Syntheses and characterization of a series of carbonylruthenium(I) and (II) complexes containing pyridyl ligands

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Abstract

The reaction of dodecacarbonyltriruthenium ($Ru_3(CO)_{12}$) with tris(2-pyridylmethyl)ammonium perchlorate ($tpa \cdot 3HClO_4$) in toluene, in the presence of acetic acid, produced a new ruthenium(II) complex of tpa $[Ru(CH_3CO_2)(CO)(tpa)]ClO_4 \cdot C_6H_5CH_3$ (**1**). A similar reaction of $Ru_3(CO)_{12}$ with 2-pyridylcarboxylic acid ($pyCO_2H$) in toluene yielded a ruthenium(II) complex $Ru(pyCO_2)_2(CO)_2$ (**2**). A related ruthenium(III) compound, $[Ru(pyCO_2)_3] \cdot H_2O$ (**3**), was obtained from the reaction of $RuCl_3 \cdot nH_2O$ and sodium 2-pyridinecarboxylate in a mixture of water and ethanol (1:1 by volume). The reaction of $Ru_3(CO)_{12}$, benzoic acid and pyridine (py) in toluene resulted in the formation of a dinuclear ruthenium(I) complex $[Ru_2(C_6H_5CO_2)_2(CO)_4(py)_2] \cdot 0.5C_6H_5CH_3$ (**4**). Compounds **1–4** have been characterized by IR, NMR and X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium complexes; Pyridyl complexes; Carboxylate complexes; Carbonyl complexes

1. Introduction

It has been known that the reactions of dodecacarbonyltriruthenium $Ru_3(CO)_{12}$, with carboxylic acids RCO_2H, produce polymeric compounds $[Ru_2(RCO_2)_2(CO)_4]_n$, which undergo depolymerization when reacting with monodentate ligands L such as tertiary phosphines to give dimers $Ru_2(RCO_2)_2(CO)_4L_2$ [1–3]. When a didentate nitrogen-containing ligand (L') like 2,2'-bipyridine (bpy) is reacted, the formation of mononuclear ruthenium(II) carbonyl complexes $Ru(RCO_2)_2(CO)_2L'$ with cis(CO)-$trans$(RCO_2) configuration, was claimed on the basis of spectroscopic data [4]. The mononuclear complexes were previously prepared from the reaction of $RuCl_2(CO)_2L'$ with silver carboxylates [5]. Similarly, $Ru(CH_3CO_2)_2(CO)_2(py)_2$ was prepared from $RuCl_2(CO)_2(py)_2$ whose geometric configuration was suggested to be $trans$(Cl)-cis(CO)-cis(py). The geometrical structure of $Ru(CH_3CO_2)_2(CO)_2(py)_2$, i.e. cis or $trans$ with respect to the pyridine ligands, could not be determined from the spectroscopic properties [5].

The direct reactions of $Ru_3(CO)_{12}$ with pyridine and polydentate nitrogen-containing ligands in the presence of carboxylic acid, which could provide a convenient route to the above pyridyl carbonyl carboxylate com-
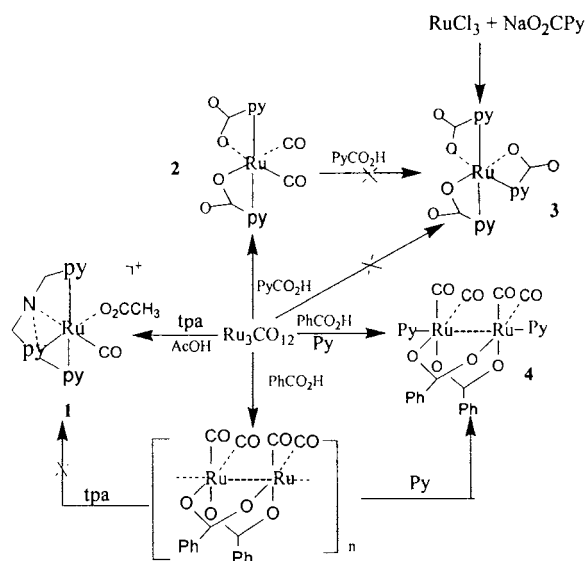
Scheme 1. Schematic view of syntheses of compounds **1–4**.

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plexes of ruthenium, have not been investigated in detail. This work deals with the reactions of dodecacarbonyltriruthenium with tris(2-pyridylmethyl)ammonium perchlorate (tpa·3HClO$_4$) in the presence of acetic acid and with 2-pyridinecarboxylic acid (pyCO$_2$H). Two new mononuclear ruthenium(II) carbonyl complexes [Ru(CH$_3$CO$_2$)(CO)(tpa)]ClO$_4$·C$_6$H$_5$CH$_3$ (**1**) and Ru(pyCO$_2$)$_2$(CO)$_2$ (**2**), respectively, were obtained. Compound **1**, which has appeared as a preliminary communication [6], represents the first example of ruthenium carbonyl complexes of tpa, although several ruthenium [7–11] and metal carbonyl complexes [12] containing tpa have been reported. The tris(pyridinecarboxylato)ruthenium(III) complex [Ru(pyCO$_2$)$_3$]·H$_2$O (**3**) was not obtained from the latter reaction, but was assessable by a quite different method. Preparation and structural studies of the dimeric pyridine derivative [Ru$_2$(C$_6$H$_5$CO$_2$)$_2$(CO)$_4$(py)$_2$]·0.5C$_6$H$_5$CH$_3$ (**4**), will also be presented in view of the absence of its structural data in the literature.

2. Results and discussion

2.1. Synthesis

Syntheses of compounds **1**–**4** are shown in Scheme 1. The pyridine complex of carbonyl ruthenium(I) Ru$_2$(C$_6$H$_5$CO$_2$)$_2$(CO)$_4$(py)$_2$ (**4**), was obtained by refluxing a mixture of Ru$_3$(CO)$_{12}$, benzoic acid and pyridine in toluene under argon atmosphere. The red–brown solution became yellow in color after several minutes, indicative of the rapid oxidation of the Ru(0) carbonyl by the acid. Evaporation of the resulting yellow solution in an open beaker led to the formation of the yellow crystals of [Ru$_2$(C$_6$H$_5$CO$_2$)$_2$(CO)$_4$(py)$_2$]·0.5C$_6$-H$_5$CH$_3$ (**4**) in about an 80% yield. Such dimeric pyridine derivatives were previously prepared from the reaction of Ru$_2$(C$_6$H$_5$CO$_2$)$_2$(CO)$_6$ or [Ru$_2$(CH$_3$CO$_2$)$_2$-(CO)$_4$]$_n$ with pyridine [1,3]. In the absence of pyridine, the reaction was reported to lead to the slow formation of the insoluble polymeric species [Ru(C$_6$H$_5$CO$_2$)$_2$(CO)$_4$]$_n$ [3].

The orange precipitate formed within several minutes when 2-pyridinecarboxylic acid (pyCO$_2$H) was used instead of benzoic acid. X-ray structure determination of the orange solid, to be described later, unambiguously show that it is a mononuclear ruthenium(II) carbonyl complex Ru(pyCO$_2$)$_2$(CO)$_2$ (**2**) rather than the polymeric species [Ru$_2$(pyCO$_2$)$_2$(CO)$_4$]$_n$. The reaction runs almost quantitatively. Further, the oxidized derivative Ru(pyCO$_2$)$_3$ (**3**), was not formed even if an excess of 2-pyridinecarboxylic acid and prolonged reflux times were employed. Neither can compound **3** be obtained from further substitution of the carbonyl groups by reacting **2** with 2-pyridinecarboxylic acid.

However, it can be easily prepared from the reaction of RuCl$_3$·nH$_2$O and sodium 2-pyridinecarboxylate in a 1:1 mixture of water and ethanol.

When a tripodal tetradentate ligand tpa was employed in the presence of acetic acid, the reaction of Ru$_3$(CO)$_{12}$ afforded the ruthenium(II) monocarbonyl complex [Ru(CH$_3$CO$_2$)(CO)(tpa)]ClO$_4$·C$_6$H$_5$CH$_3$ (**1**). A related compound [Ru(HCO$_2$)(CO)(bpy)$_2$]$^+$, was previously prepared from the reaction of Ru(CO$_3$)(bpy)$_2$ with formic acid [13]. The synthesis of compound **1** from the reaction of the polymeric species [Ru$_2$(CH$_3$CO$_2$)$_2$(CO)$_4$]$_n$ and tpa was unsuccessful, suggesting that the polymer may not be an intermediate in the formation of **1**. It should be noted that a similar reaction of the polymeric species with 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) was reported to yield the mononuclear ruthenium(II) carbonyl complexes [Ru(CH$_3$CO$_2$)$_2$(CO)$_2$L] (L = bpy or phen) on the basis of spectroscopic data [2].

2.2. Structures and IR spectra

Compounds **1**–**4** have been characterized by X-ray crystallography. Selected bond lengths and angles are listed in Table 1. Fig. 1 shows the structure of the complex cation [Ru(CH$_3$CO$_2$)(CO)(tpa)]$^+$. The cation contains an octahedrally coordinated Ru(II) ion with two axial sites occupied by the pyridine rings (N2 and N3) and four equatorial sites occupied by the tertiary amine nitrogen (N1), the other pyridyl nitrogen (N4), a carbonyl and an acetate oxygen. The structure has ideal mirror symmetry with the mirror plane defined by the RuNlCl6Cl7N4 five-membered ring. The acetate group deviates slightly from the plane. The C_s symmetry is retained in solution as indicated by the ^{1}H-NMR spectrum to be described below. The carbonyl group occupies the site *trans* to the N1 (tertiary amine) atom (N1–Ru–C1, 177.0(4)°). This may be a consequence of strong Ru(II) → CO back donation as indicated by the unusually short Ru–C bond (1.81(1) Å) and low CO stretching frequency (1938 cm^{-1}), which prefers σ or weak π donor groups occupying the site opposite to CO to favor the d–π* back donation. The Ru–C(CO) bond length is slightly shorter than that in [Ru$_3$O(CH$_3$CO$_2$)$_6$(CO)(mbpy$^+$)$_2$]$^{2+}$ (mbpy$^+$ = N-methyl-4,4′-bipyridinium ion) (1.84(2) Å) [14] and in [Ru(COOH)(CO)(bpy)$_2$]$^+$ (1.845(6) Å) [15]. On the contrary, the C–O bond (1.17(1) Å) of the former is longer than those of the latter two (1.13(3) and 1.127(6) Å, respectively). The CO stretching frequency in **1** is slightly lower than those in the Ru$_3$ compound (1940 cm^{-1}) and in the bpy species (1958 cm^{-1}), consistent with their structural data.

The acetate group is *cis* to the tertiary amine nitrogen with the Ru–O distance of 2.086(8) Å, close to those in

Table 1
Selected bond lengths (Å) and angles (°) for compounds **1–4**

1		2		3		4	
Bond lengths (Å)							
						Ru1–Ru2	2.6809(7)
Ru–C1	1.81(1)	Ru–C1	1.852(7)			Ru1–C1	1.819(5)
		Ru–C2	1.893(7)			Ru1–C2	1.823(5)
						Ru2–C3	1.808(5)
						Ru2–C4	1.819(5)
Ru–O2	2.086(8)	Ru–O3	2.071(4)	Ru–O1	2.013(5)	Ru1–O5	2.119(3)
		Ru–O5	2.065(4)	Ru–O3	2.004(4)	Ru1–O7	2.121(3)
				Ru–O5	1.998(5)	Ru2–O6	2.118(5)
						Ru2–O8	2.127(3)
Ru–N1	2.132(8)	Ru–N1	2.053(5)	Ru–N1	2.071(5)	Ru1–N1	2.216(4)
Ru–N2	2.08(1)	Ru–N2	2.073(5)	Ru–N2	2.046(5)	Ru2–N2	2.240(3)
Ru–N3	2.062(9)			Ru–N3	2.038(5)		
Ru–N4	2.064(9)						
C1–O1	1.17(1)	C1–O1	1.142(9)			C1–O1	1.150(5)
		C2–O2	1.127(9)			C1–O2	1.143(5)
						C1–O3	1.163(5)
						C1–O4	1.152(5)
Bond angles (°)							
N2–Ru–N3	162.5(4)	N1–Ru–N2	163.1(2)	N2–Ru–N3	171.1(2)	N1–Ru1–Ru2	160.07(9)
						N2–Ru2–Ru1	162.36(8)
C1–Ru–O2	96.7(4)	C1–Ru–C2	89.3(3)	O1–Ru–O3	90.3(2)	C1–Ru1–O5	93.5(2)
C1–Ru–N1	177.0(4)	C1–Ru–O3	177.3(2)	O1–Ru–O5	175.8(2)	C1–Ru1–O7	178.9(2)
C1–Ru–N4	94.4(4)	C1–Ru–O5	94.3(3)	O1–Ru–N1	78.8(2)	C1–Ru1–C2	88.0(2)
O2–Ru–N4	168.6(3)	C2–Ru–O5	175.8(2)	O3–Ru–N1	169.2(2)	C1–Ru1–O5	177.8(2)
O2–Ru–N1	86.2(3)	C2–Ru–O3	92.1(2)	O3–Ru–O5	93.8(2)	C1–Ru1–O7	92.6(2)
N1–Ru–N4	82.7(3)	C3–Ru–O5	84.3(2)	O5–Ru–N1	97.0(2)	O5–Ru1–O7	85.8(1)
Ru–C1–O1	176(1)	Ru–C1–O1	178.7(6)			Ru1–C1–O1	179.4(4)
		Ru–C2–O2	176.0(6)			Ru1–C2–O2	179.5(5)
						Ru2–C3–O3	178.5(4)
						Ru2–C4–O4	176.7(5)

$[Ru_3O(CH_3CO_2)_6(mbpy^+)_2(CO)]^{2+}$ (2.07(1) Å) [14] and $[Ru_2O(CH_3CO_2)(tpa)_2]^{3+}$ (2.085(7) Å) [9]. The N2–Ru–N3 angle is 162.5(4)°, indicating that the octahedron is distorted. The Ru–N1(amine) distance (2.132(8) Å) is significantly longer than the remaining Ru–N(py) distances (2.07(1) Å) probably due to both the *trans* influence of CO and absence of d–pπ bond. It should be noted that the former is similar to the Ru–N(py) distance (2.129(4) Å) *trans* to the CO group in $[Ru(COOH)(CO)(bpy)_2]^+$ [15].

The structure of compound $Ru(pyCO_2)_2(CO)_2$ (**2**), which has ideal C_2 symmetry, is given in Fig. 2. The complex takes *cis* configuration with respect to the two CO ligands. Two pyridyl groups lie at the *trans* sites to each other and *cis* to the carbonyl groups. Each carboxylato group is consequently *trans* to one of the two carbonyls. Similar to the case in **1**, such an arrangement seemingly reveals that σ donor ligands prefer to occupy the sites *trans* to CO. Following this fact, the actual structure of $Ru(CH_3CO_2)_2(CO)_2(py)_2$ is most likely that with *trans* arrangement of two pyridine ligands [5]. The mean N–Ru–O angle in the RuNCCO five–membered ring (79.8(8)°) is similar to the corresponding values in

compound **1**. The differences in the Ru–O and Ru–N distances in **1** and **2** are statistically insignificant. However, the Ru–C bonds in **2** (av. 1.87(2) Å) are significantly longer than that in **1** as a consequence of the fact that in compound **2** the back-donating electrons of Ru(II) are shared by the two CO groups. This observation corresponds to the higher CO stretching frequency in **2** (2062, 1998 cm^{-1}) which are close to those in the related compound, $Ru(CH_3CO_2)(CO)_2(py)_2$ (2065, 1992 cm^{-1}) [5].

Fig. 3 shows the structure of $Ru(pyCO_2)_3$ (**3**). The structure may be conveniently understood on the grounds that the two CO groups in **2** are further replaced by a pyCO$_2$ ligand. The compound thus takes *mer* (*cis–trans*) configuration. The octahedral coordination sphere of Ru(III) distorts to a lesser extent than that in **2** as indicated by the greater N2–Ru–N3 angle (171.1(2)°), the corresponding angle in **2** being 163.1(2)°. The most notable differences in structural parameters in **2** and **3** are the Ru–O(O$_2$CCH$_3$) distances, 2.068(4) Å in the former and 2.005(5) Å in the latter. This may be due to both the smaller bonding radius of Ru(III) and the absence of *trans* influence of
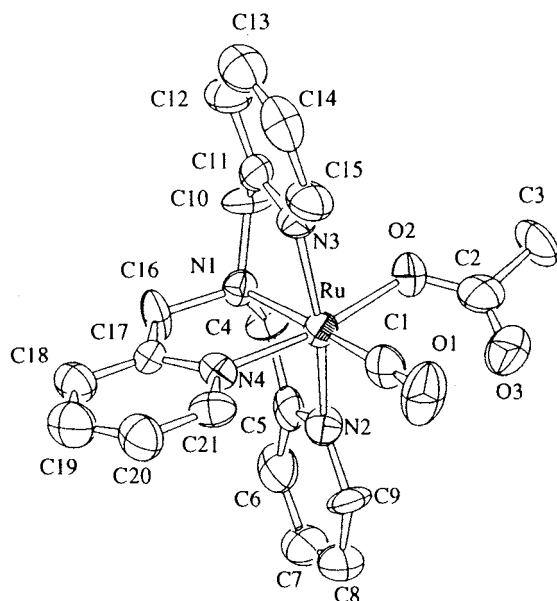
Fig. 1. ORTEP drawing of the cation [Ru(CH$_3$CO$_2$)(CO)(tpa)]$^+$ in **1** with the atomic numbering scheme. Thermal ellipsoids are drawn at the level of 50% probability.

CO in compound **3**. The Ru(III)–N bond lengths in **3** (2.05(1) Å) are not significantly shorter than the Ru(II)–N(py) ones in **1** (av. 2.07(1) Å) and **2** (av. 2.06(1) Å) as a result of the presence of d–pπ bonds in the latter species.
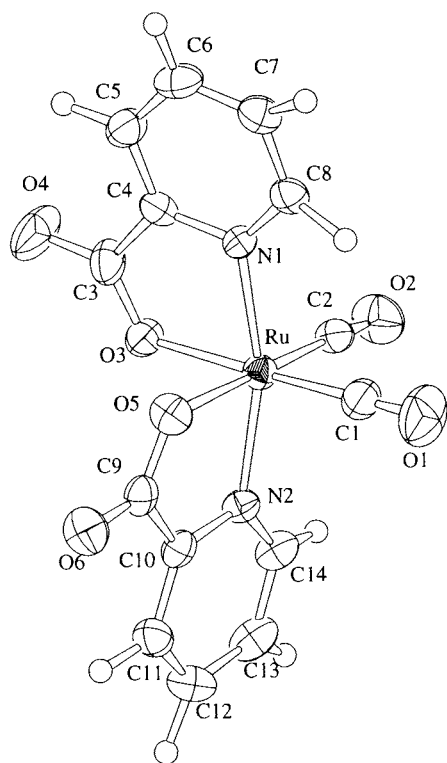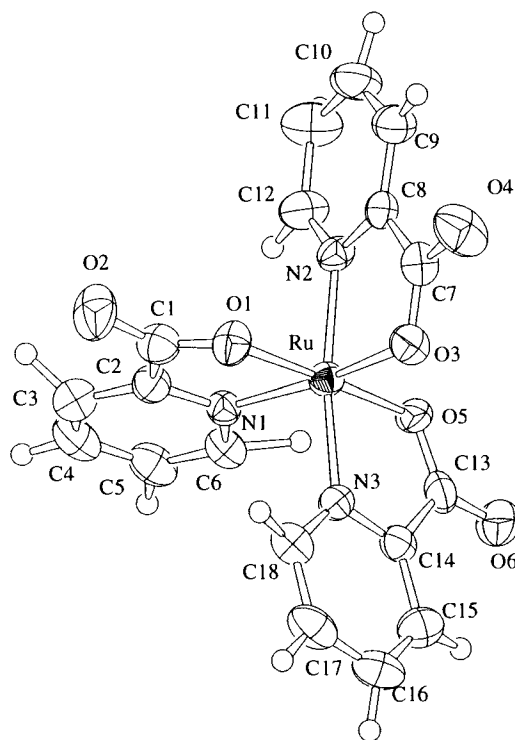

Fig. 3. ORTEP drawing of Ru(pyCO$_2$)$_3$ (**3**) with the atomic numbering scheme. Thermal ellipsoids are drawn at the level of 50% probability.

The structure of Ru$_2$(C$_6$H$_5$CO$_2$)(CO)$_4$(py)$_2$ (**4**) is given in Fig. 4. Two Ru(I) atoms are bridged by two benzoate groups. The Ru–Ru distance (2.6809(7) Å) is close to that in the acetate analogue (2.678 Å) [16], and is consistent with the existence of the Ru(I)–Ru(I) single bond. Octahedral coordination geometry of each

Fig. 2. ORTEP drawing of Ru(pyCO$_2$)$_2$(CO)$_2$ (**2**) with the atomic numbering scheme. Thermal ellipsoids are drawn at the level of 50% probability.
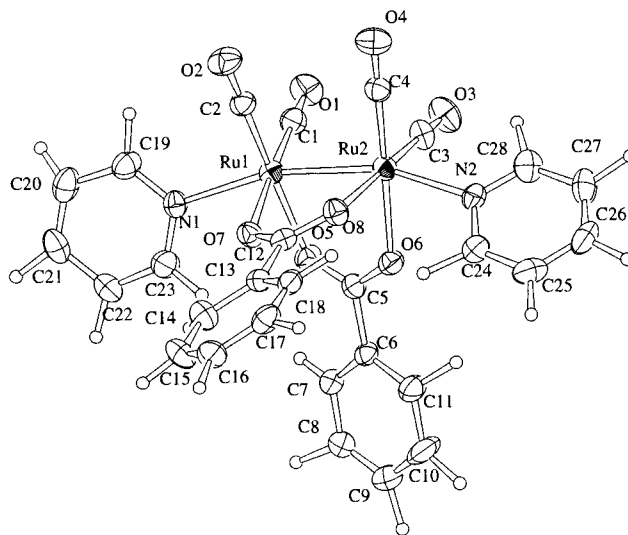
Fig. 4. ORTEP drawing of Ru(C$_6$H$_5$CO$_2$)$_2$(CO)$_4$(py)$_2$ (**4**) with the atomic numbering scheme. Thermal ellipsoids are drawn at the level of 50% probability.

Ru(I) is completed by two carbonyl groups *trans* to the benzoates and a pyridine ligand *trans* to the Ru–Ru bond. The coordination geometry of the Ru(I) is similar to that of the Ru(II) in **2**, except for the Ru–Ru bond in place of one of the Ru–N(pyridyl) bonds in **2**. The distortion of the octahedron of Ru(I) is similar to that in **2** (av. N–Ru–Ru, 161.1(9)°). The Ru(I)–CO bonds (av. 1.817(5) Å) in **4** are shorter than the Ru(II)–CO bonds in **2**, in agreement with lower CO stretching frequency in **4** (2000, 1960, 1940, 1910 cm^{-1}). The mean Ru–N bond of **4** is 2.228(10) Å, which is considerably longer than that in **2** due to both *trans* influence of the Ru–Ru bond and larger bonding radius of Ru(I). The Ru(I)–O distances (av. 2.121(5) Å) are slightly longer than that in **2**.

2.3. ^{1}H-NMR spectra

The ^{1}H-NMR spectrum of **1** in CD$_2$Cl$_2$ indicates that the compound has mirror symmetry and the basic structure found in the solid state is retained in solution. The doublets centered at 8.92 and 8.67 ppm in the integrated intensity ratio of 1:2 are attributed to the 6-*H* protons on the pyridyl rings *trans* and *cis* to the acetate group, respectively. It is thus concluded that the acetate group rotates freely along the Ru–O2 bond, leading to the equivalence of both the *cis* pyridyl rings. The other protons on the pyridyl rings show signals in the range of 7.15–7.75 ppm which are overlapped with the signals from the toluene molecule. The methylene proton signals on the pyridylmethyl groups *trans* and *cis* to the acetate ligand appear at 5.37 (s) and 5.20 (d) ppm, respectively, in the integrated intensity ratio of 1:2. The singlet at 1.78 ppm is assigned to the acetate methyl protons. The methyl proton signal from toluene appears at 1.26 ppm as a singlet.

As expected for the two-fold symmetry indicated by the solid-state structure, the ^{1}H-NMR spectrum of **2** shows two equivalent pyridyl rings, similar to the case in the closely related compound Ru(CH$_3$CO$_2$)$_2$-(CO)$_2$(py)$_2$ [5]. Two doublets centered at 8.55 and 8.21 ppm are assignable to the 6- and 3-*H* protons, respectively, and two triplets at 8.13 and 7.64 ppm are due to the 4- and 5-*H* proton resonances, respectively. Differing from compounds **1** and **2** which contain the rigid pyridyl rings, complex **4** shows only three sets of signals at 8.93 (d), 7.93 (t) and 7.57 (t) in the intensity ratio of 2:1:2 attributable to the 2- and 6-, 4-*H*, and 3- and 5-*H* protons, respectively, indicating that the pyridyl rings freely rotate along the Ru–N(py) bonds. The pyridyl proton signals of compound **3** were not observed at the corresponding region as expected for the paramagnetic nature.

3. Experimental

3.1. Materials

The ligand tris(2-pyridylmethyl)ammonium perchlorate (tpa·3HClO$_4$) was prepared as described in the literature [17]. All other commercially available reagents were used as purchased.

3.2. Preparation of the complexes

3.2.1. [Ru(CH$_3$CO$_2$)(CO)(tpa)]ClO$_4$·C$_6$H$_5$CH$_3$ (**1**)

A suspension of tpa·3HClO$_4$ (0.18 g, 0.3 mmol), Ru$_3$(CO)$_{12}$ (0.065 g, 0.1 mmol) and acetic acid (1 ml) in toluene was heated under reflux for 4 h under an argon atmosphere. The suspension changed to a red–orange and then to a yellow solution after 10 min. The resulting solution was cooled to room temperature (r.t.) and was allowed to stand in a refrigerator overnight to give yellow thin plate crystals of **1** (0.03 g, 17%). These crystals were found to be suitable for X-ray structure analysis. Anal. Found: C, 49.76; H, 4.25; N, 8.22. Calc. for C$_{28}$H$_{29}$N$_4$RuO$_7$Cl (M_W 670.08): C, 50.14; H, 4.33; N, 8.36%. UV–vis (CH$_2$Cl$_2$ (nm)), 250, 385. IR (KBr (cm^{-1})), 1938 (v(CO)), 1620(s) (v_{as}(CO$_2$)). ^{1}H-NMR (CD$_2$Cl$_2$) δ: 8.92 (1H, d, py-6-*H* *trans* to acetate), 8.67 (2H, d, py-6-*H* *cis* to acetate), 7.15–7.75 (9H, m, py-*H*, and C$_6$H$_5$CH$_3$), 5.37 (2H, s, pyridylmethyl protons *trans* to acetate), 5.20 (4H, d, pyridylmethyl protons *cis* to acetate), 1.78 (3H, s, C*H$_3$*CO$_2$), 1.26 (3H, s, C$_6$H$_5$C*H$_3$*). Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive.

3.2.2. Ru(pyCO$_2$)$_2$(CO)$_2$ (**2**)

A suspension of 2-pyridinecarboxylic acid (0.072 g, 0.6 mmol) and Ru$_3$(CO)$_{12}$ (0.065 g, 0.1 mmol) in toluene (20 ml) was refluxed under argon atmosphere for 20 min to produce an orange precipitate. The precipitate was washed with pentane (2 × 30 ml) and dried in vacuum to produce 0.08 g of **2** (yield, 70%). Single crystals suitable for X-ray structure determination were obtained by slow diffusion of pentane into the solution of CH$_2$Cl$_2$. Anal. Found: C, 41.59; H, 1.92; N, 6.83. Calc. for C$_{14}$H$_8$N$_2$RuO$_6$ (M_W 401.30): C, 41.86; H, 1.99: N, 6.98%. IR (KBr (cm^{-1})) v(CO), 2062, 1998; v_{as}(CO$_2$), 1663, 1645. ^{1}H-NMR (CD$_2$Cl$_2$) δ: 8.55 (2H, d, py-6-*H*), 8.21 (2H, d, py-3-*H*), 8.13 (2H, t, py-4-*H*), 7.64 (2H, t, py-5-*H*).

3.2.3. [Ru(pyCO$_2$)$_3$]·H$_2$O (**3**)

A mixture of RuCl$_3$·nH$_2$O (0.13 g, 0.5 mmol), sodium 2-pyridinecarboxylate (0.22 g, 0.15 mmol), water (20 ml) and ethanol (20 ml) was heated at 60°C for 3 h. The resulting solution was filtered and evaporated under vacuum and dried. The diffusion of ether

Table 2
Experimental details for crystallograpyic analyses of compounds **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{28}H_{29}N_4O_7ClRu$	$C_{14}H_8N_2O_6Ru$	$C_{18}H_{14}N_3O_7Ru$	$C_{31.5}H_{24}N_2O_8Ru_2$
Formula weight	670.08	401.30	485.39	760.68
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/c$	$Pbca$	$C2/c$	$P\bar{1}$
a (Å)	9.178(4)	15.059(4)	30.490(10)	12.988(6)
b (Å)	16.562(5)	15.310(7)	8.513(3)	14.522(7)
c (Å)	19.397(5)	12.502(4)	13.988(1)	9.371(4)
α (°)				99.14(5)
β (°)	98.63(3)		94.19(1)	108.22(4)
γ (°)				102.61(4)
V (Å)	2915(1)	2882(1)	3621(1)	1588(1)
Z	4	8	8	2
D_c (g cm^{-3})	1.53	1.85	1.78	1.59
F_{000}	1368	1584	1944	758
μ (Mo–K$_\alpha$) (cm^{-1})	6.81	11.22	9.15	10.02
Scan mode		ω–2θ		
Scan rate (deg min^{-1})	10.0	10.0	8.0	12
Scan width (°)	$0.94 + 0.30 \tan \theta$	$1.21 + 0.3 \tan \theta$	$1.23 + 0.40 \tan \theta$	$1.05 + 0.30 \tan \theta$
$2\theta_{max}$ (°)	50	50	60	55
Total reflections	5456	2546	5681	6193
No. observations ($I > 3(\sigma)I$)	2469	1773	2799	4569
Corrections		Lp, absorption		
Trans. factors	0.91–1.00	0.74–1.00	0.58–1.00	0.98–1.00
No. variables	376	208	262	381
Residuals, R; R_w	0.064, 0.054	0.036, 0.035	0.052, 0.043	0.032, 0.031
GOF	2.18	2.32	1.95	2.14
$\Delta\sigma$	0.02	0.04	0.05	0.05
$\Delta\rho$ (e Å^{-3})	0.67	0.38	0.96	0.36

into the solution of acetone gave a brown crystalline solid of **3** (0.08 g, 50%). Anal. Found: C, 44.86; H, 2.87; N, 8.46. Calc. for $C_{18}H_{14}N_3RuO_7$ (M_W 485.39): C, 44.50; H, 2.90; N, 8.64%. IR (KBr (cm^{-1})) $\nu_{as}(CO_2)$, 1675, 1657, 1625.

3.2.4. [Ru₂(C₆H₅CO₂)₂(CO)₄(py)₂]·0.5C₆H₅CH₃ (4)

A mixture of $Ru_3(CO)_{12}$ (0.065 g, 0.1 mmol), benzoic acid (0.072 g, 0.6 mmol) and pyridine (1 ml) was refluxed in toluene (50 ml) for 1 h under an argon atmosphere to give a yellow solution. The solution was evaporated in an open beaker to produce yellow crystals of **4** (0.08 g, 80%). Anal. Found: C, 49.12; H, 3.08; N, 3.52. Calc. for $C_{31.5}H_{24}N_2Ru_2O_8$ (M_W 760.68): C, 49.69; H, 3.15; N, 3.68%. IR (KBr (cm^{-1})) $\nu(CO)$, 2000, 1960, 1940, 1910; $\nu_{as}(CO_2)$, 1630; $\nu_s(CO_2)$, 1400. ^{1}H-NMR (CD$_2$Cl$_2$) δ: 8.93 (4H, d, py-2- and py-6-H), 7.86 (2H, t, py-4-H), 7.41 (4H, t, py-3- and 5-H), 7.85 (4H, d, o-ph), 7.38 (2H, t, p-ph), 7.23 (4H, t, m-ph).

3.3. X-ray crystallography

Intensity data for compounds **1**–**4** were collected on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71069$ Å) and a rotating anode generator at r.t. (23°C). Cell constants and

an orientation matrix for data collection were obtained from a least-squares refinement using setting angles of 25 carefully centered reflections. The intensities of three standard reflections were measured after every 150 reflections. No appreciable decay was observed. Data were corrected for Lorentz and polarization effects and/or an empirical absorption correction using the program DIFABS [18]. The structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps or added on ideal positions. Structures were refined by the block-diagonal-matrix followed by full-matrix least-squares (final cycle) method. The minimized function was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma_c^2(F_o) + p^2 F_o^2/4]^{-1}$. Experimental details for crystallographic analyses of compounds **1**–**4** are listed in Table 2.

3.4. Other measurements

IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. The ^{1}H-NMR spectra were obtained at 270 MHz with a Jeol JNM-EX270 spectrometer. UV–vis spectra were recorded on a Jasco Ubest-30 spectrophotometer at r.t.

4. Supporting material

A listing of the atomic coordinates and thermal parameters, complete bond lengths and angles of compounds **1**–**4** are available on request from the authors.

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