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Reactivity of cationic methyl rhodium(III) complexes *cis*-[Rh(β-diket)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] toward ligands of different character: pyridine, carbon monoxide, and triphenylphosphine

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Abstract

Cationic methyl complex of rhodium(III), *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(Py)][BPh_4] (**1**) as a single isomer with Py in the *trans* to PPh_3 position, is formed upon the reaction of *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] with pyridine in methylene chloride solution. Complex **1** was characterized by elemental analysis and by $^{31}P\{^1H\}$ and ^1H NMR spectra. Cationic pentacoordinate acetyl complexes, *trans*-[Rh(Acac)(PPh_3)$_2$($COCH_3$)][BPh_4] (**2**) and *trans*-[Rh(BA)(PPh_3)$_2$($COCH_3$)][BPh_4] (**3**), are prepared by action of carbon monoxide on *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], respectively, in methylene chloride solutions. Complexes **2** and **3** were characterized by elemental analysis and by IR, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR. According to NMR data, **2** and **3** in solution are non-fluxional trigonal bipyramids with β-diketonate and acetyl ligands in the equatorial plane and axial phosphines. In solutions, **2** and **3** gradually isomerize into octahedral methyl carbonyl complexes *trans*-[Rh(Acac)(PPh_3)$_2$(CO)(CH_3)][BPh_4] (**4**) and *trans*-[Rh(BA)(PPh_3)$_2$(CO)(CH_3)][BPh_4] (**5**), respectively. Complexes **4** and **5** were characterized by IR, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR, without isolation. Upon the action of PPh_3 on *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], reductive elimination of the methyl ligand as a phosphonium salt, [CH_3PPh_3][BPh_4], occurs to give square planar rhodium(I) complexes [Rh(Acac)(PPh_3)$_2$] and [Rh(BA)(PPh_3)$_2$], respectively. The reaction products were identified in the reaction mixtures by $^{31}P\{^1H\}$ and ^1H NMR.

Keywords: Rhodium; Methyl complexes; Acetyl complexes; Reductive elimination; IR; NMR

1. Introduction

In current publications on methyl iodide oxidative addition to square planar rhodium(I) complexes, the reaction mechanisms involving intermediates with separated charges are widely discussed [1–5]. Recently, we isolated and characterized two cationic methyl complexes of rhodium(III), *cis*-[Rh(β-diket)(PPh_3)$_2$-(CH_3)(CH_3CN)]$^+$[BPh_4]$^-$ (β-diket is acetylacetonate or benzoylacetonate ligand) [6], which may be considered as stable analogs of unstable ionic intermediates. According to X-ray data, both phosphines in these cations in the solid state lie in the same (''equatorial'') plane with the β-diketonate ligand. As might be expected, these cationic complexes showed a high reactivity with respect to acetonitrile replacement reactions and structural rearrangements. Thus, the 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, and the positions of PPh_3 ligands in the resultant complexes differ from their positions in the

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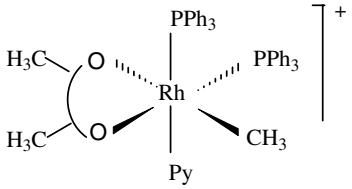
initial complexes. The ammonia complexes contain one equatorial and one axial phosphine ligand, whereas the action of I^- yields the neutral complexes *trans*-[Rh(β-diket)$(PPh_3)_2(CH_3)I$] with two axial *trans* phosphines. Here, we report reactions of the complexes *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ with three ligands, pyridine, carbon monoxide and triphenylphosphine, widely differing in their electronic properties and reactivity.

2. Results and discussion

2.1. Reaction of cis-[Rh(Acac)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ complex with pyridine

Treatment of *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ in methylene chloride with excess pyridine at ambient temperature yields *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)$(Py)][BPh_4] (**1**). Complex **1** was isolated as a yellow crystalline solid in 77% yield and was characterized by elemental analysis and by $^{31}P\{^1H\}$ and ^1H NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of **1** in chloroform represents two doublets of doublets (δ 23.1 ppm, ^1J(PRh) 134.5 Hz and δ 21.5 ppm, ^1J(PRh) 129.3 Hz, ^2J(PP) 35.2 Hz) that corresponds to the complex with two inequivalent phosphine ligands, which is present in solution as a single isomer. Spin–spin coupling constants ^1J(PRh) and ^2J(PP) of complex **1** are rather close to those of the previously reported ammonia complex *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)(NH_3)][BPh_4]$, δ 26.7 ppm, ^1J(PRh) 133.8 Hz and δ 24.0 ppm, ^1J(PRh) 128.6 Hz, ^2J(PP) 35.2 Hz [6]. The ^1H NMR spectrum of complex **1** consists of a group of signals of phenyl protons (δ 6.8–7.5 ppm), signals of coordinated pyridine (δ 6.74 and 8.09 ppm),[1] a signal from methine proton of the acetylacetonate ligand (δ 4.37 ppm) and a number of signals from methyl protons in the region δ 1–2 ppm. Two sharp signals within the last region at δ 1.88 (3H) and 1.49 ppm (3H) belong to protons of two inequivalent methyl groups of the acetylacetonate ligand. The signal at δ 1.78 ppm, which appears as a broadened singlet, should be assigned to the methyl ligand (H_3C–Rh). The coupling to ^{103}Rh and two inequivalent ^{31}P nuclei is not resolved. On the basis of NMR spectra, we assign to the cation of **1** the following structure, akin to the structure of cation *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)(NH_3)]^+$, which has been determined by NMR spectra and X-ray analysis [6].

[1] We observed only these two signals because the third one was obscured by the assemblage of phenyl proton signals; the ^1H NMR data for coordinated pyridine see, for example, in [5,7].



2.2. Reaction of cis-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ complexes with CO

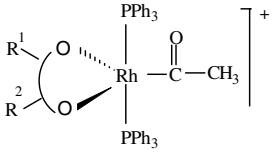
Complexes *trans*-[Rh(Acac)$(PPh_3)_2(COCH_3)][BPh_4]$ (**2**) and *trans*-[Rh(BA)$(PPh_3)_2(COCH_3)][BPh_4]$ (**3**) are easily formed at ambient temperature by passing a stream of CO for 15 min through methylene chloride solutions of complexes *cis*-[Rh(Acac)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$ and *cis*-[Rh(BA)$(PPh_3)_2(CH_3)(CH_3CN)][BPh_4]$, respectively. Complexes **2** and **3** were characterized by elemental analysis and by IR, $^{31}P\{^1H\}$ and ^1H NMR spectra. The ^{13}C NMR spectra were taken for a sample of [Rh(Acac)$(PPh_3)_2(^{13}COCH_3)][BPh_4]$ (**2′**) obtained using carbon monoxide enriched in ^{13}C (76.6%).

The IR spectra of complexes **2** and **3** display intense bands with maxima at 1726 cm^{-1} (**2**) and 1728 cm^{-1} (**3**), which correspond to the ν(CO) stretching vibration in the –C(=O)Me group of acetyl rhodium(III) complexes [3,5,8–17].

The ^{13}C NMR spectrum of a freshly prepared chloroform solution of **2′** displays doublet of triplets from acetyl carbon at δ 207.2 ppm, ^1J(CRh) 28.9 Hz, ^2J(CP) 6.2 Hz [13–17], split by spin–spin coupling with ^{103}Rh and two equivalent ^{31}P nuclei. The $^{31}P\{^1H\}$ NMR spectra of freshly prepared chloroform solutions of complexes **2** and **3** display in each case one sharp doublet at δ 30.5 ppm, ^1J(PRh) 151.9 Hz (**2**) and at δ 31.0 ppm, ^1J(PRh) 152.6 Hz (**3**). The ^{31}P NMR spectrum of **2′** shows an additional splitting arising from ^2J(PC) 6.1 Hz. No line broadening was observed which might indicate a fluxional behavior of these complexes. As is evident from these spectral data, complexes **2** and **3** exist in solutions in single isomeric forms containing two phosphine ligands in the equivalent positions *trans* to each other.

The ^1H NMR spectra of complexes **2** and **3** contain three groups of signals. In the region δ 6.8–7.8 ppm, there are signals from phenyl protons of phosphine and benzoylacetonate ligands and the $[BPh_4]^-$ anion. Signals from methine protons for complexes **2** and **3** are located at δ 5.67 and 6.44 ppm, respectively. Signals from methyl protons represent the third group lying in the region δ 1.7–2.5 ppm. In the spectrum of **2** the signal at δ 2.27 ppm (3H) should be assigned to the methyl group of the acetyl ligand as this signal is split into doublet in the spectrum of ^{13}C enriched complex **2′** (^2J(HC) 5.8

Hz). The intense signal at δ 1.73 ppm (6H) should be assigned to two equivalent methyl groups of the acetylacetonate ligand. By analogy, we assign the signals at δ 2.47 (3H) and 1.85 ppm (3H) in the spectrum of complex **3** to methyl groups of acetyl and benzoylacetonate ligands, respectively. It is easy to verify that a trigonal bipyramid with *trans*-phosphines and the acetyl group in the equatorial position fits all the experimental data:



2: $R^1 = R^2 = CH_3$

3: $R^1 = CH_3$; $R^2 = Ph$

Acyl complexes of rhodium(III) usually exist in a pentacoordinate form, and their typical solid-state geometry is square pyramid (sp) with apical acyl ligand [4,9,10,18–23]. The same geometry was evidenced for these complexes in solutions. Complexes **2** and **3** (at least in solution) belong to a less common structural type, trigonal bipyramid (tbp). The similar geometry with axial phosphine ligands was found for the neutral complex $[RhCl_2(PPh_3)_2(COCH_2Ph)]$ in solution as well as in the solid state [24]. The neutral complex $[Rh(Ph_2P(CH_2)_3PPh_2)(COCH_3)I_2]$ was described as a distorted pyramid approximated to the tbp form in the solid state [25]. Interestingly, contrary to the most pentacoordinate rhodium(III) complexes, the acyl complexes, both sp and tbp, do not exhibit fluxional behavior in solution. As mentioned above, we also did not mark any signs of fluxionality in the room-temperature NMR spectra of **2** and **3**.

We noticed that several new signals appear in the NMR spectra of solutions of complexes **2** and **3** held at ambient temperature under an inert atmosphere. As the isomerization of rhodium(III) acyl complexes into alkyl carbonyl complexes

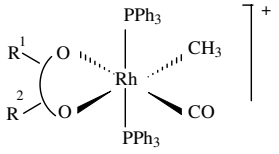
$$R–C(O)–RhL_n \rightarrow R–Rh(CO)L_n$$

is a well-documented phenomenon [9,11,12,24,26,27], we assumed that the new signals belong to the products of this kind. With this assumption, we studied the IR and NMR spectra of residues obtained by evaporation of dichloromethane solutions of **2** and **3** after 24 h storage. As expected, the IR spectra of these mixed products (in CH_2Cl_2), alongside with acetyl ν(CO) absorption bands of initial **2** and **3** at 1726 and 1728 cm^{-1}, contained ν(CO) bands at 2060 and 2058 cm^{-1}, respectively, which are characteristic of terminal carbonyl ligands in rhodium(III) complexes [3,5,8,9,11–17,27,28].

The ^{13}C NMR spectrum (in $CDCl_3$) of the mixed product obtained from complex **2′**, along with signal from acetyl carbon, showed a doublet of triplets at δ 186.2 ppm, ^1J(CRh) 61.9 Hz, ^2J(CP) 13.8 Hz, which is characteristic of carbonyl carbon in rhodium(III) bisphosphine complexes with two equivalent ^{31}P nuclei [13–17,28]. The $^{31}P\{^1H\}$ NMR spectrum of the mixed product obtained from **2**, in addition to doublet from the initial acetyl complex, contained one more doublet of sharp lines at δ 24.3 ppm, ^1J(PRh) 87.6 Hz (doublet of doublets with ^2J(PC) 13.8 Hz in the case of **2′**) that is in concordance with the above data and confirms the equivalence of two phosphine ligands in the isomerization product.

In the $^{31}P\{^1H\}$ NMR spectrum of the mixed product obtained from **3**, alongside with a doublet from the initial acetyl complex, two doublets were observed, δ 24.8 ppm, ^1J(PRh) 87.4 Hz and δ 24.4 ppm, ^1J(PRh) 86.7 Hz (Fig. 1).

Obviously in the case of the unsymmetrical β-diketonate ligand, BA, two isomeric methyl carbonyl complexes with equivalent phosphines were formed, which points to the mutual *trans* position of phosphine ligands. Taking into account the close resemblance between NMR spectra of the isomerization products, we can conclusively assign the following structures to them:



4: $R^1 = R^2 = CH_3$

5a, **5b**: R^1, $R^2 = CH_3$, Ph

The ^1H NMR spectra of mixtures of acetyl complexes and products of their isomerization are complicated, and therefore, we succeed in the complete assignment of the proton signals only for complex **4**. The methyl groups of the acetylacetonate ligand show two singlets of equal intensity, δ 1.45 and 1.38 ppm. The signal from protons of the methyl ligand (H_3C–Rh) in the spectrum of **4** at δ 1.32 ppm appears as a triplet of doublets due to spin–spin coupling with ^{103}Rh and two equivalent ^{31}P nuclei (^2J(HRh) 1.81 Hz, ^3J(HP) 4.90 Hz). All these data confirm the geometry of **4** derived from ^{31}P and ^{13}C NMR data. We did not try to make an assignment of ^1H resonances for isomers of complex **5** in the region 1–2 ppm because of abundance of partially overlapped signals. Singlets from methine protons are located at δ 4.15 ppm (**4**) and 4.91 and 4.85 ppm (isomers of **5**).

It is worth noting that acyl–alkyl isomerization of sp complexes with apical acyl ligand requires a free equatorial position capable of accepting the methyl

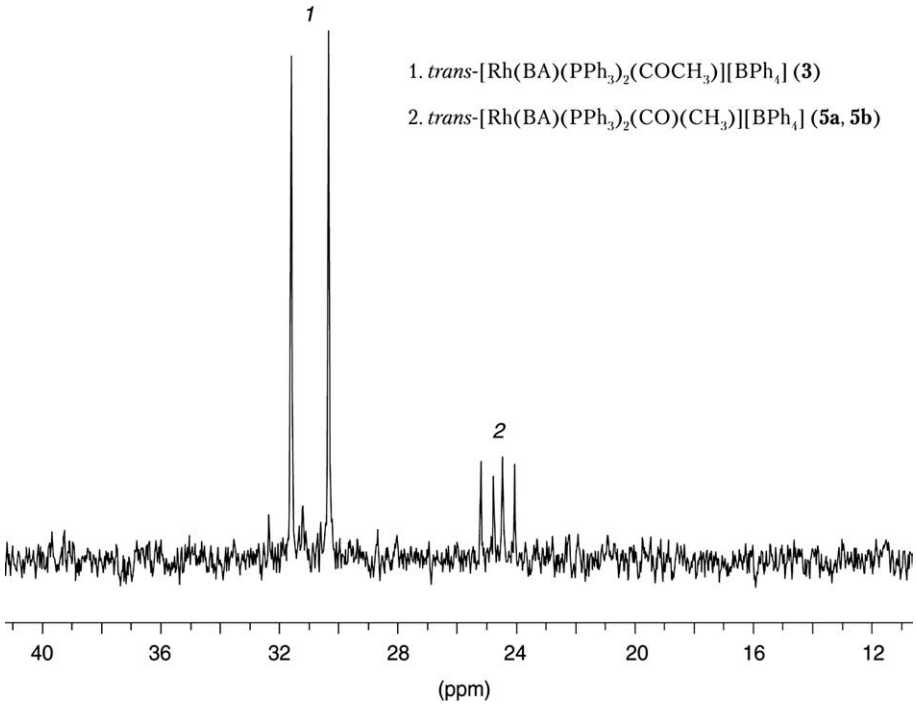


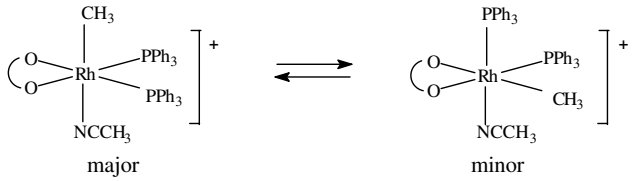
Fig. 1. The $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) spectrum of *trans*-[Rh(BA)$(PPh_3)_2(COCH_3)$][BPh_4] (**3**) after 24 h ageing of solution in CH_2Cl_2 at ambient temperature.

ligand, i.e. a considerable rearrangement of ligands should accompany this isomerization. In the case of isomerization

2 (**3**) → **4** (**5**)

the process seems to include only the methyl ligand migration within the equatorial plane, and moreover, the presence of β-diketonate ligand with a bite angle value of ∼90° [6,29–36] could facilitate this migration making two other equatorial angles more capacious then in the ideal tbp [37]. Observed incompleteness of the isomerization reactions for 24 h may be caused either by equilibrium between acyl and methyl carbonyl complexes [9,24,26,27] or by kinetic reasons. A prolonged examination of these reactions is hindered by a further transformation of carbonyl complexes that produce a number of new signals from unidentified products in NMR spectra of reaction mixtures.

The presented data allow us to make some preliminary comments concerning mechanism of the acetyl complex formation. Recently [6], we detected two dynamically exchanged isomeric forms of the cation in solution of the salt *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4]:



There is no doubt that this dynamic isomerization proceeds through acetonitrile dissociation, which produces a variety of undetectable fluxional pentacoordinate species of sp and tbp configurations. The adjunction of carbon monoxide molecule to some of these species may generate short-lived intermediates containing methyl and carbonyl ligands in *cis* position and thus appropriate to the transformation into acetyl complexes by migratory insertion. Having no positive data on the possible structure of immediate precursors of the acetyl complex, we can envision these precursors as octahedral cationic methyl carbonyl complexes containing phosphine ligands in *cis* positions. We consider the *trans*-$(PPh_3)_2$ geometry as less credible, because *trans*-$(PPh_3)_2$ carbonyl complexes were detected as relatively stable moieties **4** and **5** resulted from the isomerization of acyl complexes **2** and **3**. In the case of *cis*-$(PPh_3)_2$ precursor, the CO insertion stage obviously should be accompanied by an rearrangement of phosphine ligands.

2.3. Reaction of *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4] complexes with triphenylphosphine

Preliminary experiments have shown that the $^{31}P\{^{1}H\}$ NMR spectra of reaction mixtures of *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4] with PPh_3 in chloroform at room temperature, alongside with numerous signals of unidentified products, exhibit an intense singlet due to phosphine oxide (δ 30.5 ppm), which

points to the sensitivity of the initially formed products to oxygen traces. Therefore, to detect primary reaction products, we carried out these reactions directly in the NMR tube ($CDCl_3$ as a solvent).

The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures obtained at a molar ratio PPh_3:Rh = 1:1 show one doublet (δ 56.6 ppm, ^1J(PRh) 193.1 Hz) in the low-field region in the case of the Acac complex, and two doublets of doublets (δ 59.0 ppm, $^1J(P_1Rh)$ 195.5 Hz, and δ 54.4 ppm, $^1J(P_2Rh)$ 191.4 Hz; $^2J(P_1P_2)$ 56.4 Hz) in the case of the BA complex (Fig. 2).

These signals may be assigned with certainty to the rhodium(I) square planar complexes, [Rh(Acac)$(PPh_3)_2$] and [Rh(BA)$(PPh_3)_2$], respectively, which we studied earlier [38] and also used to obtain *cis*-[Rh(β-diket)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4] [6]. In addition, a sharp singlet (δ 22.2 ppm) is also present in the spectra of the both reaction mixtures. We ascribed this singlet to the cation $[CH_3PPh_3]^+$. This conclusion was confirmed by the synthesis of the salt $[CH_3PPh_3][BPh_4]$ and measurement of its ^1H and $^{31}P\{^1H\}$ NMR spectra [6]. The cation $[CH_3PPh_3]^+$ could form as a result of intramolecular methyl ligand transfer from the rhodium(III) to coordinated triphenylphosphine.

Thus, the main reaction occurring on action of triphenylphosphine on rhodium(III) methyl complexes can be described as reductive elimination

$$cis\text{-}[Rh(\beta\text{-diket})(PPh_3)_2(CH_3)(CH_3CN)][BPh_4] + PPh_3 \rightarrow Rh(\beta\text{-diket})(PPh_3)_2 + [CH_3PPh_3][BPh_4] + CH_3CN$$

Alongside with signals from the reaction products, the room-temperature $^{31}P\{^1H\}$ NMR spectrum of each of reaction mixtures shows signals corresponding to unconverted reactants, namely, the extremely broadened doublet centered at $\delta \sim 30$ ppm due to the initial rhodium(III) complex and the broadened singlet at δ −4.2 ppm from free triphenylphosphine (19.0 Hz as opposed to 4.0 Hz for individual PPh_3). The broadening of the last signal indicates that free triphenylphosphine takes part in an exchange process. Interestingly, signals of the rhodium(I) bisphosphine complexes in the spectra of reaction mixtures are as narrow as in the spectra of corresponding individual compounds (for instance, 4.5 Hz for [Rh(Acac)$(PPh_3)_2$]). Thus, it appears that no rhodium(I), but only rhodium(III) complexes are involved in the fast exchange with free phosphine in these conditions. Such behavior of the rhodium(I) complexes seems to be unusual, as square planar rhodium(I) complexes

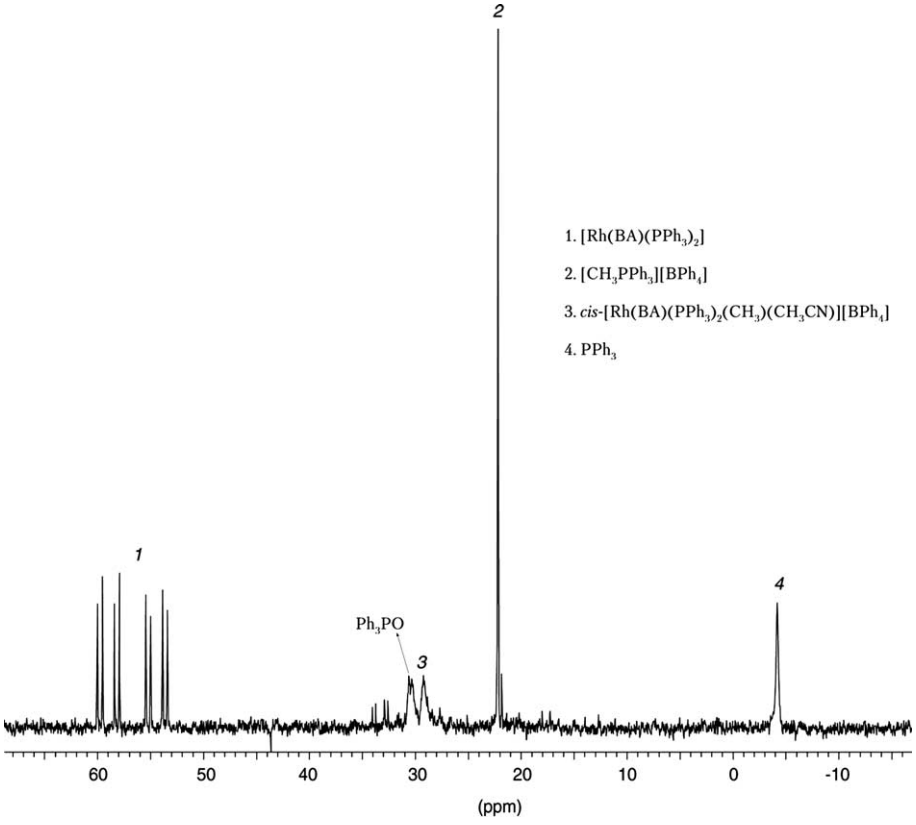


Fig. 2. The $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum of the reaction mixture {*cis*-[Rh(BA)$(PPh_3)_2(CH_3)(CH_3CN)$][BPh_4] + PPh_3} (1:1 mol) immediately after mixing of reactants.

generally are susceptible to a fast intermolecular exchange. As an example, the presence of free phosphine in a solution containing related monophosphine complex, [Rh(Acac)(PPh_3)(CO)], causes a fast exchange between free and coordinated triphenylphosphine, which leads to disappearance of the Rh–P coupling [39].

Reactions of *cis*-[Rh(β-diket)(PPh_3)$_2$(CH_3)(CH_3CN)]-[BPh_4] with triphenylphosphine were also carried out at a molar ratio PPh_3:Rh = 0.5. The $^{31}P\{^1H\}$ NMR spectra of these reaction mixtures are characterized by higher relative intensities of the signals from the initial rhodium(III) complexes.

The presence of signals of the initial rhodium(III) complexes and triphenylphosphine in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures implies that the reactions under discussion do not proceed to completion under these conditions. However, an elongation of reaction time led to the appearance of signals presumably related to products of decomposition of the formed rhodium(I) bisphosphine complexes, Rh(β-diket)(PPh_3)$_2$, as a result of their interaction with traces of oxygen (the singlet of phosphine oxide at δ 30.5 ppm) [40] and chlorinated solvent [36,41].

The reaction mixtures have been examined by ^1H NMR spectroscopy. As it could be expected, in the region δ 5–6.5 ppm we observed singlets from methine protons of β-diketonate ligands both of formed rhodium(I) complexes, 5.26 ppm (Acac) and 6.02 ppm (BA) [38], and of initial rhodium(III) complexes, 5.34 ppm (Acac) and 6.04 ppm (BA) [6]. The intensity of singlets from methine protons of rhodium(I) complexes increased with increasing PPh_3:Rh molar ratio in reaction mixtures.

In the region 1–2 ppm, where signals due to CH_3 groups of the initial complex and final products could be expected [6,38], the ^1H NMR spectra of the reaction mixtures were complicated owing to overlapping of numerous signals. The use of rhodium(III) complexes with a deuterated methyl ligand (D_3C–Rh) allowed us to identify a part of these signals. Thus, it was possible to distinguish a doublet due to the cation $[CH_3PPh_3]^+$ (δ 1.39 ppm, ^2J(HP) 12.7 Hz), and singlets of methyl groups of β-diketonate ligands in [Rh(β-diket)(PPh_3)$_2$]: δ 1.41 ppm (Acac) and 1.53 ppm (BA). In the spectra of reaction mixtures at a molar ratio PPh_3:Rh = 0.5, we could detect resonances of initial rhodium(III) complexes: broadened singlets due to methyl ligand, H_3C–Rh, at δ 1.90 ppm (Acac) and 2.04 ppm (BA), and sharp singlets due to methyl groups of the β-diketonate ligand at δ 1.70 (Acac) and 1.84 (BA). In the ^1H NMR spectra of 1:1 reaction mixtures, signals from the methyl ligand, CH_3–Rh, could not be detected, whereas the positions of sharp singlets at δ 1.70 ppm (Acac) and 1.84 ppm (BA) remained unchanged. We ascribe this peculiarity to chemical exchange processes in rhodium(III) complexes, which also were evidenced by the $^{31}P\{^1H\}$ NMR spectra.

3. Concluding remarks

In this work and in our previous paper [6], we have reported the reactions of the cationic methyl complexes *cis*-[Rh(β-diket)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] with several ligands of different nature, namely I^-, NH_3, pyridine, CO, PPh_3. As shown above, these complexes readily react with all these ligands at ambient temperature. The high rate of these reactions seems to be caused by the fact that the acetonitrile ligand is easily detached from the starting complex to give pentacoordinate moieties, which are involved into a fast interconversion. It suggests that in these reactions the first and the slowest stage of a substitution reaction occurs spontaneously on the dissolution of a starting compound, and hence the entire reaction has a very low activation barrier. It is worth noting that both NH_3 and pyridine derivatives are formed as a single isomer each. It is very likely that in the all cases an entering ligand does occupy the position *cis* to the CH_3 ligand. In the cases of ligands, which are subject to methylation (CO, PPh_3), this location is of the key importance because it provides a possibility for further transformations, namely migratory insertion or reductive elimination.

4. Experimental

4.1. Preparation of complexes

All operations were performed under an atmosphere of dry argon. The rhodium complexes *cis*-[Rh(Acac)-(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4], *cis*-[Rh(Acac)(PPh_3)$_2$-(CD_3)(CH_3CN)][BPh_4], *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3-CN)][BPh_4], *cis*-[Rh(BA)(PPh_3)$_2$(CD_3)(CH_3CN)][BPh_4] were synthesized by published procedures [6]. Gaseous CO was prepared by standard method [42]. Carbon monoxide enriched in ^{13}C (76.6%) was obtained from commercial sources. Solvents were dried and purified by known procedures [43] and distilled under argon. Elemental analyses were performed on a Hewlett–Packard 185 microanalyzer.

4.1.1. Preparation of cis-[Rh(Acac)(PPh_3)$_2$(CH_3)-(Py)][BPh_4] (1)

Mixture of *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (0.13 g, 0.11 mmol), excess pyridine (0.7 ml, 8.7 mmol) and methylene chloride (2 ml) was stirred at ambient temperature for 2 h. Then solvent and excess pyridine were removed in vacuo. Recrystallization from methylene chloride/diethyl ether provided yellow crystals of **1**. Yield: 0.10 g (77%). *Anal.* Calc. for $C_{71}H_{65}BNO_2P_2Rh$: C, 74.81; H, 5.75. Found: C, 74.31; H, 5.66%. ^1H NMR ($CDCl_3$): δ 6.8–7.5 (m, C_6H_5), 8,09 (s, 2H), 6.74 (s, 2H) (C_5H_5N), 1.78 (br s, 3H,

H_3C–Rh), 4.37 (s, 1H), 1.88 (s, 3H), 1.49 (s, 3H) ($OC(CH_3)CH(CH_3)CO$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.1 (dd, ^1J(PRh) 134.5 Hz, ^2J(PP) 35.2 Hz), 21.5 (dd, ^1J(PRh) 129.3 Hz, ^2J(PP) 35.2 Hz).

4.1.2. Preparation of trans-[Rh(Acac)(PPh_3)$_2$-($COCH_3$)][BPh_4] (2)

A stream of CO was passed through a solution of complex *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (0.30 g, 0.26 mmol) in methylene chloride (4 ml) for 15 min at ambient temperature. Then solvent was removed in vacuo, and yellow solid **2** was thus obtained. Yield: 0.26 g (91%). *Anal*. Calc. for $C_{67}H_{60}BO_3P_2Rh$: C, 73.90; H, 5.55. Found: C, 73.83; H, 5.75%. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 1726s. ^1H NMR ($CDCl_3$): 6.8–7.5 (m, C_6H_5), 5.67 (s, 1H), 1.73 (s, 6H) ($OC(CH_3)CH(CH_3)CO$), 2.27 (s, 3H, CH_3(CO)–Rh). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.5 (d, ^1J(PRh) 151.9 Hz). *trans*-[Rh(Acac)(PPh_3)$_2$($^{13}COCH_3$)][BPh_4] (**2**). ^1H NMR ($CDCl_3$): δ 6.8–7.5 (m, C_6H_5), 5.67 (s, 1H), 1.73(s, 6H) ($OC(CH_3)CH(CH_3)CO$), 2.27 (d, 3H, ^2J(HC) 5.8 Hz, $CH_3(^{13}CO)$–Rh). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 207.2 (dt, ^1J(CRh) 28.9 Hz, ^2J(CP) 6.2 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.5 (dd, ^1J(PRh) 151.9 Hz, ^2J(PC) 6.1 Hz).

4.1.3. Preparation of trans-[Rh(BA)(PPh_3)$_2$($COCH_3$)]-[BPh_4] (3)

A stream of CO was passed through a solution of the complex *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (0.47 g, 0.38 mmol) in methylene chloride (5 ml) for 20 min at ambient temperature. Then solvent was removed in vacuo, and yellow solid complex **3** was thus obtained as CH_2Cl_2 0.5:1 solvate. Yield: 0.44 g (97%). *Anal*. Calc. for $C_{72}H_{62}BO_3P_2Rh \cdot \frac{1}{2}CH_2Cl_2$: C, 72.96; H, 5.32. Found: C, 72.52; H, 5.38%. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 1728s. ^1H NMR ($CDCl_3$): δ 6.8–7.8 (m, C_6H_5), 6.44 (s, 1H), 1.85 (s, 3H), ($OC(CH_3)CH(C_6H_5)CO$), 2.47 (s, 3H, CH_3(CO)–Rh), 5.30 (s, 1H, $\frac{1}{2}CH_2Cl_2$, solvent molecules in the solvated crystals). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 31.0 (d, ^1J(PRh) 152.6 Hz).

4.1.4. Isomerization of trans-[Rh(Acac)(PPh_3)$_2$-($COCH_3$)][BPh_4] (2)

The solution of complex **2** (0.1 g, 0.09 mmol) in methylene chloride (1.5 ml) was stored for 24 h at ambient temperature. Then solvent was removed in vacuo. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 1726, 2060. ^1H NMR ($CDCl_3$): δ 6.8–7.5 (m, C_6H_5), 5.67 (s), 1.73 (s) ($OC(CH_3)CH(CH_3)CO$), 2.27 (s, CH_3(CO)–Rh) (complex **2**); 4.15 (s), 1.45 (s), 1.38 (s) ($OC(CH_3)CH(CH_3)$-CO), 1.32 (td, ^2J(HRh) 1.81 Hz, ^3J(HP) 4.90 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.5 (d, ^1J(PRh) 151.9Hz) (complex **2**), 24.3 (d, ^1J(PRh) 87.6 Hz); intensities of signals of **2** and resultant carbonyl complex are in ratio 1.7:1.

4.1.5. Isomerization of trans-[Rh(Acac)(PPh_3)$_2$-($^{13}COCH_3$)][BPh_4] (2′)

^1H NMR ($CDCl_3$): δ 6.8–7.5 (m, C_6H_5), 5.67 (s), 1.73 (s) ($OC(CH_3)CH(CH_3)CO$), 2.27 (d, $CH_3(^{13}CO)$–Rh, ^2J(HC) 5.8 Hz) (complex **2′**); 4.15 (s), 1.45 (s), 1.38 (s), 1.32 (td, ^2J(HRh) 1.81 Hz, ^3J(HP) 4.90 Hz). $^{31}P\{^1H\}$ ($CDCl_3$): δ 30.5 (dd, ^1J(PRh) 151.9 Hz, ^2J(PC) 6.1 Hz) (complex **2′**), 24.3 (dd, ^1J(PRh) 87.6 Hz, ^2J(PC) 13.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 207.2 (dt, ^1J(CRh) 28.9 Hz, ^2J(CP) 6.2 Hz) (complex **2′**); 186.2 (dt, ^1J(CRh) 61.9 Hz, ^2J(CP) 13.8 Hz).

4.1.6. Isomerization of trans-[Rh(BA)(PPh_3)$_2$-($COCH_3$)][BPh_4] (3)

The solution of complex **3** (0.1 g, 0.08 mmol) in methylene chloride (1.5 ml) was stored for 24 h at ambient temperature. Then solvent was removed in vacuo. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 1728, 2058. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.0 (d, ^1J(PRh) 152.6 Hz) (complex **3**), 24.8 (d, ^1J(PRh) 87.4 Hz), 24.4 (d, ^1J(PRh) 86.7 Hz); intensities of signals of **3** and resultant carbonyl complexes are in ratio 3:1.

4.1.7. The reaction 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] with PPh_3 in $CDCl_3$

$CDCl_3$ (0.6 ml) was added directly in the NMR tube to a mixture of complex *cis*-[Rh(Acac)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (0.014 g, 0.012 mmol) or complex *cis*-[Rh(BA)(PPh_3)$_2$(CH_3)(CH_3CN)][BPh_4] (0.016 g, 0.013 mmol) with appropriate amount of PPh_3 at ambient temperature. The mixtures was intensively shaken for 10–15 s and immediately after that transferred to NMR probe.

4.2. NMR and IR measurements

The NMR spectra were measured in deuterochloroform solutions at room temperature on Bruker AM-300 spectrometer operating in the Fourier-transform mode with noise proton decoupling for ^{31}P and ^{13}C. The ^1H and ^{13}C spectra were recorded with solvent as internal standards (δ ^1H of residual proton 7.25 ppm; δ ^{13}C 77.0 ppm in $CDCl_3$). The ^{31}P chemical shifts were measured with 85% phosphoric acid as external standard, δ ^{31}P 0.0 ppm. The IR spectra were recorded on a Specord 75 IR spectrometer.

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