Preparation of Rhodium Pentasulfido(2−) Complexes with Hydrotris(3,5-dimethylpyrazol-1-yl)-borato Coligand

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Treatment of [Tp*Rh(coe)(MeCN)] (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate; coe = cyclooctene) with S_8 in MeCN afforded a complex with a chelating pentasulfido(2−) ligand [Tp*Rh(S_5)(MeCN)], which was converted further to [Tp*Rh(S_5)(CNXy)] (**3**; Xy = 2,6-$Me_2C_6H_3$) by the reaction with XyNC. An X-ray analysis was carried out for **3**, which disclosed a chair conformation for the RhS_5 ring.

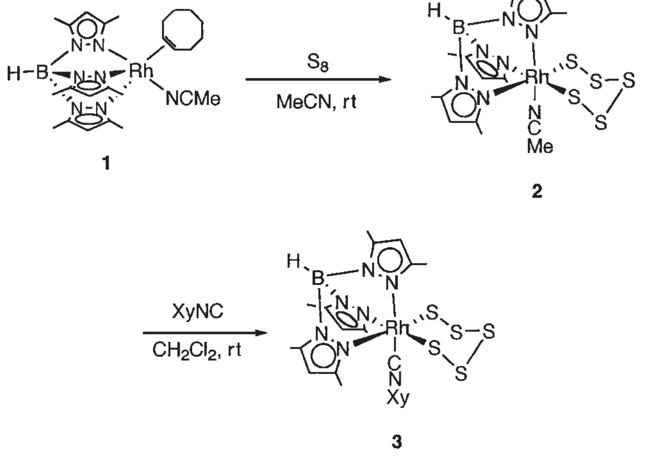
Our recent studies have focused on the chemistry of noble metal complexes with sulfur-donor ligands.[1] Much effort has been paid to synthesizing thiolato- and sulfido-bridged multimetallic complexes and clarifying their reactivities. During the course of these studies, it turned out that the multinuclear complexes containing Cp*M units (M = Ru, Rh, Ir; Cp* = η^5-C_5Me_5) showed remarkable structural diversities and numerous intriguing reactivities. Such interesting findings spurred us more recently to extend these studies to complexes having the Tp′ ligands (Tp′ = hydrotris(pyrazol-1-yl)borate (Tp) and its congeners),[2] which are isoelectronic with ubiquitous cyclopentadienyls, but are still being studied poorly compared to cyclopentadienyls.

In a previous paper,[3] we reported on the syntheses of a series of mononuclear and dinuclear thiolato complexes containing Tp′Rh units (Tp′ = Tp or Tp*; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) from [Tp′Rh(coe)(MeCN)] (coe = cyclooctene) and certain thiolate sources. These included, for example, [Tp*Rh(SR)$_2$(MeCN)] (R = Ph, 4-MeC_6H_4), obtained by the reaction of [Tp*Rh(coe)(MeCN)] (**1**) with one equiv of RSSR. Now we have found that the reaction of **1** with elemental sulfur gives a Rh^{III} complex with a chelating pentasulfido(2−) ligand [Tp*Rh(S_5)(MeCN)] (**2**). In this paper, we wish to describe the synthesis and characterization of **2** and its XyNC derivative [Tp*Rh(S_5)(XyNC)] (**2**; Xy = 2,6-$Me_2C_6H_3$), which represent the still-rare examples of transition metal S_5 complexes containing organic coligands.

When **1** was treated with ca. 5/8 equiv of S_8 in MeCN at room temperature, a pentasulfido(2−) complex **2** was obtained in moderate yield as a brown solid (Scheme 1). Attempts to prepare the crystals of **2** for X-ray diffraction led to the isolation of some single crystals by recrystallizing the product from CH_2Cl_2–hexane. However, due to their poor quality, only the preliminary X-ray results were available. Nevertheless, the atom-connecting scheme shown in Scheme 1 has been unambiguously demonstrated. The ^{1}H NMR spectrum of **2** is consistent with this structure, showing the CH_3 and CH protons in the Tp* ligands as two sets of signals with the intensity ratio of 2:1. The presence of one MeCN coordinated to Rh was confirmed by a singlet resonance at δ 1.01 in the ^{1}H NMR spectrum and the characteristic ν(C≡N) band at 2304 cm^{-1} in the IR spectrum, both shifting from δ 1.54 of MeCN in C_6D_6 and 2254 cm^{-1} of neat MeCN. Unfortunately, in spite of many attempts to purify **2**, we could not obtain **2** in an analytically pure form.

To fully characterize the core structure with the pentasulfido(2−) ligand by the X-ray analysis, reactions of **2** with certain π-acceptor ligands were carried out, and it has been found that the substitution product **3**, derived by treating **2** with 1 equiv of XyNC in CH_2Cl_2 at room temperature, was available as single crystals suitable for X-ray diffraction.

As shown in Fig. 1, **3** has the expected octahedral structure containing a chelating S_5 ligand together with the *fac*-Tp* and end-on XyNC ligands. The RhS_5 ring has a chair conforma-



Scheme 1.

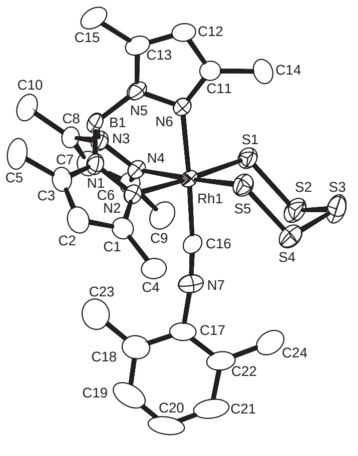


Fig. 1. An ORTEP drawing for **3** at 30% probability level. Hydrogen atoms are omitted for clarity.

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Table 1. Selected Bond Distances (Å) and Angles (°) in **3**

Rh–S(1)	2.341(1)	Rh–S(5)	2.337(1)
Rh–N(2)	2.139(2)	Rh–N(4)	2.129(2)
Rh–N(6)	2.119(2)	Rh–C(16)	1.911(3)
S(1)–S(2)	2.022(1)	S(2)–S(3)	2.073(1)
S(3)–S(4)	2.070(1)	S(4)–S(5)	2.027(1)
C(16)–N(7)	1.153(4)		
S(1)–Rh–S(5)	92.48(3)	Rh–S(1)–S(2)	110.76(4)
Rh–S(5)–S(4)	110.77(5)	S(1)–S(2)–S(3)	106.49(6)
S(2)–S(3)–S(4)	100.94(6)	S(3)–S(4)–S(5)	105.90(6)
Rh–C(16)–N(7)	174.6(3)	C(16)–N(7)–C(17)	172.1(3)

tion, in which the Rh–S–S bonds are bent in a manner that the β-S atoms are oriented away from the Tp* group to avoid any steric repulsion. The Rh–S bond lengths are 2.341(1) and 2.337(1) Å, while the S–Rh–S angle is 92.48(3)°. In the CpRh counterpart, $[CpRh(S_5)(PPh_3)]$ (**4**; Cp = η^5-C_5H_5), which is obtained as the major product from the reaction of $[CpRh(PPh_3)_2]$ with S_8, the RhS_5 ring has a chair structure with the β-S atoms oriented toward the Cp group, where the Rh–S bond lengths are reported to be 2.359(2) and 2.351(2) Å, with the S–Rh–S angle being 92.09°.[4] These values in the Rh pentasulfido(2−) complexes are also comparable to those in the closely related Tp*Rh dithiolato complex $[Tp^*Rh(SC_6H_4Me\text{-}4)_2(MeCN)]$ at 2.342(1) and 2.338(1) Å, and 94.38(5)°, respectively.[3] With respect to the XyNC ligand, the Rh–C(16)–N(7) and C(16)–N(7)–C(17) linkages are bent only slightly (174.6(3) and 172.1(3)°), and these as well as the Rh–C(16) and C(16)–N(7) bond distances at 1.911(3) and 1.153(4) Å, respectively, are not exceptional for the η^1-XyNC ligand (Table 1).

In addition to **3** and **4**, $[Rh(S_5)(edpp)_2]^+$ (edpp = (2-aminoethyl)diphenylphosphine)[5] and $[Rh(S_5)_3]^{3-}$[6] are known as well-defined Rh complexes with a chelating S_5 ligand. The X-ray analyzed S_5 complexes of other transition metals include, for example, $[Cp_2Ti(S_5)]$,[7] $[Cp_2V(S_5)]$,[8] $[Fe(NO)_2(S_5)]^-$,[9] $[(S_5)Fe(\mu\text{-}S)_2Fe(S_5)]^{2-}$,[10] $[CpCo(PMe_3)(S_5)]$,[11] and $[Pt(S_5)_3]^{2-}$,[12] all having a chair conformation, whereas $[Cp^*Th(S_5)]$[13] and $[\{Ti(Bu^t{}_3PN)_2\}(S_5)]$[14] contain the twist-boat MS_5 rings, which are observed less commonly. In contrast, a bicyclic structure with the coordination of three S atoms at the α-, β-, and ω-positions has been demonstrated for $[Ru(S_5)\{P(OR)_3\}_3]$ (R = Me, Et).[15]

Experimental

General. All manipulations were carried out under N_2 using standard Schlenk techniques. Solvents were dried by common methods and distilled under N_2 before use. Complex **1** was prepared according to literature methods,[16] while other chemicals were obtained commercially and used as received.

NMR and IR spectra were measured on a JEOL alpha-400 or a JASCO FT/IR-420 spectrometer at room temperature. Elemental analyses were conducted with a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of 2. A mixture of **1** (99 mg, 0.18 mmol) and S_8 (70 mg, 0.11 mmol) in MeCN (5 mL) was stirred at room temperature for 3 h. The resultant red mixture was dried up in vacuo and the residue was extracted with toluene. The addition of hexane to the concentrated extract afforded **2** as a brown solid in 80% yield. IR (KBr): 2530 (B–H), 2304 (C≡N) cm^{-1}; ^1H NMR (C_6D_6): δ 5.63 (s, 2H, CH in Tp*), 5.36 (s, 1H, CH in Tp*), 3.60 (s, 3H, Me in Tp*), 2.63 (s, 6H, Me in Tp*), 2.07 (s, 6H, Me in Tp*), 1.95 (s, 3H, Me in Tp*), 1.01 (s, 3H, MeCN).

Table 2. X-ray Crystallographic Data

Empirical formula	$C_{24}H_{31}N_7BS_5Rh$
Formula weight	691.57
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a/Å	9.758(2)
b/Å	10.549(2)
c/Å	15.800(3)
α/°	81.960(6)
β/°	72.619(5)
γ/°	86.338(6)
V/Å^3	1536.4(5)
Z	2
μ(Mo Kα)/cm^{-1}	9.22
Number of reflections used [$I > 3\sigma(I)$]	5395
Number of variables	374
$R1^{a)}$	0.035
$wR2^{b)}$	0.102
GOF$^{c)}$	1.05

a) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$. c) GOF $= [\Sigma w(|F_o| - |F_c|)^2/\{(\text{No. observed}) - (\text{No. variables})\}]^{1/2}$.

Preparation of 3. Into a CH_2Cl_2 solution (8 mL) of **2** (121 mg, 0.200 mmol) was added XyNC (27 mg, 0.21 mmol), and the mixture was stirred overnight at room temperature. The addition of hexane to the concentrated product solution gave **3** as orange crystals (50 mg, 36% yield). IR (KBr): 2530 (B–H), 2187 (N≡C) cm^{-1}; ^1H NMR (C_6D_6): δ 6.67 (t, 1H, 4-H in XyNC), 6.51 (d, 2H, 3- and 5-H in XyNC), 5.51 (s, 2H, CH in Tp*), 5.47 (s, 1H, CH in Tp*), 3.52 (s, 3H, Me in Tp*), 2.63 (s, 6H, Me in Tp*), 2.20, 2.01 (s, 6H each, Me in Tp* and XyNC), 2.00 (s, 3H, Me in Tp*). Anal. Calcd for $C_{24}H_{31}N_7BS_5Rh$: C, 41.68; H, 4.52; N, 14.18%. Found: C, 41.95; H, 4.45; N, 14.54%.

X-ray Crystallography. A single crystal of **3** was sealed in a glass capillary under argon and mounted on a Rigaku Mercury-CCD diffractometer equipped with a graphite-monochromatized Mo Kα source. All diffraction studies were done at 23 °C, the details of which are listed in Table 2.

Structure solution and refinements were carried out by using the CrystalStructure program package.[17] The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY)[18] and subsequent Fourier synthesis (DIRDIF 99).[19] These were refined with anisotropic thermal parameters by full-matrix least-squares techniques. Hydrogen atoms were placed at the calculated positions and included at the final stages of the refinements with isotropic thermal parameters.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-271751 for **3**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit @ccdc.cam.ac.uk).

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