Heterometallic cyanide-bridged complexes containing Rh^{I}Ru^{II}Rh^I triad: NMR data on exchange reactions and ligand effect transmission

Yu.S. Varshavsky [a,*], T.G. Cherkasova [a], M.R. Galding [a], V.N. Khrustalev [b], I.S. Podkorytov [a], V.A. Gindin [a], S.N. Smirnov [a], A.B. Nikol'skii [a]

[a] St. Petersburg State University, Inorganic Chemistry Department, Universitetskii pr. 26, Petrodvorets, St. Petersburg 198504, Russia
[b] Nesmeyanov Iinstitute of Organoelement Compounds, Vavilova Str., 28, Moscow 117813, Russia

ABSTRACT

Trans-[RuPy$_4$(CN)$_2$] cleaves chloro-rhodium bridges in rhodium(I) binuclear complexes, [Rh(CO)$_2$Cl]$_2$, [Rh(Cod)Cl]$_2$, and [(Cod)RhCl$_2$Rh(CO)$_2$] yielding heterometallic triad complexes, [(CO)$_2$ClRh(NC)Ru-Py$_4$(CN)RhCl(CO)$_2$] (**I**), [(Cod)ClRh(NC)RuPy$_4$(CN)RhCl(Cod)] (**II**), and [(Cod)ClRh(NC)RuPy$_4$(CN)RhCl(CO)$_2$] (**III**), respectively. In solutions, **III** coexists with equilibrium amounts of **I** and **II** in the near-binomial proportions. Under action of [Rh(CO)$_2$Cl]$_2$, **II** transforms into **I** with parallel formation of [Rh(Cod)Cl]$_2$. Ligand effect transmission along the L-Rh-NC-Ru-CN-Rh-L′ chain is studied by ^{1}H and ^{13}C NMR. Chemical shifts δ^1H and δ^{13}C of Ru-bound Py ligands are sensitive to the nature of Rh-bound ligands. Values of δ^1H and δ^{13}C of Cod and ^{13}C of CO ligands are sensitive to the ligands at the remote end of the L-Rh-NC-Ru-CN-Rh-L′ chain. Reaction of trans-[RuPy$_4$(CN)$_2$] with Rh$_2$(OAc)$_4$ yields an apparently linear polymer [-Rh(OAc)$_4$Rh-NCRuPy$_4$CN-]. Upon action of [Rh(CO)$_2$Cl]$_2$, the polymer decomposes yielding **I** and Rh$_2$(OAc)$_4$. X-ray structure data for **I** are given.

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1. Introduction

During the last two decades, transition metal cyanide complexes have attracted considerable interest as organonitrile-like metalloligands, L$_x$M-CN. Entering the coordination sphere of another metal, M′, such a metalloligand forms a cyanide-bridged binuclear complex, M-CN-M′ [1]. Dicyanide complexes, NC-(L$_x$M)-CN, being capable of forming two cyanide bridges, are widely used as building blocks in the construction of metallocyanide chains consisting of M-NC-M′-CN- fragments. The key concepts concerning cyanide-bridged transition metal complexes and a variety of strategies to synthesize them were thoroughly discussed in the literature (see e.g. [2–15] and numerous refs. therein). One may mark, however, that contrary to the great body of the X-ray structural, magnetic, UV–Vis spectral, and electrochemical ox/red characteristics of polynuclear cyanide-bridged complexes, only meagre data on their NMR spectra, reactivity in solutions, and ligand effects transmission are available. In this paper we used ^{1}H and ^{13}C chemical shift values of ligand nuclei as a probe of sensibility of each specific atom or group in the central and terminal units of triad to variations in its remote parts. The presented data demonstrate subtle but clearly defined remote ligand effects transferred along the L-Rh-NC-Ru-CN-Rh-L′ chain.

We report here on new complexes belonging to the triad family Rh^I(NC)Ru^{II}(CN)Rh^I, namely [(CO)$_2$ClRh(NC)RuPy$_4$(CN)RhCl(CO)$_2$] (**I**) and [(Cod)ClRh(NC)RuPy$_4$(CN)RhCl(Cod)] (**II**), as well as a "hybrid" complex [(Cod)ClRh(NC)RuPy$_4$(CN)RhCl(CO)$_2$] (**III**), which, in solutions, is in equilibrium with **I** and **II**. Reactions of the terminal fragments exchange including transformation of **II** and **III** into **I** under the action of [Rh(CO)$_2$Cl]$_2$ are also described. The preliminary data on these complexes including their spectral (IR and ^{13}C NMR) parameters and X-ray data for **I** were briefly reported in our presentations [16]. The first example of the family, [(Cod)ClRh(NC)Ru(Bu^{t}NC)$_4$(CN)RhCl(Cod)], has been structurally characterized recently [17].

2. Results and discussion

Ruthenium(II) dicyanide complex, trans-[RuPy$_4$(CN)$_2$], readily reacts with [Rh(CO)$_2$Cl]$_2$ in chloroform solution cleaving chloro-rhodium bridges to form heterometallic triad complex [(CO)$_2$ClRh(NC)RuPy$_4$(CN)RhCl(CO)$_2$] (**I**) in high yield:
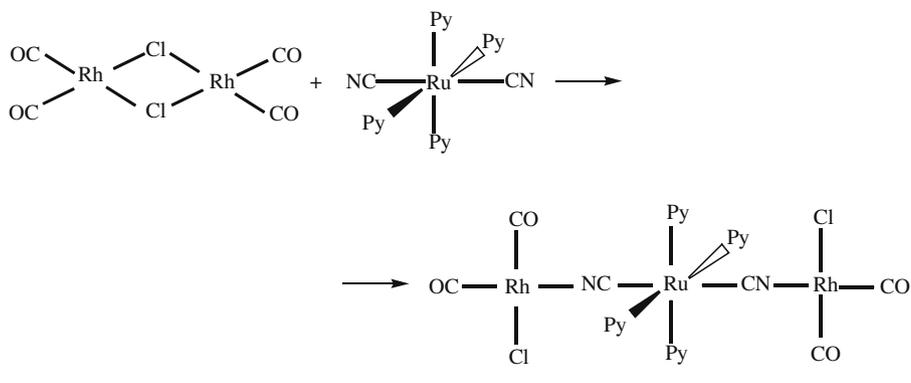
In this reaction, ruthenium(II) complex behaves like organodinitriles, NC-{R}-CN, which convert $[Rh(CO)_2Cl]_2$ into $[(CO)_2ClRhNC-\{R\}-CNRhCl(CO)_2]$ [18]. The IR and NMR spectral parameters of $RhCl(CO)_2$ fragments in **I** are typical for rhodium(I) dicarbonyl complexes: two strong $\nu(CO)$ stretching bands in the IR spectrum (CHCl$_3$ solution) separated by 70 cm^{-1}, at 2086 cm^{-1} (*sym*) and 2016 cm^{-1} (*asym*); two doublets from non-equivalent carbonyl carbons in the ^{13}C NMR spectrum (CDCl$_3$ solution), δ 183.4 ppm, $^1J(CRh)$ 66.4 Hz and δ 180.4 ppm, $^1J(CRh)$ 71.8 Hz with additional doublet splitting of each doublet in the spectrum of highly ^{13}C enriched preparation, $^2J(CC)$ ~6 Hz. On the basis of the lower $^1J(CRh)$ value [19,20] for the doublet at 183.4 ppm, we assign it to the carbonyl carbon *trans* to cyanide nitrogen.

As usually observed, the $\nu(CN)$ stretching frequency of bridging cyanide groups in the spectrum of **I** (2100 cm^{-1} in CHCl$_3$) is markedly higher as compared with the value for terminal CN groups in the starting *trans*-$[RuPy_4(CN)_2]$, 2058 cm^{-1} in CHCl$_3$ (2062 cm^{-1} in KBr pellet [14]). The increase in $\nu(CN)$ values upon bridging two metal atoms was discussed widely, but the issue seems to remain far from clarity; for references, criticism, and some new ideas see [21]. The ^{13}C resonance of cyanide carbons in the spectrum of **I** appears in the normal spectral region [22], at 172.2 ppm, (2C, d), $^2J(CRh)$ ~6 Hz and is close to the ^{13}C resonance in the spectrum of *trans*-$[RuPy_4(CN)_2]$, 168.4 ppm (singlet).

Pyridine proton chemical shifts in the spectrum of **I** (in CDCl$_3$) are usual for pyridine ligand and close to the values for "free" *trans*-$[RuPy_4(CN)_2]$ [14]). Chemical shifts of pyridine carbons in the spectrum of **I** are also close to the values for $[RuPy_4(CN)_2]$.

The X-ray data for **I** presented below (Fig. 1 and Table 1) show typical octahedral coordination for ruthenium(II) and planar tetragonal coordination for rhodium(I) centers.

Four pyridine ligands are posed in the usual propeller orientation around ruthenium atom with Ru–N distances close to those in free *trans*-$[RuPy_4(CN)_2]$ [14]. The RuCN, CRuC, and CNRh angles in **I** (average values are given), ~173.0(2)°, 174.43(8)°, and ~170.3(2)°, respectively, are all considerably reduced from 180°. Thus the NCRuCN fragment in **I** is far from the perfectly linear configuration observed [14] in the solvated ruthenium complex, *trans*-$[RuPy_4(CN)_2]$·2MeCN. The most notable deflections show CNRh angles, 171.3(2)° and 169.3(2)°, which values fall in-between those found for (Cod)ClRhNC and (CO)$_2$ClRhNC fragments in the structures studied earlier [17,23]. Accumulation of these unidirectional deflections, together with those of RhCO (~177.5(2)° for *trans*-N carbonyl groups) and CRhN (~175.44(8)°) angles, makes the (OC)Rh(NC)Ru(CN)Rh(CO) chain markedly bow-shaped, what, to some extent, can be seen also in the structure [(Cod)ClRh(NC)-Ru(Bu^{t}NC)$_4$(CN)RhCl(Cod)] [17]. Contrary to *anti*-(Cl, Cl) configuration in the last structure, chlorido ligands in **I** are nearly *syn*-
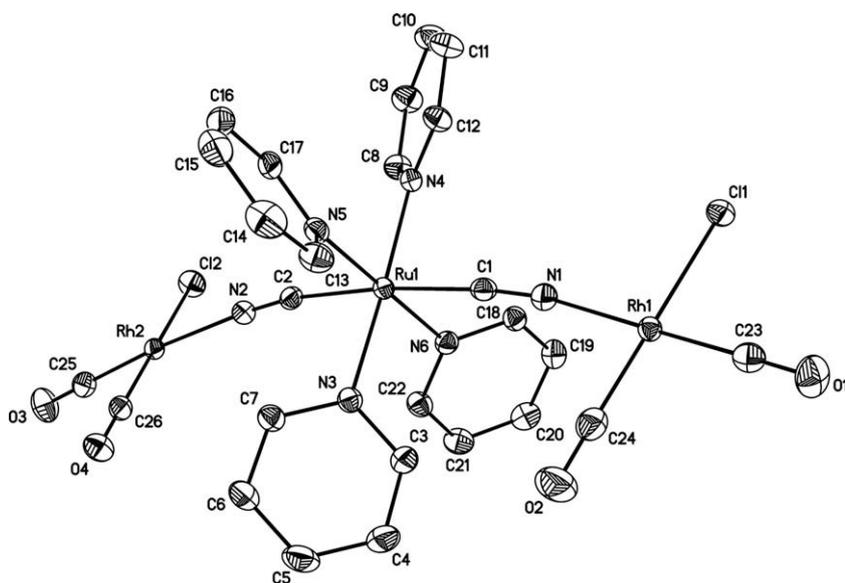

Fig. 1. Molecular structure of $[(CO)_2ClRh(NC)RuPy_4(CN)RhCl(CO)_2]$ (**I**). Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for the complex [(CO)₂ClRh-(NC)RuPy₄(CN)-RhCl(CO)₂] (**I**) with estimated standard deviations in parentheses.

Bond lengths (Å)		Bond angles (°)	
Rh(1)–C(23)	1.850(2)	C(23)Rh(1)C(24)	89.18(9)
Rh(2)–C(25)	1.845(2)	C(25)Rh(2)C(26)	91.55(9)
Rh(1)–C(24)	1.842(2)	C(23)Rh(1)Cl(1)	91.26(6)
Rh(2)–C(26)	1.855(2)	C(25)Rh(2)Cl(2)	86.45(7)
Rh(1)–N(1)	2.046(2)	C(23)Rh(1)N(1)	176.03(8)
Rh(2)–N(2)	2.064(2)	C(25)Rh(2)N(2)	174.84(8)
Rh(1)–Cl(1)	2.3560(5)	C(24)Rh(1)Cl(1)	179.37(8)
Rh(2)–Cl(2)	2.3492(5)	C(26)Rh(2)Cl(2)	177.67(6)
O(1)–C(23)	1.136(3)	Rh(1)C(23)O(1)	178.0(2)
O(3)–C(25)	1.131(3)	Rh(2)C(25)O(3)	177.0(2)
O(2)–C(24)	1.116(3)	Rh(1)C(24)O(2)	178.7(2)
O(4)–C(26)	1.130(3)	Rh(2)C(26)O(4)	178.8(2)
Ru(1)–C(1)	2.018(2)	C(24)Rh(1)N(1)	89.67(9)
Ru(1)–C(2)	2.041(2)	C(26)Rh(2)N(2)	89.97(8)
Ru(1)–N(Py) avg	2.097(2)	N(1)Rh(1)Cl(1)	89.92(5)
		N(2)Rh(2)Cl(2)	91.92(5)
N(1)–C(1)	1.162(3)	C(1)N(1)Rh(1)	171.3(2)
N(2)–C(2)	1.154(3)	C(2)N(2)Rh(2)	169.4(2)
		C(1)Ru(1)C(2)	174.43(8)
		Ru(1)C(1)N(1)	174.4(2)
		Ru(1)C(2)N(2)	171.5(2)

oriented. Owing to relatively short intermolecular metal-metal separations (3.1570(2) Å (cf. 3.317(2) Å for intermolecular and 3.136(2) Å for intramolecular contacts in the [Rh(CO)₂Cl]₂ crystal [25]), molecules I form an infinite ladder-shaped sequence along the c-axis of the crystal (Fig. 2). The geometric and IR characteristics of the tetragonal dicarbonyl rhodium fragments, (CO)₂ClRhNC, in I are close to the corresponding data for di- and trinuclear rhodium–manganese complexes containing the same structural unit [24].

Similarly, trans-[RuPy₄(CN)₂] readily reacts with binuclear chloro bridged rhodium(I) complex, [Rh(Cod)Cl]₂ (Cod = cyclo-octadiene-1,5), to give triad complex [(Cod)ClRh(NC)RuPy₄(CN)-RhCl(Cod)] (**II**). The cyanide stretching frequencies and ¹³C (CN), ¹³C (pyridine) and ¹H (pyridine) chemical shifts are very close to those for **I** (see Section 3). The ¹H NMR spectrum of Cod ligand is typical for Cod complexes: two singlets from the protons of two non-equivalent (trans-Cl and trans-N) HC=CH groups, 3.93 ppm (4H) and 4.39 ppm (4H), and two multiplets from methylene group protons, 2.38 ppm (8H) and 1.73–1.72 ppm (8H). The ¹³C spectrum also exhibits two different signals from olefin groups (trans-Cl and trans-N), both being split into doublets due to the ¹³C¹⁰³Rh spin–spin coupling: 75.55 ppm (4C), ¹J(CRh) 13.5 Hz and 82.72 ppm (4C), ¹J(CRh) 11.5 Hz; methylene carbons show singlets at 31.10 ppm (4C) and 30.38 ppm (4C). The non-equivalence of two kinds of methylene carbons in **II** indicates that methylene groups are sensitive to the trans-Cl versus trans-N position of the adjacent olefine group. Similar spectral patterns were observed [26] for
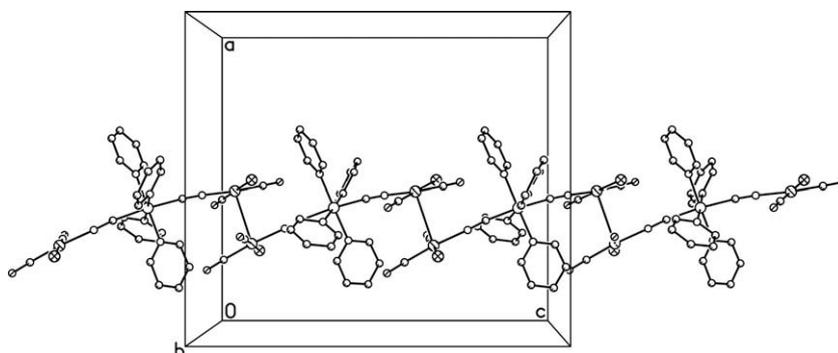

Fig. 2. A fragment of the crystal packing of [(CO)₂ClRh(NC)RuPy₄(CN)RhCl(CO)₂] (**I**) along c-axis demonstrating the infinite ladder-shaped sequence.
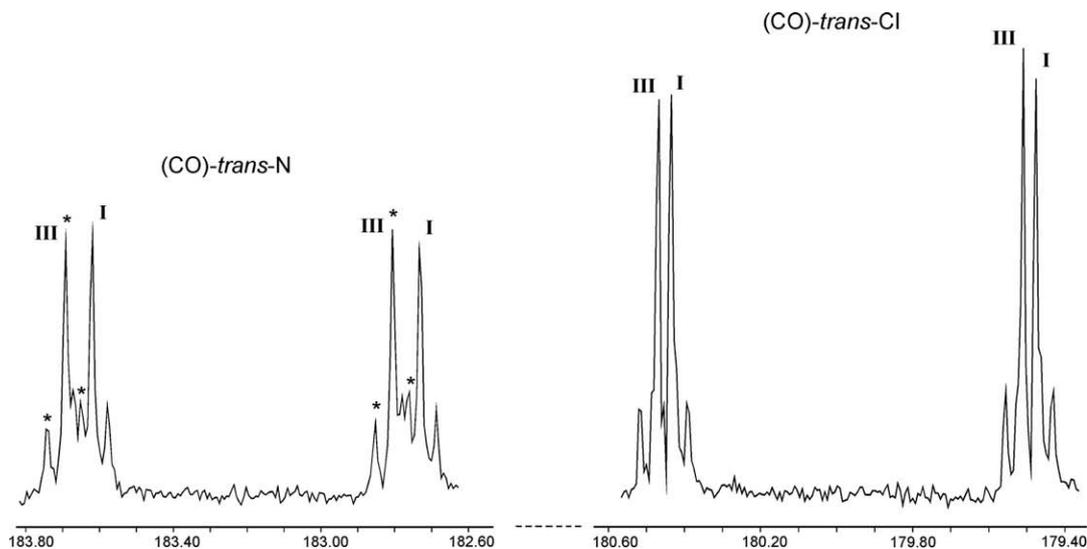
Fig. 3. 75 MHz ¹³C{¹H} NMR spectra of the equilibrium solution of [(Cod)ClRh(NC)RuPy₄(CN)RhCl(CO)₂] (**III**) in the carbonyl carbon area (−30 °C, solvent CDCl₃, ¹³C enrichment ~40%). In the (CO)-trans-N part, where the ¹³C¹³C splitting is better pronounced; the components of intense doublet from the ¹²C¹³C isotopomer of [(Cod)ClRh(NC)RuPy₄(CN)RhCl(CO)₂] (**III**) and of corresponding doublet of doublets from its ¹³C¹³C isotopomer are marked with asterisks.

other rhodium(I) cyclooctadiene complexes with *trans*-Cl and *trans*-N olefinic groups.

Unexpectedly, ^{1}H NMR spectrum of the 1:1 molar ratio mixture {**II** + [Rh(CO)$_2$Cl]$_2$} in chloroform showed only one olefin proton signal, 4.21 ppm, from equivalent HC≡CH groups of Cod ligand symmetrically coordinated in [Rh(Cod)Cl]$_2$ complex [27]. The IR spectrum of the mixture displayed only CO stretching bands of **I**, 2086 and 2016 cm^{-1}, and no absorption maxima distinctive for the starting dimeric rhodium(I) carbonyl chloride, 2104, 2092, and 2036 cm^{-1}. These observations suggest that the ligand exchange reaction in this case is virtually irreversible:
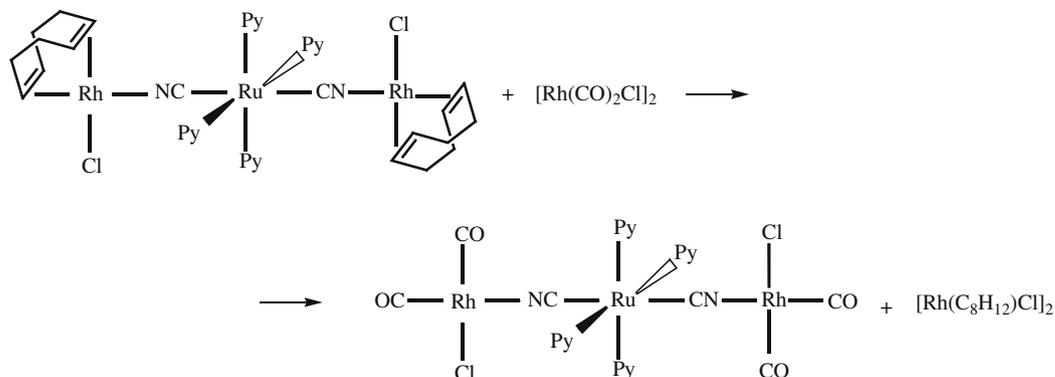

Trans-[RuPy$_4$(CN)$_2$] readily cleaves chloro bridges in other rhodium(I) binuclear complexes. Specifically, with an asymmetrical ("hybrid") complex, [Rh(Cod)Cl$_2$Rh(CO)$_2$] [28–30], it yields [(Cod)ClRh(NC)RuPy$_4$(CN)RhCl(CO)$_2$] (**III**). The NMR spectra of **III** resemble combinations of the spectra **I** and **II**, but at ambient temperature all ^{1}H and ^{13}C NMR signals appear broadened and ill-resolved which is indicative of a dynamic behaviour. The

and **III**, are very close, the signals are clearly discernible in the recorded spectra and may be unambiguously assigned to these three species (see Section 3 and Fig. 3).

The slight but distinct spectral differences between three complexes reflect the transfer of the ligand effects along the chain L-Rh-NC-Ru-CN-Rh-L'. The action of [Rh(CO)$_2$Cl]$_2$ on the hybrid triad complex **III** proceeds like the reaction (*) leading to gathering the dicarbonyl units in the symmetrical RhRuRh triad, and Cod units in the [Rh(Cod)Cl]$_2$ dimer.

On stirring the dirhodium(II)tetraacetate suspension in a chloroform solution of *trans*-[RuPy$_4$(CN)$_2$], the initial sea-green colour of the suspension changed to lilac. The lilac solid product so

formed is insoluble in every solvent we tried. Its elemental analysis is consistent with 1:1 ratio of reactants, and we formulate it tentatively as a linear polymer [-Rh(OAc)$_4$Rh-NCRuPy$_4$CN-]$_n$. This kind of Rh(OAc)$_4$Rh unit coordination is well documented, see e.g. [31,32]. Rhodium(I) dicarbonyl complex easily disrupts rhodium(II)-cyano nitrogen bonds in the chain polymer complex yielding **I** with recovery of unchanged dirhodium(II)tetraacetate:
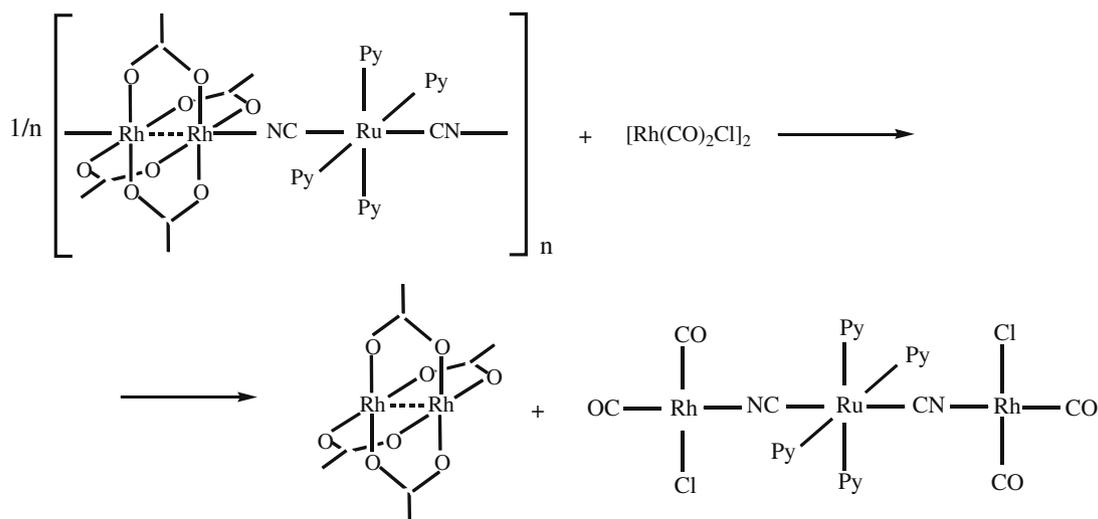
examination of the ^{1}H and ^{13}C NMR spectra of **III** in the CHCl$_3$ solution measured at −30 °C evidenced the presence of three complexes in the near-binomial proportion, **III** (predominant form), **I**, and **II**, and allowed us to determine spectral parameters of **III**. Although the chemical shifts δ[1]H and δ^{13}C for Py ligands in **I**, **II**, and **III**, as well as the values of δ^{13}C for CO ligands in the spectra of **I** and **II** and δ[1]H and δ^{13}C for Cod ligand in the spectra of **II**

3. Experimental

All operations were carried out in a dry argon atmosphere using classical Schlenk techniques. All solvents were purified according to the standard procedures [33]. [RuPy$_4$(CN)$_2$], [Rh(CO)$_2$Cl]$_2$, [Rh(Cod)Cl]$_2$, [Rh(Cod)Cl$_2$Rh(CO)$_2$] and [Rh$_2$(OAc)$_4$] were prepared by the published procedures [[14,34,27,29,35], respectively]. The

^{13}C-enriched samples of carbonyl complexes were produced using an enriched sample of $[Rh(CO)_2Cl]_2$ prepared by action of 40–99% enriched ^{13}CO on a solution of $[Rh(C_2H_4)_2Cl]_2$ [36] in benzene. The ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on Bruker spectrometers DPX-300 and AM-500 at 300 and 500 MHz for ^1H; 75 and 125 MHz for ^{13}C, respectively, using CDCl$_3$ as solvent. The ^1H and ^{13}C chemical shifts were measured with solvent as internal standard (δ^1H 7.25 ppm; $\delta^{13}C$ 77.0 ppm) and referenced to TMS. IR spectra (CHCl$_3$ solutions and Nujol mulls) were recorded on a Specord 75 IR instrument. Elemental analyses were performed by Dr. E.G. Rumjanceva with Hewlett–Packard 185 microanalyzer.

3.1. $[(CO)_2ClRhNCRuPy_4CNRhCl(CO)_2]$ (I)

The solution of $[Rh(CO)_2Cl]_2$ (0.116 g, 0.3 mmol) in CHCl$_3$ (5 ml) was added to the solution of *trans*-$[RuPy_4(CN)_2]$ (0.14 g, 0.3 mmol) in CHCl$_3$ (5 ml). In 40 min the solvent was removed under reduced pressure, diethyl ether was added to the residue, and the yellow crystalline solid was transferred to a filter. After filtration, the product was washed with diethyl ether (2 × 5 ml) and dried *in vacuo*. Yield 0.23 g (90%). Anal. Found: C, 36.30; H, 2.23; Cl, 8.09; N, 9.98%. Calc. for $C_{26}H_{20}Cl_2N_6O_4Rh_2Ru$: C, 36.38; H, 2.35; Cl, 8.26; N, 9.79%. IR (in CHCl$_3$): ν(CN) 2100 cm^{-1}; ν(CO) 2086, 2016 cm^{-1} (natural ^{13}C abundance); For the sample with 99% ^{13}CO enrichment: ν(CN) 2100 cm^{-1}; ν(CO) 2038, 1970 cm^{-1}. NMR (ppm, Hz, CDCl$_3$): $\delta^{13}C$ (carbonyl) 183.4, ^1J(CRh) 68.2; 180.4, ^1J(CRh) 71.8, ^2J(CC) 6; $\delta^{13}C$ (Py) 157.11 (8C, $C^{2,6}$), 136.22 (4C, C^4), 125.06 (8C, $C^{3,5}$); $\delta^{13}C$ (CN) 172.2, (2C, d) ^2J(CRh) 6.0; δ^1H (Py) 8.51 (8H, d, $H^{2,6}$), 7.66 (4H, t, H^4), 7.15 (8H, t, $H^{3,5}$). Complex I is soluble in benzene, methylene chloride, hexane and is stable on storage in an inert gas atmosphere.

Crystals of I suitable for X-ray analysis were obtained by dethyl ether diffusion into chloroform solution of I.

3.2. $[(Cod)ClRhNCRuPy_4CNRhCl(Cod)]$ (II)

$[RhCod)Cl]_2$ (0.148 g, 0.3 mmol) was added to the solution of *trans*-$[RuPy_4(CN)_2]$ (0.14 g, 0.3 mmol) in CHCl$_3$ (5 ml). In 40 min the solvent was removed under reduced pressure, to the residue was added diethyl ether, and the yellow crystalline solid was transferred to the filter. After filtration the product was washed with diethyl ether (2 × 5 ml) and dried *in vacuo*. Yield 0.24 g (92%). Anal. Found: C, 47.50; H, 4.53; Cl, 7.30; N, 8.77%. Calc. for $C_{38}H_{44}Cl_2N_6O_4Rh_2Ru$: C, 47.41; H, 4.61; Cl, 7.37; N, 8.73%. IR: ν(CN) 2096 cm^{-1} (in CHCl$_3$); 2094 cm^{-1} (in Nujol). NMR (ppm, Hz, CDCl$_3$): $\delta^{13}C$ (Py) 157.17 (8C, $C^{2,6}$), 135.62 (4C, C^4), 124.69 (8C, $C^{3,5}$); $\delta^{13}C$ (CN) 170.1, (2C, d) ^2J(CRh) 6.0; $\delta^{13}C$ (Cod) 82.59 (4C, d, CH), ^1J(CRh) 12.0, 75.19 (4C, d, CH), ^1J(CRh) 13.5, 31.29 (4C, s, CH$_2$), 30.54 (4C, s, CH$_2$); δ^1H (Py) 8.50 (8H, d, $H^{2,6}$), 7.59 (4H, t, H^4), 7.09 (8H, t, $H^{3,5}$); δ^1H (Cod) 4.39 (4H, s, HC), 3.93 (4H, s, HC), 2.38 (8H, m, CH$_2$), 1.73–1.72 (8H, m, CH$_2$). Complex II is soluble in benzene and methylene chloride and is stable on storage in an inert gas atmosphere.

3.3. Interaction of $[(Cod)ClRhNCRuPy_4CNRhCl(Cod)]$ (II) with $[Rh(CO)_2Cl]_2$

$[Rh(CO)_2Cl]_2$ (0.027 g, 0.07 mmol) was added to the solution of II, $[(Cod)ClRhNC\{RuPy_4\}CNRhCl(Cod)]$, (0.067 g, 0.07 mmol) in CHCl$_3$ (3 ml). In 40 min the solvent was removed under reduced pressure. IR (in CHCl$_3$): ν(CN) 2098sh cm^{-1}; ν(CO) 2086, 2016 cm^{-1} (natural ^{13}C abundance). For the sample with 99% ^{13}CO enrichment: ν(CN) 2100 cm^{-1}; ν(CO) 2038, 1970 cm^{-1}. NMR spectra (ppm, Hz, CDCl$_3$) of the residue solution correspond to the mixture of I (*vide supra*, Section 3.1) and [Rh(Cod)Cl]$_2$, δ^1H, ppm: 4.21 (8H, s, HC), 2.47 (8H, m, CH$_2$), 1.73–1.74 (8H, m, CH$_2$).

3.4. $[(Cod)ClRh(NC)RuPy_4(CN)RhCl(CO)_2]$ (III)

$[(Cod)RhClClRh(CO)_2]$ (0.066 g, 0.15 mmol) was added to the solution of *trans*-$[RuPy_4(CN)_2]$ (0.07 g, 0.15 mmol) in CHCl$_3$ (3 ml). In 40 min the solvent was removed under reduced pressure. IR of the residue (in CHCl$_3$): ν(CN) 2098 cm^{-1}; ν(CO) 2086, 2016 cm^{-1}. For the sample with 99% ^{13}CO enrichment: ν(CN) 2096 cm^{-1}; ν(CO) 2039, 1966 cm^{-1}. NMR (ppm, Hz, CDCl$_3$, ambient temperature): $\delta^{13}C$ 183.4, ^1J(CRh) 66.4, $\delta^{13}C$ 180.4, ^1J(CRh) 71.8. The both signals are broad, with unresolved CC coupling. At -30 °C, in the spectrum of the ~40% ^{13}C enriched sample the carbonyl carbon resonances showed better resolution, enhanced further by Lorentz to Gauss transformation, and were assigned to the complexes I and III; carbonyl carbons (ppm, Hz) $\delta 13C$, ^1J(CRh), and ^2J(CC): 183.15, 67.3 and 179.95, 72.3 for I; 183.24, 66.8 and 180.00, 72.3 for III, ^2J(CC) ~6.0, for all *cis*-Rh(CO)$_2$ fragments (see Fig. 3). The assignments was proved by the increase of the relative intensities of the signals assigned to I upon addition excess $[Rh(CO)_2Cl]_2$ (0.25 mol per 1 mol III) to the equilibrium solution of III. The ^{13}C (Py) resonances from three complexes appeared: at 156.80 with two unresolved shoulders ($C^{2,6}$); at 135.94 (predominant, III), 136.22 (I), and 135.65 (II) ppm (C^4); at 124.87 (predominant, III), 125.05 (I), and 124.69 (II) ppm ($C^{3,5}$). ^1H (Py): partially resolved, superimposed groups of signals at 8.49 (8H, $H^{2,6}$), 7.64 (4H, H^4), and 7.14(8H, $H^{3,5}$) ppm; δ^1H (Cod): 4.37 (2H, s, HC); 3.93 (2H, s, HC), 2.36 (4H, m, CH$_2$), 1.73–1.68 (4H, m, CH$_2$). All values assigned to the complexes I and II agreed well with the data for individual I and II at -30 °C.

3.5. $[-Rh(OAc)_4Rh-NCRuPy_4-CN-]_n$

$[Rh_2(OAc)_4]$ (0.088 g, 0.2 mmol) was added to the solution of $[RuPy_4(CN)_2]$ (0.094 g, 0.2 mmol) in CHCl$_3$ (3 ml). On stirring, the green starting solid suspended in the reaction mixture gradually transformed into a lilac precipitate. After stirring the reaction mixture for 2 h, the lilac product was separated by filtration, washed with diethyl ether, and dried *in vacuo*. Yield 0.16 g (87.9%). Anal. Found: C, 39.30; H, 3.67; N, 9.22. Calc. for $C_{38}H_{44}N_6O_{16}Rh_2Ru$: C, 39.53; H, 3.54; N, 9.22. IR (in Nujol): ν(COO) 1600, 1448, 1428 cm^{-1}; ν(CN) 2082sh, 2066 cm^{-1}.

$[RuPy_4(CN)_2Rh_2(OAc)_4]_n$ (0.045 g, 0.05 mmol) was added to the solution of $[Rh(CO)_2Cl]_2$ (0.0194 g, 0.05 mmol) in CHCl$_3$ (2 ml). On stirring the suspension, the starting lilac solid dissolved rapidly, the solution turned green, and the green precipitate of $[Rh_2(OAc)_4]$ formed. The IR spectrum of the resulting solution coincided with the spectrum of the reference solution prepared from complex I.

3.6. X-ray crystal structure determination

Crystal of I ($C_{26}H_{20}Cl_2N_6O_4Rh_2Ru$, $M = 858.27$) orthorhombic, space group *P*bca, at $T = 100$ K: $a = 17.8821(5)$, $b = 16.5594(9)$, $c = 20.5639(11)$ Å, $V = 6089.3(5)$ Å^3, $Z = 8$, $F(0\,0\,0) = 3344$, $d_{calc} = 1.872$ g/cm^3, $\mu = 1.778$ mm^{-1}. Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1K CCD detector (λ(MoKα)-radiation, graphite monochromator, φ and ω scan mode, $\theta_{max.} = 30°$) and corrected for Lorentz and polarization effects and for absorption [37]. The structure was determined by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined in riding mode with fixed thermal parameters. The final *R*-factors are $R_1 = 0.0221$ for 7282 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0507$ for all 8925 independent reflections. All calculations were carried out using the SHELXTL PLUS program (PC Version 5.10) [38].

Appendix A. Supplementary material

CCDC 705030 contains the supplementary crystallographic data for **I**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.028.

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