Notes

New Rhodium(II) Complexes with 2,2′:6′,2″-Terpyridine

**Florian P. Pruchnik,*,† Francis Robert,‡
Yves Jeannin,‡ and Suzanne Jeannin‡**

Faculty of Chemistry, University of Wrocław,
Joliot-Curie 14, 50-383 Wrocław, Poland, and
Laboratoire de Chimie des Metaux de Transition,
Universite P. et M. Curie, 4, Place Jussieu,
75252 Paris Cedex 05, France

The development of chemistry of the rhodium(II) dimers observed recently, is due to the interest in the spectroscopy, reactivity,[1−7] possible practical applications in catalysis,[1−4,8−10] and promising antitumor properties of these compounds.[1−4,11] The Rh(II) complexes $[Rh_2(OOCR)_2(N-N)_2L_2]^{2+}$ with heterocyclic nitrogen ligands are effective and selective catalysts for hydrogenation of ketones and alkenes[4,9] and show higher cytostatic activity than $[Rh_2(OOCR)_4]$ complexes.[4,11] The current interest in complexes of polypyridyl ligands, 2,2′-bipyridine, 1,10-phenanthroline, 2,2′:6′,2″-terpyridine (terpy), etc., is associated with the extremely interesting electrochemical, photophysical, and photoelectrochemical properties that they exhibit.[12−17] Complexes with these ligands are also DNA intercalators, showing an ability to inhibit nucleic acid synthesis in vivo.[18] 2,2′:6′,2″-Terpyridine can in principle exhibit a variety of bonding modes to metals, viz. monodentate, bidentate, terdentate, or bridging. However, the majority of terpy complexes involve terdentate bonding.

The X-ray structure only few compounds with terpy acting as a bidentate chelate ligand, has been determined,[13,19] but

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† University of Wrocław.
‡ Universite P. et M. Curie.
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complexes with monodentate terpy have, at least to our knowledge, never been observed up to now although their presence has been postulated occasionally. In $[AuBr(CN)_2(terpy)]$ the coordination is distorted square-pyramidal and terpyridine acts as a quasi-bidentate ligand with one N atom in the basal square (Au−N = 2.078 Å) and the other in the apical position at a distance of 2.839 Å, which is intermediate between the sum of the covalent and van der Waals radii.[20] We describe herein new dinuclear Rh(II) complexes $[Rh_2(\mu\text{-OOCMe})_4(\eta^1\text{-terpy})_2]$, **1**, and $[Rh_2Cl_2(\mu\text{-OOCMe})(\eta^3\text{-terpy})_2](H_3O)Cl_2 \cdot 9H_2O$, **2**, with terpy coordinating as a monodentate and as a terdentate ligand, respectively. The complex **1** was prepared by refluxing $Rh_2(OAc)_4$ (0.2 mmol) with terpy (0.4 mmol) in ethanol (7 cm³) for 2 h. After evaporation of the solution to ca 2 cm³, a dark-violet crystalline product was obtained (¹H NMR (300 MHz, CDCl₃, 293 K): δ 1.61 (s, 3H, CH₃), 1.70 (s, 9H, CH₃), 7.36 (ddd, 4H, H5 + H5″), 7.85(t, 2H, H4′), 7.87 (dt, 4H, H4 + H4″), 8.42 (d, 4H, H3′ + H5′), 8.55(d, 4H, H3 + H3″), 8.76 (dd, 4H, H6 + H6″). IR (in KBr): ν^s(RhO) 337 cm⁻¹, ν^{as}(RhO) 382 cm⁻¹, ν^s(COO) 1440 cm⁻¹, ν^{as}(COO) 1592 cm⁻¹. UV−vis (CHCl₃): 1.67 μm⁻¹ (ε = 260), 2.30 μm⁻¹ (ε = 160)). The compound **2** was prepared by refluxing $Rh_2(OAc)_4$ (0.2 mmol) with terpy (0.4 mmol) and NaCl (2 mmol) in ethanol (5 cm³) for 6 h. The red product was filtered off and recrystallized from water (¹H NMR (300 MHz, D₂O, 293 K): 2.72 (s, 3H, CH₃), 7.44 (ddd,, 4H, H5 + H5″), 7.83−8.03 (m, 14H), 8.13 (d, 4H, H6 + H6″). IR (in KBr): ν^s(COO) 1447 cm⁻¹, ν^{as}(COO) 1545 cm⁻¹. UV−vis (H₂O): 1.82 μm⁻¹ (ε = 420), 2.29 μm⁻¹ (ε = 3950), 2.58 μm⁻¹ (ε = 4400) sh, 2.90 μm⁻¹ (ε = 9850), 3.17 μm⁻¹ (ε = 20700), 3.55 μm⁻¹ (ε = 26 800) sh, 3.65 μm⁻¹ (ε = 28000), 4.33 μm⁻¹ (ε = 28 900).

The X-ray structure of complex **1** (Figure 1) shows monodentate binding of the terpy ligand to Rh(II) along Rh−Rh axis via terminal pyridine ring. The Rh−Rh and Rh−N distances (2.401(1) and 2.337(7) Å, respectively) are longer than those in $[Rh_2(OAc)_4(py)_2]$ (2.3963(2) and 2.227(3) Å). The CCN angles between pyridine rings in $[Rh_2(OAc)_4(terpy)_2]$ are similar to those in the free 4′-phenyl-2,2′:6′,2″-terpyridine ligand[13] apart from the N^1CC angle (N^1 is coordinated with rhodium), which is higher. This indicates that relatively strong repulsion exists between central noncoordinating pyridine ring of terpy and the carboxylato ligands.

In complex **2** terpy acts as a terdentate ligand (Figure 2). The coordination geometry about each Rh(II) center is pseudooctahedral with equatorial coordination sites occupied by nitrogen atoms of terpy and the oxygen atom of the bridging acetato ligand. The Rh−Rh distance (2.6341(9) Å) is 0.238 and 0.080 Å longer than that in $[Rh_2(OAc)_4(py)_2]$ and $[Rh_2Cl_2(OAc)_2(phen)_2] \cdot 10.5H_2O$,[1,21] respectively. The compound **2** is the first Rh(II) complex containing only one carboxylato bridging ligand to be analyzed crystallographically. Two planar [Rh(terpy)] units are rotated about Rh−Rh axis by 23° from eclipsed configuration. It seems that this is the highest possible rotation in complexes with bridging carboxylato ligand. In Rh(II) dimers $[Rh_2Cl_2(OOCR)_2(N-N)_2]$ (N-N = bpy, phen) and $[Rh_2(dmgH)_2(OAc)_2(PPh_3)_2]$ containing two carboxylato bridges the Rh(N-N) units are rotated by 11−20°.[10,21] Complexes

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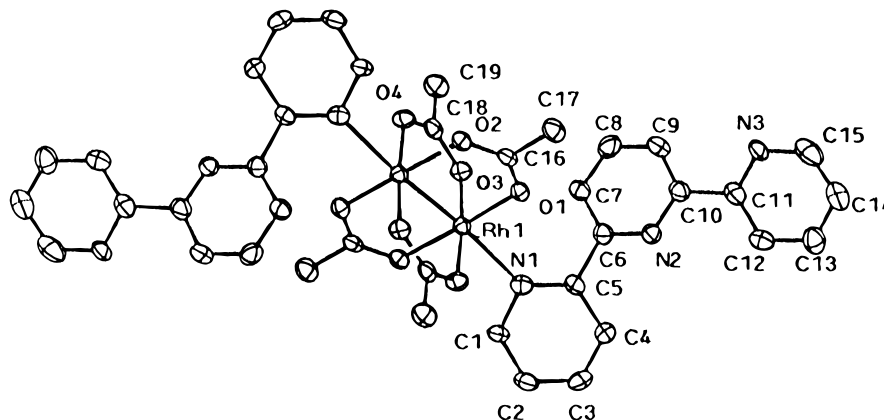
Figure 1. Ortep representation of complex **1**. Selected bond lengths (Å) and angles (deg): Rh(1)−Rh(1), 2.401(1); Rh(1)−N(1), 2.337(7); Rh(1)−O(1), 2.027(5); Rh(1)−O(2), 2.036(5); Rh(1)−O(3), 2.032(5); Rh(1)−O(4), 2.043(5); N(1)−Rh(1)−Rh(1), 174.5(2); O(1)−Rh(1)−Rh(1), 88.1(2); O(1)−Rh(1)−N(1), 92.1(2); O(3)−Rh(1)−O(1), 91.1(2); O(2)−Rh(1)-O(1), 175.9(2).
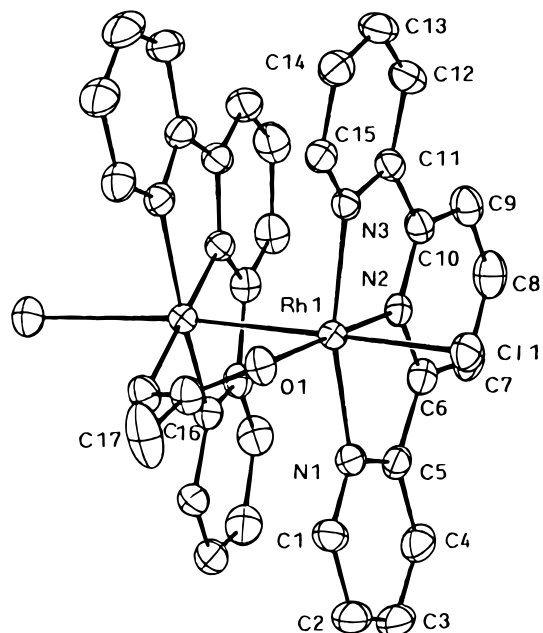

Figure 2. Ortep representation of complex **2**. Selected bond lengths (Å) and angles (deg): Rh(1)−Rh(1), 2.6341(9); Rh(1)−Cl(1), 2.517-(2); Rh(1)−N(1), 2.033(5); Rh(1)−N(2), 1.921(5); Rh(1)−N(3), 2.029-(5); Rh(1)−O(1), 2.062(4); Cl(1)−Rh(1)−Rh(1), 173.28(4); N (1)−Rh(1)−Rh(1), 93.8(1); N(2)−Rh(1)−Rh(1), 96.5(1); O(1)−Rh(1)−Rh(1), 82.6(1); O(1)−Rh(1)−Cl(1), 90.8(1); O(1)−Rh(1)−N(1), 97.4(2); O(1)−Rh(1)−N(2), 178.0(2).

Table 1. Crystallographic Data for $Rh_2(OAc)_4(terpy)_2$ (**1**) and $[Rh_2Cl_2(OAc)(terpy)_2](H_3O)Cl_2 \cdot 9H_2O$ (**2**)

	1	**2**
formula	$C_{38}H_{34}N_6O_8Rh_2$	$C_{32}H_{46}Cl_4N_6O_{12}Rh_2$
fw	908.53	1054.37
cryst syst	monoclinic	monoclinic
space group	*C2/c*	*C2/c*
unit cell dimens		
a (Å)	28.371(5)	18.531(3)
b (Å)	9.820(2)	19.345(3)
c (Å)	13.734(3)	13.637(2)
β (deg)	99.40(3)	120.71(1)
V (Å^3)	3775(3)	4202(3)
Z	4	4
temp	room temp	room temp
ρ_{calcd} (g cm^{-3})	1.60	1.67
abs coeff, μ (cm^{-1})	9.17	10.91
R^a	0.039	0.043
R_w^b	0.043	0.049
GOF^c	4.6	5.8

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. ^{c} GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

containing only terminal ligands, e.g. $[Rh_2(NCMe)_{10}]^{4+}$ and $[Rh_2(NCMe)_8(H_2O)_2]^{4+}$ show staggered conformation, two planar Rh(NCMe)$_4$ units are twisted by 45° from eclipsed geometry. The Rh−Rh distances in these complexes are 2.624-(1) and 2.625(1) Å, respectively,[22,23] and are very close to that in complex **2**. This confirms that a distance of ca. 2.60 Å is reliable measure of a Rh(II)−Rh(II) single bond and indicates that one carboxylate bridge is supporting the Rh−Rh bond only weakly, or not supporting at all, contrary to complexes containing two, three, or four μ-OOCR ligands. The Rh−Cl distances, 2.517(2) Å, are long, thus showing that chloro ligands are weakly coordinated. Crystal data for **1** and **2** are given in Table 1.

Titration of complex **2** with 0.01 M NaOH solution confirmed the presence of 1 equiv of H_3O^+. The chemical shift of CH_3

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group (2.72 ppm) in **2** is ca. 1 ppm higher than that in **1** and similar to that in $[Rh_2(OAc)_2(N-N)_2(H_2O)_2]^{2+}$ (N-N = bpy, phen).

The ^1H NMR spectrum of **1** in CDCl$_3$ showed equivalence of terminal pyridyl rings. It consisted of six multiplets arising from terpy hydrogens. The coordination chemical shifts (ppm) $\Delta\delta(H) = \delta_{complex} - \delta_{terpy}$ are relatively small: +0.07 (H6, H6″), +0.05 (H5, H5″), +0.04 (H4, H4″), −0.05 (H3, H3″), −0.09 (H4′) and −0.03 (H3′, H5′). This suggests a rather weak interaction of the terpy ligand with the rhodium atom. The observed spectrum clearly points to the terpyridyl being involved in a fluxional process in which the monodentate ligand is changing coordination with Rh via the nitrogen atoms of the terminal pyridyl rings. The fluxional process is observed up to 213 K.

The weak Rh−terpy bonding in **1** was also confirmed by electronic spectra of this compound in CHCl$_3$ and acetone. The energy of the first band assigned to the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition depends on the ligand field strength of the axial ligand.[1-4,7] This transition for $[Rh_2(OAc)_4L_2]$ complexes with nitrogen ligands should be observed at ca. 550 nm ($\sim$1.82 μm^{-1}) and with oxygen axial ligands at ca. 590 nm ($\sim$1.69 μm^{-1}). The spectrum of complex **1** in a KBr pellet shows the first band at 549 nm while in CHCl$_3$ solution it is at 597 nm. Thus electronic spectra of **1** suggest that the dynamic properties of terpy in **1** result from weak coordination of this ligand in solutions in organic solvents, most probably from fast dissocia-

tion−association of the ligand. The electronic spectrum of **2** in the visible region is very similar to the spectra of [Rh_2X_2-$(OOCR)_2(N-N)_2$] (N-N = bpy, phen). The first band should be assigned, in a similar manner as for the above complexes with bpy and phen, to the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition and the second one to the MLCT $\sigma(Rh_2) \rightarrow \pi^*(terpy)$ transition.[4,7] Complex **2** in solutions in water is at room temperature slowly oxidized to the Rh(III) terpy complexes, which however can be reduced to the Rh(II) dimers by means of alcohols at elevated temperatures. Alcohols are oxidized to appropriate aldehydes and acids. Compound **2** in basic solutions in alcohols catalyze hydrogenation of ketones. Rate of reduction of acetone (2 cm^3 of Me_2CO in 8 cm^3 of 0.3 M NaOH in MeOH, 5×10^{-6} mole of **2**, room temperature, $p(H_2)$ = 0.09 MPa) is 180 mol of H_2 (mol of **2**)$^{-1}$ h^{-1}. Thus complex **2** belongs to the most active catalysts for reduction of ketones.

Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates and thermal parameters, and intramolecular bond lengths and angles for **1** and **2** (10 pages). Ordering information is given on any current masthead page.

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