent was removed from filtrate. Then, chloroform (9 ml) was added to the solid and white precipitate was filtered off. The solution was concentrated to give a red-orange solid (0.263 g). Yellow crystals of **1** as CH_3CN 1:1 solvate could be obtained by dissolving the red-orange solid in acetonitrile (2 ml), adding toluene (7 ml) and layering the solution with 8 ml of petroleum (b.p. range 70–100 °C). Yield: 0.12 g (40%). Anal. Calc. for $C_{70}H_{63}BF_3N_2O_2P_2Rh$: C, 70.24; H, 5.31. Found: C, 70.31; H, 5.31%.

4.1.2. Preparation of cis-[Rh(TFA)(PPh_3)$_2$(CH_3)(NH_3)][BPh_4] (**2**)

Methyl iodide (0.1 ml, 1.6 mmol) was added to a suspension of [Rh(TFA)(PPh_3)$_2$] (0.208 g, 0.27 mmol) in acetonitrile (15 ml) at −20 °C with stirring. The reaction mixture was allowed to warm to +10 °C. After 1 h the starting complex was entirely dissolved, and the yellow-orange solution was formed. The solution thus obtained was mixed with $NaBPh_4$ (0.5 g, 1.46 mmol) in acetonitrile (10 ml). The resulting reaction mixture was stirred for 10 min, filtered, and volatiles were removed in vacuo. Methylene chloride (15 ml) was added to the oily residue, and the white precipitate was filtered off. The volume of filtrate was reduced to about 5 ml, and a steam of gaseous NH_3 was passed through the solution for 5 min at room temperature. Then, the solvent was removed in vacuo and the oily residue was recrystallized from methylene chloride/diethyl ether to form pale-yellow bright crystals of solvate **2**·(C_2H_5)$_2$O. Yield: 0.16 g (50%). Anal. Calc. for $C_{70}H_{70}BF_3NO_3P_2Rh$: C, 69.72; H, 5.85. Found: C, 69.36; H, 5.85%.

4.1.3. Preparation of cis-[Rh(TFA)(PPh_3)$_2$(CH_3)Py][BPh_4] (**3**)

Methyl iodide (0.1 ml, 1.6 mmol) was added to a suspension of [Rh(TFA)(PPh_3)$_2$] (0.190 g, 0.24 mmol) in acetonitrile (15 ml) at −20 °C with stirring. The reaction mixture was allowed to warm to +10 °C. After 1 h the starting complex was entirely dissolved and the yellow-orange solution was formed. The solution thus obtained was mixed with $NaBPh_4$ (0.44 g, 1.3 mmol) in acetonitrile (12 ml). The resulting reaction mixture was stirred for 10 min, filtered, and volatiles were removed in vacuo. Methylene chloride (20 ml) was added to the oily residue, and the white precipitate was filtered off. The volume of filtrate was reduced to about 5 ml, and excess pyridine (0.1 ml, 1.24 mmol) was added. The reaction mixture was stirred for 10 min at room temperature. Then excess pyridine and the solvent were removed in vacuo, and the oily residue was recrystallized from methylene chloride/diethyl ether to form pale-yellow crystals of solvate **3**·0.75 $C_2H_2Cl_2$. Yield: 0.23 g (76%). Anal. Calc. for $C_{71.75}H_{63.50}BCl_{1.5}F_3NO_2P_2Rh$: C, 68.52; H, 5.10. Found: C, 68.98; H, 5.36%.

4.1.4. Preparation of cis-[Rh(TFA)(PPh_3)$_2$(CH_3)I] (**4**)

Methyl iodide (0.4 ml, 6.3 mmol) was added to a suspension of [Rh(TFA)(PPh_3)$_2$] (0.17 g, 0.22 mmol) in acetonitrile (3 ml) at −20 °C with stirring. The reaction mixture was allowed to warm to 0 °C. After stirring the suspension for 30 min at 0 °C a bright-yellow bulk solid was formed. To complete the reaction, reaction mixture was stirred for 1 h at 0 °C. Then excess methyl iodide was removed in vacuo without heating. Acetonitrile (3 ml) was added at 0 °C. The product was filtered off and washed with cold acetonitrile and cold methanol, and dried in vacuo. Yield: 0.15 g (75%). Anal. Calc. for $C_{42}H_{37}F_3IO_2P_2Rh$: C, 54.68; H, 4.04. Found: C, 54.42; H, 3.91%.

4.1.5. Preparation of cis-[Rh(TFA)(PPh_3)$_2$(CD_3)I]

The complex was prepared similarly to **4** starting from [Rh(TFA)(PPh_3)$_2$] (0.10 g, 0.13 mmol) and CD_3I (0.1 ml, 1.6 mmol) in CH_3CN (3 ml). Yield: 0.07 g (57%).

4.1.6. Preparation of cis-[Rh(Acac)(PPh_3)$_2$(CH_3)I](**5**)

A mixture of complex *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (0.25 g, 0.22 mmol), NaI (0.11 g, 0.73 mmol), and acetone (5 ml) was

stirred at −15 °C for 1.5 h. The initial pale-yellow suspension turned bright-yellow. The solid was isolated by filtration, washed with cold methanol (3 ml) and dried in vacuo. Yield: 0.18 g (92%). Anal. Calc. for $C_{42}H_{40}IO_2P_2Rh$: C, 58.08; H, 4.64. Found: C, 57.75; H, 4.68%.

4.1.7. Preparation of cis-[Rh(Acac)(PPh_3)$_2$(CD_3)I]

The complex was prepared similarly to **5** starting from *cis*-[Rh(Acac)(PPh_3)$_2$(CD_3)(CH_3CN)][BPh_4] (0.20 g, 0.18 mmol) and NaI (0.10 g, 0.67 mmol) in acetone (5 ml). Yield: 0.14 g (89%).

4.2. NMR measurements

^1H (300.1 MHz) and ^{31}P (121.5 MHz) NMR spectra were measured on a Bruker DPX-300 spectrometer operating in the Fourier-transform mode with CPD proton decoupling for ^{31}P. ^1H chemical shifts were referenced with respect to TMS using solvent ($CDCl_3$) residual proton as internal standard, δ $^1H = 7.28$ ppm. ^{31}P chemical shifts were referenced with respect to external 85% H_3PO_4. ^{19}F NMR spectra (470.6 MHz) were measured on a Bruker AM-500 spectrometer. ^{19}F chemical shifts were referenced with respect to $CFCl_3$ using external C_6F_6, δ $^{19}F = -162.9$ ppm.

4.3. X-ray structure determinations

Data were collected on a Bruker SMART APEX II CCD (for **2**) and a Bruker SMART 1 K CCD (for **3**) diffractometers (λ(MoK_α)-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the SADABS program (versions 2.03 [26] for **2** and 2.01 [27] for **3**). For details, see Table 7. The structures were solved by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The trifluoromethyl group in **3** is disordered over two sites with equal occupancies. The asymmetric unit of **2** contains one diethyl ether solvate molecule, and the asymmetric unit of **3** contains two methylene chloride solvate molecules. The diethyl ether solvate molecule in **2** is strongly disordered, and attempts to model its position were unsatisfactory. The contribution to the scattering by this molecule was removed by use of the utility SQUEEZE in PLATON98 [28]. One of the two methylene chloride solvate molecules in **3** is disordered over two sites connected by an inversion center, with the total positional occupancy of 0.5. The other molecule is also disordered over two sites with the occupancies of 0.25:0.25. The hydrogen atoms of the NH_3-group in **2** were localized in the difference-Fourier map and included in the refinement with fixed positional and isotropic displacement parameters. The other hydrogen atoms in both compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement 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 using the SHELXTL program [29].

Appendix A. Supplementary material

Crystallographic data for **2**·$(C_2H_5)_2O$ and **3**·0.75 CH_2Cl_2 have been deposited with the Cambridge Crystallographic Data Center. CCDC 818787 and CCDC 818788 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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