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Syntheses of ruthenium hydridotris(1-pyrazoryl)borate complexes having sulfur-donor coligands

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Abstract

Treatment of $[TpRuCl(PPh_3)_2]$ ((1); Tp = hydridotris(1-pyrazolyl)borate) with NaS₂CNMe₂ afforded the dithiocarbamate complex $[TpRu(\eta^2-S_2CNMe_2)(PPh_3)]$ (2) in high yield. The structure of 2 has been determined unambiguously by X-ray diffraction study. Complex 1 also reacted with a mixture of excess TolSSTol (Tol = p-MeC₆H₄) and Zn powder to give a novel trinuclear complex with bridging thiolate ligands [{TpRu(PPh_3)(μ -STol)₂}Zn] (3) in moderate yield, which has been characterized spectroscopically and by elemental analyses. Initial treatment of 1 with an equimolar amount of AgBF₄ followed by the reaction with a mixture of TolSSTol and Zn also resulted in the formation of 3 as the major product. However, from this reaction mixture, a dinuclear complex closely related to 3, [TpRu(PPh_3)-(μ -STol)₂Zn(STol)(MeOH)], was able to be isolated in quite a low yield, which has also been fully characterized by the X-ray analysis. $(0 \ 1998 \ Elsevier \ Science \ S.A. \ All \ rights \ reserved.$

Keywords: Ruthenium complexes; Zinc complexes: Pyrazolylborate complexes; Dithiocarbamate complexes; Crystal structures

1. Introduction

For some years, we have been developing the chemistry of a series of thiolate-bridged diruthenium complexes obtained from the reactions of $[(Cp^*Ru)_4(\mu_3-Cl)_4]$ or $[Cp^*Ru Cl(\mu-Cl)_2RuCp^*Cl]$ ($Cp^* = \eta^5-C_5Me_5$) with certain thiolate compounds [1]. These studies have already shown that complexes containing Ru(II) and/or Ru(III) centers such as $[Cp^*Ru(\mu-SR)_2RuCp^*], [Cp^*Ru(\mu-SR)_3RuCp^*]$, and $[Cp^*RuCl(\mu-SR)_2RuCp^*(H_2O)]^+$ can promote numerous stoichiometric and catalytic transformations of organic and inorganic substrates represented by alkynes [2], alkyl halides [3], hydrazines [4], etc., with retention of the dinuclear cores owing to the presence of firmly bound thiolate bridges. A recent investigation in this area has also been directed toward the syntheses and reactivities of related Ir and Rh complexes, some results of which have already appeared elsewhere [5].

Another intriguing extension of our studies on diruthenium thiolate complexes has gone to the replacement of the Cp* ligand by the hydridotris(1-pyrazolyl)borate (Tp) ligand [6]. In spite of the similarity of the Tp ligand to the Cp (Cp = η^{5} -C₅H₅) and Cp* ligands with respect to the number

of donating electrons and the charge, the chemistry of the ruthenium complexes containing Tp ligands [6,7] is less explored than that for complexes having Cp and Cp* ligands. To our knowledge, the (pyrazolyl)borate complexes of Ru with sulfur-donor coligands are still unknown, although several well-defined complexes have been reported for other metals such as Mo [8], W [9], Zn [10], and Cu [11].

Despite much effort in this laboratory, the dinuclear TpRu thiolate complexes analogous to the Cp*Ru complexes cited above have remained unattainable. However, we have very recently isolated two types of the ruthenium compounds containing both Tp and sulfur-donor ligands by the use of $[TpRuCl(PPh_3)_2]$ (1) as the starting Ru source; one is the mononuclear dithiocarbamate complex [TpRu(η^2 -S₂CN- Me_2 (PPh₃) (2) and the other includes the thiolatebridged mixed metal complexes $[{TpRu(PPh_3)} (\mu$ -STol)₂]₂Zn] ((3); Tol=p-MeC₆H₄) and [TpRu(PPh₃)- $(\mu$ -STol)₂Zn(STol)(MeOH)] (4). In this paper, we wish to describe the syntheses and characterization of these new complexes.

2. Experimental

2.1. General

All manipulations were carried out under a nitrogen atmosphere. Complex 1 was prepared according to the literature

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[12], while the chemicals commercially obtained were used as received. IR and ¹H NMR spectra were recorded on a Shimadzu 8100M or JEOL EX-270 spectrometer, respectively. Elemental analyses were done using a Perkin-Elmer 2400II CHN analyzer. For **3**, the atomic ratio with respect to Ru, Zn, P, and S was determined by electron-probe microanalysis (EPMA) using a Kevex μ X 7000 energy dispersivetype X-ray analyzer.

2.2. Preparation of $[TpRu(\eta^2-S_2CNMe_2)(PPh_3)]$ (2)

A mixture of **1** (88 mg, 0.10 mmol) and NaS₂-CNMe₂·2H₂O (44 mg, 0.24 mmol) in THF (4 cm³) was refluxed for 2 h. After cooling, the mixture was dried up in vacuo and the residue was extracted with CH₂Cl₂. Addition of EtOH to the concentrated extract gave **2** as orange crystals (62 mg, 88%). IR (KBr, cm⁻¹): 2500 [ν (BH)]. ¹H NMR (CDCl₃, ppm): 3.00 (s, 6H), NMe₂; 5.68 (t, 2H), 6.62 (2H, d), and 7.60 (2H, d), pyrazolyl (Pz) *trans* to S: 6.13 (t, 1H), 7.61 (d, 1H), and 7.75 (d, 1H), Pz *trans* to P; 7.1– 7.3 (m, 15H), PPh₃. *Anal*. Found: C, 51.75; H. 4.65; N, 13.88. Calc. for C₃₀H₃₁N₇PS₂BRu: C, 51.73; H. 4.49; N, 14.08%.

2.3. Preparation of $[{TpRu(PPh_3)(\mu-STol)_2}_2Zn](3)$ and $[TpRu(PPh_3)(\mu-STol)_2Zn(STol)(MeOH)](4)$

(a) A mixture containing 1 (87 mg, 0.10 mmol), Tol-SSTol (123 mg, 0.50 mmol), and Zn powder (129 mg, 1.97 mmol) in THF (8 cm³) was refluxed for 2 h. The resultant mixture was dried up in vacuo and the residue was extracted with benzene. Addition of EtOH to the concentrated extract afforded **3** as yellow microcrystals (54 mg, 32%). IR (KBr, cm⁻¹): 2500 [ν (BH)]. ¹H NMR (CD₂Cl₂, ppm): 1.95 (s, 6H) and 2.21 (s, 6H), C₆H₄*Me*; 5.65 (d, 4H), 5.67 (d, 4H), 6.15 (d, 4H), and 6.50 (d, 4H), C₆H₄Me; 5.13 (t, 2H), 5.52 (t, 2H), 5.54 (t, 2H), 5.71 (d, 2H), 6.95(d, 2H), 7.56 (d, 2H), 7.61 (d, 2H), 7.62 (d, 2H), and 7.68 (d, 2H), Pz; 7.1–7.3 (m, 30H), PPh₃. EPMA: atomic ratio of Ru:Zn:S:P=2:1:4:2. *Anal.* Found: C, 57.66; H, 5.00; N, 9.32. Calc. for C₈₂H₇₈N₁₂P₂S₄B₂Ru₂Zn: C, 57.36; H, 4.93; N, 9.03.

(b) A mixture containing 1 (44 mg, 0.050 mmol) and $AgBF_4$ (10 mg, 0.050 mmol) in THF (4 cm³) was stirred at room temperature for 30 min. The resultant suspension was filtered and the filtrate was poured into a mixture of ToISSToI (62 mg, 0.25 mmol) and Zn powder (26 mg, 0.40 mmol) in THF (4 cm³). After refluxing for 2 h, all volatile materials were removed in vacuo and the residue was extracted with benzene. Addition of MeOH to the concentrated extract gave microcrystalline **3** as the major product, together with a small amount of **4** as the yellow prismatic crystals. The yield of each compound could not be specified.

2.4. X-ray crystallography of 2 and 4

Single crystals of 2 and 4 mounted in glass capillaries under N_2 were transferred to a Rigaku AFC7R diffractometer equipped with a graphite-monochromated Mo K α source. Cell constants and orientation matrices were derived from the least-squares fit of 25 machine-centered reflections of $35 < 2\theta < 40^\circ$. Data collections were carried out at room temperature and intensity data were corrected for the Lorentz-polarization effects and for absorption. Intensities of three check reflections were measured every 150 reflections, which showed no significant decay for both compounds.

All calculations were performed by the use of the teXsan program package [13]. Structures were solved by a combination of the Patterson methods and Fourier syntheses [14], and refined by full-matrix least-squares techniques using anisotropic parameters for all non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and included at the final stage of refinements with fixed parameters $[d(C-H) = 0.95 \text{ Å}; B_{eq} (H) = 1.2B_{eq} (attached C)]$. Details of X-ray crystallography are given in Table 1.

3. Results and discussion

3.1. Synthesis and X-ray structure of $[TpRu(\eta^2-S_2CNMe_2)-(PPh_3)](2)$

Extensive studies in this laboratory have already demonstrated that $[(Cp^*Ru)_4(\mu-Cl)_4]$ and $[Cp^*RuCl(\mu-Cl)_2-$ RuCp*Cl] react readily with various thiolate sources including HSR [15], Me₃SiSR [15a], NaSR [16], and RSSR [17] to give a series of thiolate-bridged diruthenium complexes. Reactivities of the related phosphine (L) adducts such as $[Cp'Ru(L)_2Cl]$ and $[Cp'Ru(L)Cl_2]$ (Cp' = Cp or Cp^{*}) towards thiolate compounds have also been studied by us and others though less extensively, which disclosed, for example, the formation of mononuclear thiolate complexes $[CpRu(PPh_3)_2SR]$ (5) from the reactions of [CpRu- $(PPh_3)_2CI$ (6) with LiSR (R = alkyl, aryl) [18] or $Bu^{n}_{3}SnSPh$ [19], and $[Cp^{*}Ru(PR'_{3})(SR)_{2}]$ by treatment of $[Cp^*Ru(PR'_3)Cl_2]$ with NaSR (R, R' = Ph, Me) [15a]. In the reaction mixture of 6 with LiSR, dimeric and trimeric products are formed as well as complex 5, which are considered to include a well-defined trimeric compound $[(CpRu)_3(\mu_2-SPr^n)_3]$ and a dimeric complex $[\{CpRu (PPh_3)_2(\mu$ -SPrⁿ)₂ not yet available in a pure form [20].

In contrast to the high reactivities of Cp'Ru precursors towards various thiolate compounds, complex 1 did not react with RSH, Me₃SiSR, or RSSR, and the reactions of 1 with NaSR resulted in the formation of untractable products. However, in the course of these studies, we have found that 1 reacts with NaS₂CNMe₂ in THF at reflux to give the η^2 dithiocarbamate complex 2 in high yield (Eq. (1)).

Table 1					
Crystallographic	data	for	2	and	4

	2	4	
Crystal data			
Formula	$C_{30}H_{31}N_7BPS_2Ru$	C49H50N6OS3PBRuZn	
Formula weight	696.6	1043.4	
Crystal system	triclinic	triclinic	
Space group	<i>P</i> Ī (No. 2)	<i>P</i> 1 (No. 2)	
$a(\mathbf{\ddot{A}})$	10.373(2)	12.876(3)	
$b(\dot{\mathbf{A}})$	16.259(2)	19.052(3)	
c (Å)	9.979(2)	10.686(2)	
α (°)	99.31(1)	92.83(2)	
β (°)	112.10(1)	112.56(2)	
γ (°)	87.58(1)	87.83(2)	
$V(\dot{\mathbf{A}}^3)$	1538.4(4)	2417.4(9)	
Z	2	2	
$D_{\rm code}$ (g cm ⁻³)	1.504	1.433	
F(000)	712	1072	
μ (Mo K α , cm ⁻¹)	7.31	10.14	
Data collection			
Sean type	$\omega - 2\theta$	ω-2θ	
Scan rate (° min ⁻¹)	16	16	
$2\theta_{\rm max}(2)$	55	50	
No. unique reflections measured	7061	8537	
Transmission factors	0.978-1.00	0.715-1.00	
Solution and refinements			
No. data used $(1 > 3.0\sigma(1))$	3573	4962	
No. variables	379	568	
Data/parameter ratio	9.43	8.74	
Weighting scheme	$1/\sigma^2(F_{\rm o})$	$1/\sigma^2(F_o)$	
$R_{\rm e}R_{\rm w}$	0.026, 0.053	0.048, 0.034	
Maximum residual (e Å $^{-3}$)	0.41	1.45	



Analogous reaction carried out in CH₂Cl₂ at room temperature overnight afforded the desired product **2** in only 23% yield. Related Cp' complexes [Cp'Ru(η^2 -S₂CNRR')-(PPh₃)] [Cp'=Cp, η^5 -CH₃C₅H₄, η^5 -CH₃COC₅H₄; R, R'=Et₂, (CH₂)₄] have previously been synthesized from [Cp'Ru(PPh₃)₂Cl] and NaS₂CNRR' in refluxing MeOH or CHCl₃ [21], and the closely relevant complex [CpRu(η^2 -S₂CNMe₂)(PPh₃)] (7) has been obtained from [CpRu(PPh₃)₂(HSC₃H₇)] ' by treatment with NaS₂CNMe₂ in CH₂Cl₂ [22]. Since the single crystals were readily obtained for **2**, its detailed structure has been determined by the X-ray crystallography.

The ORTEP drawing of **2** is shown in Fig. 1, while pertinent bonding parameters of **2** are listed in Table 2. Complex **2** has a distorted octahedral structure in which the Tp ligand



Fig. 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 30% probability level.

coordinates to the Ru atom in an η^3 fashion with the N–Ru– N angles varying from 83.9(2) to 88.3(2)°. The dithiocarbamate ligand is planar and bound to Ru in a bidentate manner but not symmetrically; one Ru–S bond distance [Ru–S(1): 2.423(2) Å] is somewhat longer than the other [Ru–S(2): 2.360(2) Å], presenting a marked contrast to the almost symmetrical coordination found in the S₂CNMe₂ ligand of 7 [Ru-S: 2.397(3) and 2.394(3) Å] [22] as well as the related S₂CSPrⁿ ligand of [CpRu(η^2 -S₂CSPrⁿ)(PPh₃)] (8) [Ru-S: 2.374(4) and 2.362(2) Å] [18]. However, in the ¹H NMR spectrum of **2** the methyl protons are recorded as a sharp singlet, indicating that two methyl groups in the dithiocarbamate ligand are equivalent in solution. The S-Ru-S angle at 72.38(5)° and two S-Ru-P angles at 89.96(5) and $93.51(5)^{\circ}$ in **2** are comparable with those in **7** [S-Ru-S: $71.88(9)^{\circ}$, S-Ru-P: 89.82(9) and 95.18(9) $^{\circ}$ and 8 [S-Ru-S: 71.47(11)°, S-Ru-P: 90.76(12) and 93.35(9)°], which indicates that the Tp ligand with a much greater cone angle (close to 180°) than that of the Cp moiety (100°) [7c.23] causes little difference in the coordination geometry of the remaining three ligands between the Tp complex 2 and the Cp complexes 7 and 8.

3.2. Synthesis of mixed-metal complex [{TpRu(PPh₃)-(µ-STol)₂}₂Zn] (3) and X-ray structure of [TpRu(PPh₃)-(µ-STol)₂Zn(STol)(MeOH)] (4)

As described already, complex 1 did not react with RSSR (R = alkyl, aryl) even under forcing conditions. However, when treated with TolSSTol in the presence of Zn in THF at reflux, 1 was converted to a trinuclear Ru_2Zn complex 3 having four bridging thiolate ligands (Eq. (2)).



The elemental analysis as well as the EPMA data strongly suggested the formula $| \{TpRu(PPh_3) (\mu-STol)_2\}_2Zn |$ for **3**, and the ¹H NMR spectrum also confirmed this formulation. The inequivalent nature of the three pyrazolyl groups in the Tp ligand as well as the appearance of two sets of thiolate resonances demonstrated by the ¹H NMR spectrum can be interpreted in terms of the structure having a two-fold symmetry imposed on the tetrahedral Zn atom. The plausible structure for **3** is shown in Eq. (2), which illustrates one enantiomer, and **3** must exist as a mixture of two enantiomers. Unfortunately, despite many trials, single crystals of **3** suitable to X-ray crystallography have not been obtained.

To improve the yield of **3**, another procedure involving the treatment of **1** with $AgBF_4$ prior to the reaction with a Zn–TolSSTol mixture was followed. Although this did not provide a better route to **3**, a new product (**4**) was isolated as good-quality crystals in trace amounts together with microcrystalline **3** (Eq. (3)).

 Table 2

 Selected bond distances and angles in 2 and 4

2			
Bond distances $(\hat{\Lambda})$			
Ru-S(1)	2.423(2)	Ru-S(2)	2.360(2)
Ru–P	2.292(2)	Ru-N(1)	2.143(4)
Ru-N(3)	2.096(4)	Ru-N(5)	2.132(4)
$S(1) \sim C(10)$	1.723(6)	S(2) - C(10)	1.697(6)
Bond angles (°)			
S(1)-Ru-S(2)	72.38(5)	S(1)-Ru-P	89.96(5)
S(1)-Ru=N(1)	104.9(1)	S(1)-Ru-N(3)	165.0(1)
S(1)=Ru=N(5)	90.3(1)	S(2)Ru-P	93.51(5)
S(2)=Ru=N(1)	173.1(1)	S(2)-Ru-N(3)	93.6(1)
S(2)-Ru-N(5)	88.5(1)	Ru-S(1)-C(10)	86.6(2)
Ru-S(2)-C(10)	89.2(2)	S(1)-C(10)-S(2)	111.4(3)
4			
Bond distances (Å)			
Ru-S(1)	2.417(2)	Ru-S(2)	2.399(2)
Ru–P	2.349(2)	Ru-N(1)	2.122(6)
Ru-N(3)	2.110(6)	Ru=N(5)	2.079(6)
Zn-S(1)	2.338(2)	Zn-S(2)	2.331(2)
Zn=S(3)	2.260(2)	Zn-O(1)	2.042(5)
Bond angles (°)			
S(1)-Ru-S(2)	83.68(7)	S(1)-Ru-P	91.51(7)
S(1)-Ru-N(1)	98.5(2)	S(1)-Ru-N(3)	91.4(2)
S(1)-Ru-N(5)	172.6(2)	S(2)-Ru-P	95.94(7)
S(2) = Ru = N(1)	174.2(2)	S(2)-Ru-N(3)	91.3(2)
S(2)-Ru-N(5)	89.3(2)	P-Ru-N(1)	89.4(2)
P-Ru-N(3)	172.5(2)	P-Ru-N(5)	91.6(2)
S(1)-Zn-S(2)	86.94(7)	S(1) = Zn = S(3)	129.19(8)
S(1)-Zn-O(1)	104.7(2)	S(2) - Zn - S(3)	134.08(8)
S(2)-Zn=O(1)	102.5(1)	S(3) - Zn - O(1)	94.8(2)
Ru=S(1)=Zn	93.21(7)	Ru-S(1)-C(1)	119.2(3)
Zn-S(1)-C(1)	109.1(2)	Ru=S(2)=Zn	93.87(8)
Ru=S(2)=C(8)	119.2(3)	Ru = S(2) = C(8)	107.7(2)



Although the paucity of 4 hampered the analytical and spectroscopic characterization, its structure has been determined unequivocally by single-crystal X-ray diffraction study. As shown in Fig. 2, the structure of 4 may relate intimately to that proposed for 3 in that the former may be derived from the latter by replacing one TpRu(STol) fragment with MeOH. This structural relationship might support, though indirectly, the proposed structure of 3.

Selected bond distances and angles in **4** are given in Table 2. Complex **4** consists of the Ru(II) and Zn(II) atoms separated by 3.46 Å, which indicates the absence of any direct interaction. These two metal centers were connected by two bridging STol ligands and the four-membered ring constituted by one Ru, one Zn, and two S atoms is slightly puckered with the dihedral angle of $\sim 12^\circ$ along the S–S vector. Two Tol substituents are attached to this ring in mutually syn



Fig. 2. Molecular structure of **4**. Thermal ellipsoids are drawn at the 30% probability level.

orientation. For the bridging STol ligands, the Ru–S bonds [2.417(2) and 2.399(2) Å] are considerably elongated from the corresponding Zn–S bonds [2.338(2) and 2.331(2) Å], but both are not exceptional for bond distances between the Ru² or Zn³ atom and the bridging thiolate.

The Ru atom has a slightly distorted octahedral configuration and the facial Tp ligand is bound to Ru with the N– Ru–N angles of $83.3(2)-88.2(2)^\circ$, which are comparable with those in **2** (vide supra). Around the essentially tetrahedral Zn atom, the S(terminal)–Zn–S(bridging) angles [129.19(8) and 134.08(8)°] are much wider than the S(bridging)–Zn–S(bridging) angle of $86.94(7)^\circ$. It is also worth noting that the Zn–S(bridging) bond distances described above are considerably longer than the Zn– S(terminal) bond length at 2.260(2) Å. Analogous feature has previously been observed in the dinuclear Zn complex with benzene-1,2-dithiolate ligands [Zn₂(C₆H₄S₂)₂-(C₈H₆N₄)₂] [2.433(3) and 2.475(3) Å versus 2.303(3) Å] [28].

4. Supplementary material

Tables listing atom coordinates, anisotropic displacement parameters for non-hydrogen atoms, extensive bond distances and angles, and observed and calculated structure factors are available from author (Y.M. or M.H.) upon request.

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 $^{^2}$ The Ru–SR(bridging) bond distances observed in various dinuclear Cp*Ru complexes cited above fall in the range 2.28–2.42 Å.

³ For example, the Zn–SR(terminal) distances observed in $[Zn(SPh)_4]^2 = [24]$ and $[Zn(SPh)_3(MeIm)]^{++} [25]$ are 2.31–2.37 Å, while the Zn–SR(bridging) bond lengths found in $[Zn_{10}S_4(SPh)_{16}]^4 = [26]$, $[Zn_{10}S_4(SEt)_{12}(C_5NH_4Me_2)_4] = [27]$, and $[Zn_2(C_6H_4S_2)_2 + (C_8H_6N_4)_2] = [28]$ are 2.39–2.48 Å.

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