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Synthesis and X-ray structures of hydridotris(1-pyrazolyl)borate carbonyl complexes of ruthenium

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Abstract

A series of new hydridotris(1-pyrazolyl)borate (Tp) carbonyl complexes of ruthenium were synthesized. Treatment of [TpRu(CO)$_2$X] (X = Br, I) with Me$_3$NO in MeCN afforded [TpRu(CO)(NCMe)X] (X = Br (**1**), I (**2**)). The reactions of **1** and **2** with either neutral isocyanides or anionic dialkyldithiocarbamates to produce [TpRu(CO)(CNR)X] (X = Br, R = PhCH$_2$ (**3**); X = Br, R = ^{t}Bu (**4**); X = I, R = PhCH$_2$ (**5**) X = I, R = ^{t}Bu (**6**)) and [TpRu(CO)(η^2-S$_2$CNR$_2$)] (R = Me (**7**), Et (**8**)), respectively. Compounds **1** and **2** reacts with RSH–Et$_3$N in THF or 1,2-dimethoxyethane at reflux to give mono- and dithiolato diruthenium products, (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-X)(μ-SR)] (X = I, R = ^{i}Pr (**11**); X = Br, R = ^{t}Bu (**13**); X = I, R = ^{t}Bu (**14**)), (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**9**), (*cis*, *syn*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**10**), (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{t}Bu)$_2$] (**12**), and (*cis*, *anti*-2)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)(μ-S^{t}Bu)] (**15**). Compound **11** reacts with Me$_3$NO to form stereo- and chemospecifically the first diruthenium sulfenate, (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-I)(μ-S(O)^{i}Pr)] (**16**) with the S=O bond at the *endo* position with respect to carbonyls. Structures **8**, **9**, **10**, **12**, **14**, **15**, and **16** are described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Hydridotris(1-pyrazolyl)borate; Thiolates; Isocyanides; Dialkyl dithiocarbamates; Carbonyl

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1. Introduction

Since the discovery of the pyrazolylborate ligands by Trofimenko in 1966 [1], an extensive transition-metal chemistry that utilizes these ligands has emerged [2]. Due to the apparent similarity in coordination and electronic structure to the cyclopentadienyl (Cp) ligand, much chemistry developed with the hydridotris(L-pyrazolyl)borate (Tp) ligand has involved compounds whose Cp analogues were well established. Despite these similarities, there were for many years few and scattered reports of mixed-ligand complexes of ruthenium containing a Tp ligand, a carbonyl ligand, and other ligands [3], in contrast with numerous corresponding CpRu(CO) complexes [4]. The obvious reason is the lack of TpRu(CO) starting compounds. Previous attempts, as well as our own attempts (vide infra) to synthesize the mixed-ligand Ru compounds using [TpRu(CO)$_2$X] (X = Br, I) [3a,3d] were frustrated by low or no conversion. However, we wish to report here that [TpRu(CO)(MeCN)X] (X = Br (**1**), I (**2**)) can be obtained readily and serve as a better starting material, leading to a series of new TpRu(CO) products.

2. Results and discussion

2.1. Preparation of [TpRu(CO)(MeCN)X] (X = Br (1), I (2))

The Tp ligand, with its steric bulk (cone angle 180°) and unique electronic properties [5], is known to bias formation of the octahedral six-coordinate complexes of transition-metal atoms. It is hence not unexpected that no genuine seven-coordinate TpRu compounds were described in the literature [3,6]. This propensity of the ligand apparently accounts for the observed poor

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reactivity of [TpRu(CO)$_2$X] (X = Br, I) toward various nucleophiles even under forced conditions. Thus, it usually allows only a partial conversion (ca. 30–50%), shown in the sequentially measured solution IR spectra, from [TpRu(CO)$_2$X] into other derivatives, even when the reaction mixture of [TpRu(CO)$_2$X] and nucleophiles in MeCN was heated at 82 °C for 3 days. Unfortunately, there were for many years no reports in the literature concerning any other {TpRu(CO)} complexes as good starting material [3]. We have now found that employment of [TpRu(CO)(MeCN)X] (X = Br (**1**), I (**2**)), prepared in a high yield from decarbonylation of [TpRu(CO)$_2$X] with Me$_3$NO in MeCN, as the starting compounds can allow a complete conversion into the derived products. Apparently compounds **1** and **2** are the lightly stabilized complexes [7], and can serve as a good starting material leading to other substituted compounds.

2.2. Formation of monomeric TpRu(CO) complexes

No apparent reaction between [TpRu(CO)$_2$X] and neutral alkyl isocyanides in MeCN was observed, monitored by sequential solution IR spectra, even under reflux for a week. However, treatment of **1** and **2** with a slight excess of RNC under reflux for 12 h gave the expected complexes [TpRu(CO)(CNR)X] (X = Br, R = PhCH$_2$ (**3**), ^{t}Bu (**4**); X = I, R = PhCH$_2$ (**5**), ^{t}Bu (**6**)) in 60–70% yield. Likewise, reaction between **2** and anionic dialkyldithiocarbamate produced as expected [TpRu(CO)(η^2-S$_2$CNR$_2$)] (R′ = Me (**7**), Et (**8**)) in a satisfactory yield within a reasonable period of time. The monomeric feature of **8** was also confirmed by its crystal structure (Fig. 1). The C–N distance of the coordinated diethyldithiocarbamate, d(C(11)–N(7)) = 1.329(3) Å, is within the typical range of 1.31–1.36 Å [8] for containing a partial double-bond character, and the distance is found compatible with the C–N stretching frequency of 1501 cm^{-1} measured in CH$_2$Cl$_2$.

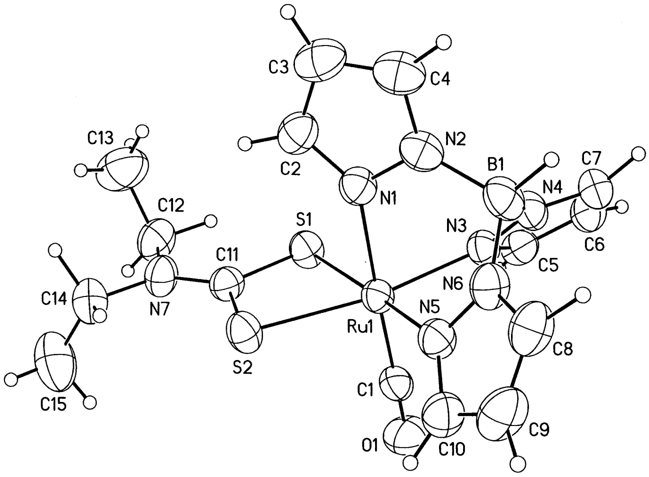
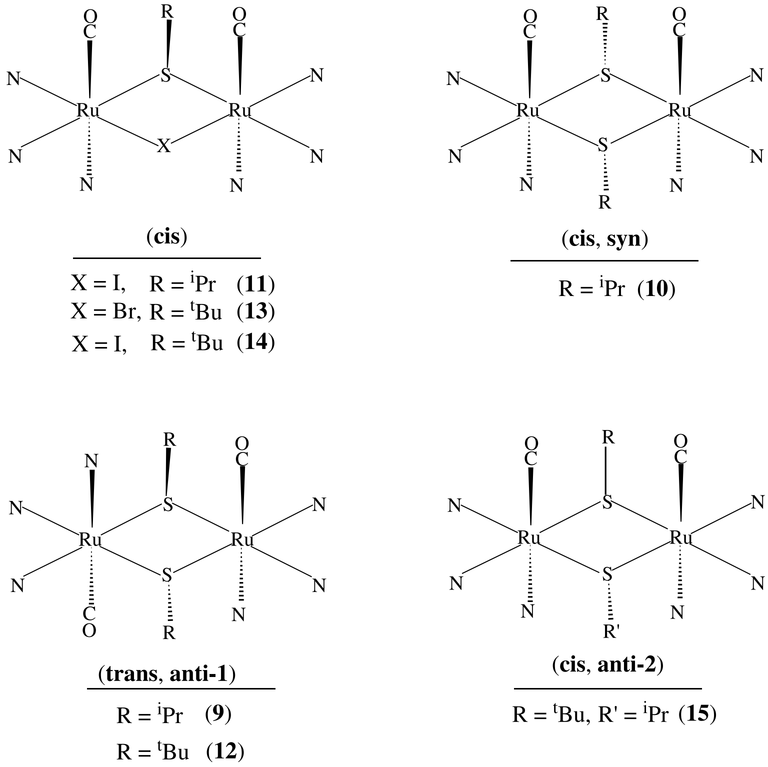


Fig. 1. ORTEP drawing of [TpRu(CO)(η^2-S$_2$CNEt$_2$)] (**8**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°) are as follows: Ru(1)–C(1), 1.834(3); Ru(1)–N(1), 2.158(2); Ru(1)–N(3), 2.101(2); Ru(1)–N(5), 2.113(2); Ru(1)–S(1), 2.3811(7); Ru(1)–S(2), 2.4013(7); S(1)–C(11), 1.725(3); S(2)–C(11), 1.724(3); C(11)–N(7), 1.329(3); C(1)–O(1), 1.146(3); S(1)–Ru(1)–S(2), 72.93(2); Ru(1)–C(1)–O(1), 178.7(2); S(1)–C(11)–S(2), 123.9(2).

2.3. Formation of dimeric TpRu(CO) complexes

Prior to studying the reactions between [TpRu(CO)-(MeCN)X] and thiolates, it was expected to obtain dimeric {Tp$_2$Ru$_2$} products with exclusively *trans*-disposed Tp ligands, based on the steric bulk of this ligand. However, to our surprise, seven different products were obtained with five *cis* and two *trans* compounds, containing one and two thiolato bridges: (*cis*)-[Tp$_2$Ru$_2$(CO)(μ-X)(μ-SR)] (X = I, R = ^{i}Pr (**11**); X = Br, R = ^{t}Bu (**13**); X = I, R = ^{t}Bu (**14**)), (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**9**), (*cis*, *syn*)-[Tp$_2$Ru$_2$(CO)$_2$-(μ-S^{i}Pr)$_2$] (**10**), (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{t}Bu)$_2$] (**12**), and (*cis*, *anti*-2)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)(μ-S^{t}Bu)] (**15**). For the compounds containing two thiolato bridges, except the common *syn* orientation [9], there are two types of *anti* orientations: *anti*-1 for the geometry containing one thiolato R group above plane Ru$_2$S$_2$ and the other group below, and *anti*-2 for the geometry with one thiolato R group below plane Ru$_2$S$_2$ and the other group coplanar with Ru$_2$S$_2$ (Chart 1). [Tp$_2$Ru$_2$(CO)$_2$(μ-Br)(μ-S^{i}Pr)] was not isolated in the reaction between **1** and ^{i}PrSH–Et$_3$N. Clearly with the exception of the steric effect of the Tp ligand, the formation of different products is also dependent on the effect of the halo ligand, X, of [TpRu(CO)-(MeCN)X] and that of the thiolato R group. Using a thiol reagent with a bulkier ^{t}Bu group, or using **2** with a larger iodo ligand, mono-thiolato products [Tp$_2$Ru$_2$(CO)$_2$(μ-X)(μ-SR)] (X = I, R = ^{i}Pr (**11**); X = Br, R = ^{t}Bu (**13**); X = I, R = ^{t}Bu (**14**)) were then observed. The geometries of these mono-thiolato complexes are similar to each other: each displays two carbonyl stretching bands in the IR spectrum, and one set of six doublets in an intensity ratio of 1:1:1:1:1:1 for hydrogen nuclei at the 3- and 5-positions of the pyrazolyl rings of the Tp ligand and a set of three triplets in an intensity ratio of 1:1:1 for those at the 4-positions in the ^{1}H-NMR spectrum. The crystal structure of **14** was determined, and two Tp ligands were found to adopt the *cis* positions (Fig. 2). Sum in the metallacycle Ru(1)/S(1)/Ru(2)/I is 345.50°, deviated largely from the theoretical value of 360° required for planar four-membered ring. It indicates that the four atoms, Ru$_2$SX (X = I, in **14**), are not coplanar. Apparently, [TpRu(CO)(MeCN)X] reacted with RSH–Et$_3$N to form an intermediate [TpRu(CO)(SR)] first, and either dimerization of this intermediate or a subsequent reaction between [TpRu-



(cis)

X = I, R = ^{i}Pr (**11**)
X = Br, R = ^{t}Bu (**13**)
X = I, R = ^{t}Bu (**14**)

(cis, syn)

R = ^{i}Pr (**10**)

(trans, anti-1)

R = ^{i}Pr (**9**)
R = ^{t}Bu (**12**)

(cis, anti-2)

R = ^{t}Bu, R' = ^{i}Pr (**15**)

Chart 1.

(CO)(SR)] and [TpRu(CO)(MeCN)X] then took place to form [$Tp_2Ru_2(CO)_2(\mu$-$SR)_2$] and [$Tp_2Ru_2(CO)_2(\mu$-X)(μ-SR)] (Scheme 1).

The reaction of **1** or **2** with ^{i}PrSH–Et_3N was heated in either THF or 1,2-dimethoxyethane under reflux, giving several products. Two typical reactions as shown in the Section 3 produced (*trans*, *anti*-1)-[$Tp_2Ru_2(CO)_2(\mu$-S^{i}Pr$)_2$] (**9**), (*cis*, *syn*)-[$Tp_2Ru_2(CO)_2(\mu$-S^{i}Pr$)_2$] (**10**), and (*cis*)-[$Tp_2Ru_2(CO)_2(\mu$-I)(μ-S^{i}Pr)] (**11**). The crystal structures of **9** (Fig. 3) and **10** (Fig. 4) were also determined by X-ray diffraction methods to confirm the (*trans*, *anti*-1) and (*cis*, *syn*-1) geometries assigned for **9** and **10**, respectively. Sum in the metallacycle Ru(1)/S(1A)/Ru(1A)/S(1) is 360° in **9**, indicating that unlike Ru_2SX in **14** (Fig. 2), the four atoms, Ru_2S_2 in **9** (Fig. 3) are coplanar, with one thiolato R group above this plane and the other below, probably due to the fact that this structure contains a crystallographically imposed inversion center. Although, structure **10** has a crystallographically imposed mirror plane containing two sulfur atoms, S(1) and S(2), and two carbon atoms, C(11) and C(13), the four Ru_2S_2 atoms (i.e. Ru(1), Ru(1A), S(1), and S(2)), in **10** are not coplanar with sum in the metallacycle Ru(1)/S(2)/Ru(1A)/S(1) of 356.94°.

Except the mono-thiolato complexes, (*cis*)-[$Tp_2Ru_2(CO)_2(\mu$-Br)(μ-S^{t}Bu)] (**13**) and (*cis*)-[$Tp_2Ru_2(CO)_2(\mu$-I)(μ-S^{t}Bu)] (**14**), (*trans*, *anti*-1)-[$Tp_2Ru_2(CO)_2(\mu$-S^{t}Bu$)_2$] (**12**) was separated successfully from the reactions of **1** or **2** with ^{t}BuSH–Et_3N. Compound **12** shows similar features in both IR and ^{1}H-NMR spectra to compound **9**. Like **9**, compound **12** also adopts a (*trans*, *anti*-1) geometry as confirmed by X-ray diffraction methods.

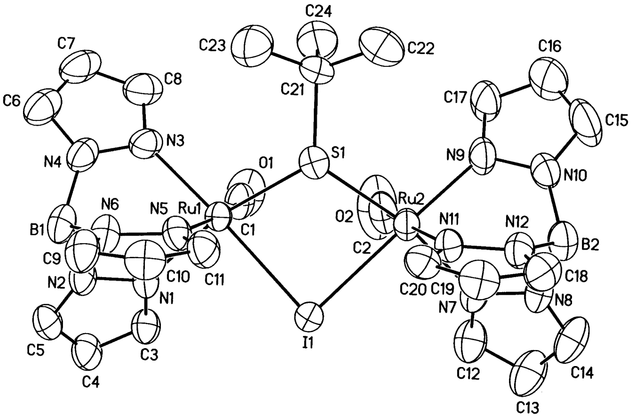
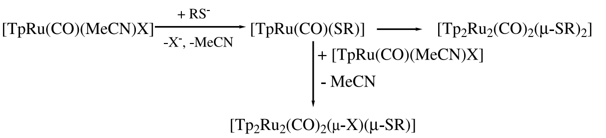


Fig. 2. ORTEP drawing of (*cis*)-[$Tp_2Ru_2(CO)_2(\mu$-I)(μ-S^{t}Bu)] (**14**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Ru(1)–C(1), 1.844(8); Ru(1)–N(1), 2.102(6); Ru(1)–N(3), 2.099(6); Ru(1)–N(5), 2.148(6); Ru(1)–S(1), 2.423(2); Ru(1)–I(1), 2.7288(7); C(1)–O(1), 1.115(10); Ru(2)–C(2), 1.825(9); Ru(2)–N(7), 2.089(6); Ru(2)–N(9), 2.100(7); Ru(2)–N(11), 2.173(6); Ru(2)–S(1), 2.452(2); Ru(2)–I(1), 2.7338(7); C(2)–O(2), 1.152(12); S(1)–C(21), 1.828(8); S(1)–Ru(1)–I(1), 76.07(5); Ru(1)–I(1)–Ru(2), 89.60(2); I(1)–Ru(2)–S(1), 75.53(5); Ru(2)–S(1)–Ru(1), 104.30(8); Ru(1)–C(1)–O(1), 173.2(8); Ru(2)–C(2)–O(2), 171.4(9).



$$\begin{tikzcd}[\mathrm{TpRu(CO)(MeCN)X}] \arrow[r, "+\mathrm{RS}^-", "-\mathrm{X}^-\text{, -MeCN}"'] & [\mathrm{TpRu(CO)(SR)}] \arrow[r] \arrow[d, "+\ [\mathrm{TpRu(CO)(MeCN)X}]", "-\ \mathrm{MeCN}"'] & [\mathrm{Tp_2Ru_2(CO)_2(\mu\text{-}SR)_2}] \\ & [\mathrm{Tp_2Ru_2(CO)_2(\mu\text{-}X)(\mu\text{-}SR)}] & \end{tikzcd}$$

Scheme 1.

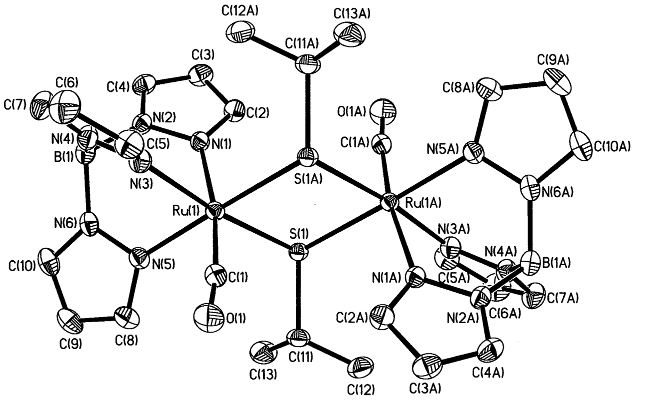


Fig. 3. ORTEP drawing of (*trans*, *anti*-1)-[$\mathrm{Tp_2Ru_2(CO)_2(\mu\text{-}S^{\mathit{i}}Pr)_2}$] (**9**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Ru(1)–C(1), 1.826(3); Ru(1)–N(1), 2.165(2); Ru(1)–N(3), 2.104(3); Ru(1)–N(5), 2.127(3); Ru(1)–S(1), 2.4264(7); S(1)–C(11), 1.858(3); C(1)–O(1), 1.152(4); S(1)–Ru(1)–S(1A), 79.90(3); Ru(1)–S(1)–Ru(1A), 100.10(3); Ru(1)–C(1)–O(1), 172.6(3).

The asymmetric unit of the single crystal used contains one half dinuclear molecule for **9** (Fig. 3), but two such half molecules, **12A** and **12B**, for **12**. Both **9** and **12** contain a crystallographically imposed inversion center. Although structure **12A** is similar to structure **12B**, two methyl groups of the ^{t}Bu group in **12B** were found to be disordered in two positions with an occupancy ratio of 0.726:0.274. Molecule **12A** was drawn in Fig. 5. The fact that the ^{t}Bu singlet for **14** or **13** is at the further upfield position, with δ 0.88 for **14** and δ 1.02 for **13** relative to that of δ 1.74 for **12**, is probably caused by the different shielding ring-current effect of the nearby pyrazolyl moieties of the Tp ligands.

To obtain some diruthenium complexes with mixed thiolato ligands, the reaction of **1** with ^{i}PrSH, ^{t}BuSH, and $\mathrm{Et_3N}$ was also carried out in 1,2-dimethoxyethane. Since a ^{t}Bu group is much larger than an ^{i}Pr group, more ^{t}BuSH than ^{i}PrSH was used in the reaction. Except three homo-dithiolato compounds of **9**, **10**, and **12**, only one hetero-dithiolato product [$\mathrm{Tp_2Ru_2(CO)_2(\mu\text{-}S^{\mathit{i}}Pr)(\mu\text{-}S^{\mathit{t}}Bu)}$] (**15**) was isolated. The crystal structure of **15** was determined and found to contain a crystallographically imposed mirror plane consisting of atoms S(1), S(2), C(11), C(13) and C(15) (Fig. 6). It is worthy to note that structure **15** adopts a unique (*cis*, *anti*-2) geometry with a large R group, ^{t}Bu, rather than a small one, ^{i}Pr, at a position close to the plane $\mathrm{Ru_2S_2}$ (Fig. 6). Like structure **10**, the four atoms, $\mathrm{Ru_2S_2}$, in structure **15** are not coplanar with sum in the metallacycle Ru(1)/S(1)/Ru(1A)/S(2) of 351.03°. In order to find an explanation for **15** to adopt such a geometry, structures, **9**, **10**, **12**, **14**, and **15** were compared with each other again, and a unique feature was then rediscovered as shown in Scheme 2. If the carbon and oxygen atoms of each carbonyl in these structures, the ligated Ru atom, and one *trans*-pyrazolyl nitrogen atom are connected in one imaginary line segment, two such segments in **9** and **12** are found to be almost parallel to each other, but the two segments in **10**, **14**, and **15** are not, forming a small angle of 2.6° in **10**, 8.0° in **14** and 4.4° in **15**. Apparently, the molecular strain resulting from repulsive non-bonded interactions between a bulky Tp ligand and a thiolato group (or a halo group) cannot be relieved in a

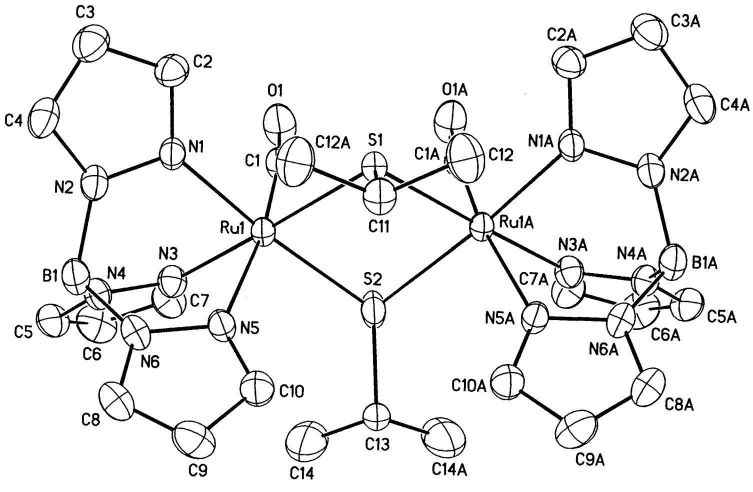


Fig. 4. ORTEP drawing of (*cis*, *syn*)-[$\mathrm{Tp_2Ru_2(CO)_2(\mu\text{-}S^{\mathit{i}}Pr)_2}$] (**10**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Ru(1)–C(1), 1.820(6); Ru(1)–N(1), 2.098(4); Ru(1)–N(3), 2.113(4); Ru(1)–N(5), 2.192(4); Ru(1)–S(1), 2.4146(12); Ru(1)–S(2), 2.415(2); S(1)–C(11), 1.840(7); C(1)–O(1), 1.155(7); S(1)–Ru(1)–S(2), 80.49(6); Ru(1)–S(1)–Ru(1A), 98.00(6); Ru(1)–S(2)–Ru(1A), 97.96(8); Ru(1)–C(1)–O(1), 172.6(5).

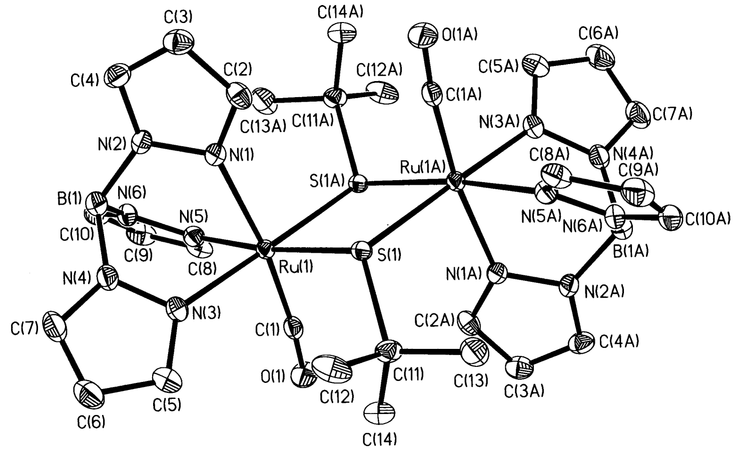


Fig. 5. ORTEP drawing of (*trans*, *anti*-1)-[$Tp_2Ru_2(CO)_2(\mu\text{-}S^tBu)_2$] (**12A**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Ru(1)–C(1), 1.829(3); Ru(1)–N(1), 2.167(3); Ru(1)–N(3), 2.139(3); Ru(1)–N(5), 2.107(3); Ru(1)–S(1), 2.4527(8); S(1)–C(11), 1.895(3); C(1)–O(1), 1.162(4); S(1)–Ru(1)–S(1A), 78.87(3); Ru(1)–S(1)–Ru(1A), 101.13(3); Ru(1)–C(1)–O(1), 173.3(3).

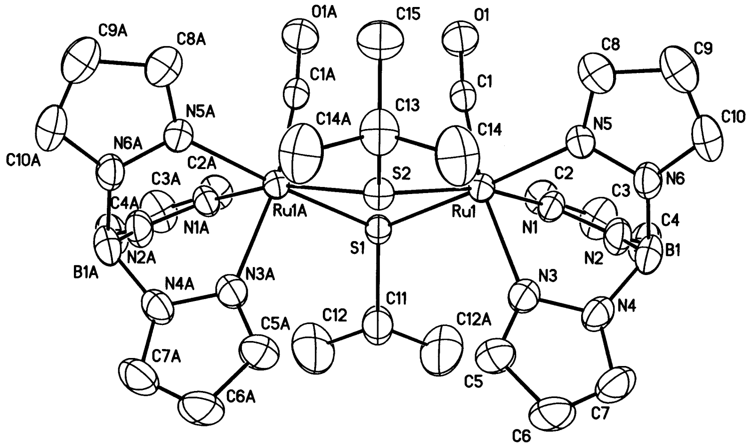


Fig. 6. ORTEP drawing of (*cis*, *anti*-2)-[$Tp_2Ru_2(CO)_2(\mu\text{-}S^iPr)(\mu\text{-}S^tBu)$] (**15**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Ru(1)–C(1), 1.817(5); Ru(1)–N(1), 2.103(4); Ru(1)–N(3), 2.186(4); Ru(1)–N(5), 2.126(4); Ru(1)–S(1), 2.4222 (11); Ru(1)–S(2), 2.4040(11); S(1)–C(11), 1.832(9); S(2)–C(13), 1.828(7); C(1)–O(1), 1.150(5); S(1)–Ru(1)–S(2), 75.40(5); Ru(1)–S(1)–Ru(1A), 99.60(6); Ru(1)–S(2)–Ru(1A), 100.63(6); Ru(1)–C(1)–O(1), 172.1(4).

trans geometry such as **9** or **12**. However, the strain can be relieved more or less in a *cis* geometry such as **10**, **14**, or **15** by twisting two line segments toward the carbonyl side. This twisting also shifts four atoms of Ru_2SX in **14** or Ru_2S_2 in **10** and **15** away from coplanarity (Scheme 2). The strain relieving is probably effective, and there are five-versus-two *cis* reaction products favorably formed from **1** and **2** Chart 1. By comparison of the structure models for **15** and a hypothetical one, **15′**, with ^iPr and ^tBu positions interchanged, there is non-bonding repulsive interaction between the lone pair electrons of the S atom of ^iPrS and a methyl group of ^tBuS.

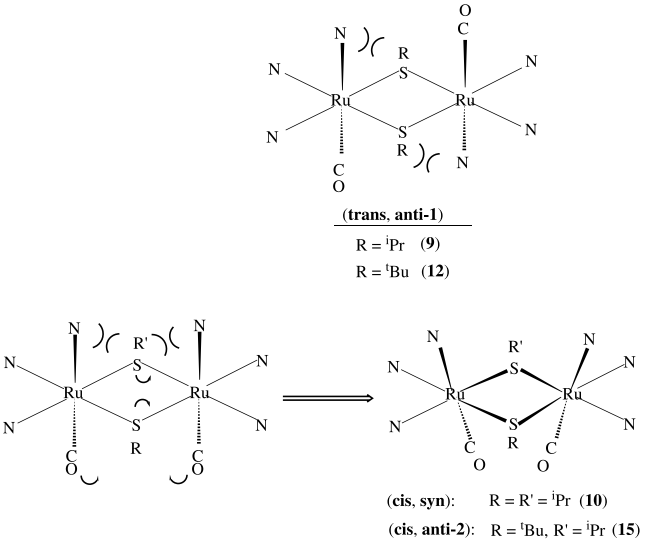
2.4. Reaction of (cis)-[$Tp_2Ru_2(CO)_2(\mu\text{-}I)(\mu\text{-}S^iPr)$] (**11**) with Me_3NO

Following a recent focus of research on the formation of a transition-metal sulfenate (MS(=O)R) [10], oxygenation of (*cis*)-[$Tp_2Ru_2(CO)_2(\mu\text{-}I)(\mu\text{-}S^iPr)$] (**11**) with trimethylamine oxide was also carried out. Two new carbonyl stretching bands at 1979s and 1945m cm^{-1} and one strong band at 943 cm^{-1}, assigned to ν(S=O), appeared almost immediately as shown in an IR spectrum measured in CH_2Cl_2. The ruthenium sulfenate, (*cis*)-[$Tp_2Ru_2(CO)_2(\mu\text{-}I)(\mu\text{-}S(O)^iPr)$] (**16**) was obtained as the only product, which is the first diruthenium sulfenate, to the best of our knowledge [11]. The asymmetric unit of the single crystal used contains two molecules, **16A** and **16B**, for **16**. Both structures are similar to each other, and only structure **16A** is shown in Fig. 7. The molecular structure confirms that the mono-oxygenation process is probably stereo- and chemospecific to give the product with an S=O bond at an *endo* rather than *exo* position with respect to carbonyls (Scheme 3). The S–O distances of

1.509(6) Å in **16A** and 1.534(6) Å in **16B** are similar to that of 1.548(8) Å in a nickel sulfenate complex [10a].

3. Experimental

All solvents were dried and purified by standard methods and were freshly distilled under N_2 immediately before use. All reactions and manipulations were carried out in standard Schlenk ware, connected to a switchable double manifold providing vacuum and N_2. The compound $[TpRu(CO)_2X]$ (X = Br, I) was prepared by the literature method [3d]. Reagents were used as supplied by Aldrich, Fluka, or Strem. ^1H- and ^{31}P-NMR spectra were measured on a Brueker AMC-400 (^1H, 400 MHz; ^{31}P, 162 MHz) NMR spectrometer. ^1H chemical shifts (δ in ppm, J in Hz) are defined as positive downfield relative to internal Me_4Si (TMS) or the deuterated solvent, while ^{31}P chemical shifts are referred to external 85% H_3PO_4. The IR spectra were recorded on a BioRad FTS 175 instrument. The following abbreviations were used: s, strong (IR); m, medium; w, weak; s, singlet (NMR); d, doublet; br, broad; m, multiplet. Microanalyses were carried out by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.



Scheme 2.

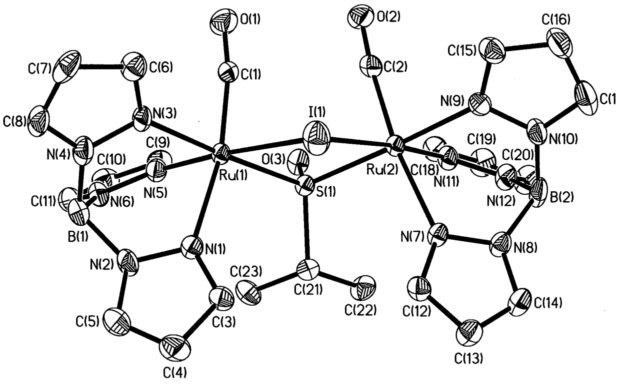


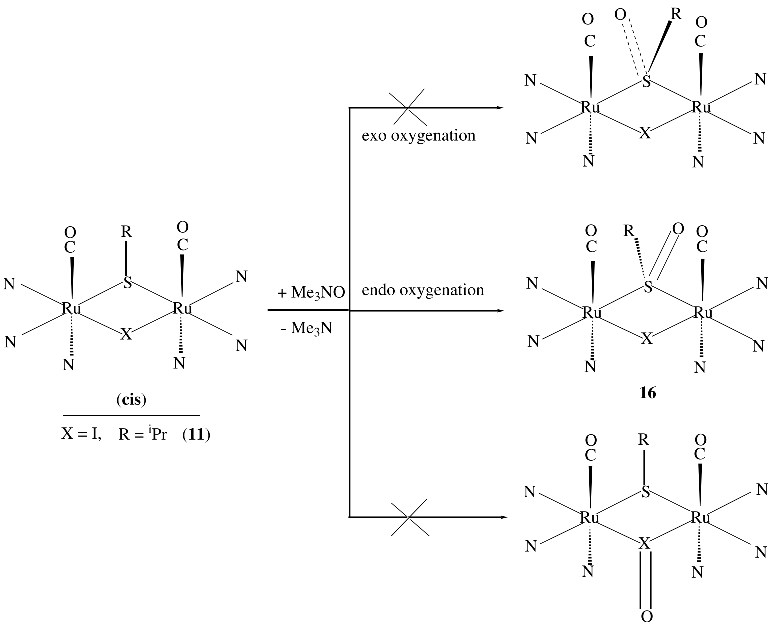
Fig. 7. ORTEP drawing of (*cis*)-$[Tp_2Ru_2(CO)_2(\mu\text{-}I)(\mu\text{-}S(O)^iPr)]$ (**16A**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: Ru(1)–C(1), 1.840(10); Ru(1)–N(1), 2.171(8); Ru(1)–N(3), 2.129(8); Ru(1)–N(5), 2.066(8); Ru(1)–S(1), 2.347(2); Ru(1)–I(1), 2.7054(12); S(1)–C(21), 1.828(10); C(1)–O(1), 1.137(12); Ru(2)–C(2), 1.840(10); Ru(2)–N(7), 2.163(8); Ru(2)–N(9), 2.142(8); Ru(2)–N(11), 2.085(8); Ru(2)–S(1), 2.344(2); Ru(2)–I(1), 2.7082(11); S(2)–C(44), 1.817(10); C(2)–O(2), 1.139(12); S(1)–O(3), 1.509(6); O(3)–S(1)–C(21), 104.1(4); S(1)–Ru(1)–I(1), 82.35(6); Ru(1)–S(1)–Ru(2), 104.18(9); S(1)–Ru(2)–I(1), 82.33(6); Ru(2)–I(1)–Ru(1), 86.26(3); Ru(1)–C(1)–O(1), 170.0(9); Ru(2)–C(2)–O(2), 174.8(9).

*3.1. Synthesis of [TpRu(CO)(NCMe)X] (X = Br (**1**), I (**2**))*

A solution of complex $[TpRu(CO)_2X]$ (1.90 mmol) in MeCN (45 ml) was added dropwise with the Me_3NO solution, prepared from 0.245 g of $Me_3NO\cdot 2H_2O$ (2.21 mmol) in 30 ml of MeCN. The solution was stirred at room temperature (r.t.) for 10 min, and the solvent was removed under vacuum. Recrystallization from CH_2Cl_2–MeOH gave pure product. [TpRu(CO)(NCMe)Br] (**1**): yellow; yield 87%. Anal. Calc. for $C_{12}H_{13}BBrN_7ORu$: C, 31.13; H, 2.83; N, 21.17. Found: C, 31.09; H, 2.87; N, 21.13%. ^1H-NMR ($CDCl_3$): δ 2.33 (s, 3H), 6.15 (t, 1H, $^3J_{H,H} = 2.2$), 6.22 (t, 1H, $^3J_{H,H} = 2.1$), 6.33 (t, 1H, $^3J_{H,H} = 2.0$), 7.53 (d, 1H, $^3J_{H,H} = 2.0$), 7.61 (d, 1H, $^3J_{H,H} = 2.4$), 7.69 (d, 1H, $^3J_{H,H} = 2.4$), 7.73 (d, 1H, $^3J_{H,H} = 2.4$), 7.80 (d, 1H, $^3J_{H,H} = 2.0$), 8.16 (d, 1H, $^3J_{H,H} = 2.0$). IR (CH_2Cl_2): ν_{B-H}, 2495w; ν_{CO}, 1981s cm^{-1}. [TpRu(CO)(NCMe)I] (**2**): yellow; yield 84%. Anal. Calc. for $C_{12}H_{13}BIN_7ORu$: C, 28.26; H, 2.57; N, 19.22. Found: C, 28.03; H, 2.54; N, 18.95%. ^1H-NMR ($CDCl_3$): δ 2.40 (s, 3H), 6.13 (t, 1H, $^3J_{H,H} = 2.8$), 6.23 (t, 1H, $^3J_{H,H} = 2.8$), 6.32 (t, 1H, $^3J_{H,H} = 2.8$), 7.54 (d, 1H, $^3J_{H,H} = 2.4$), 7.60 (d, 1H, $^3J_{H,H} = 2.4$), 7.67 (d, 1H, $^3J_{H,H} = 2.4$), 7.70 (d, 1H, $^3J_{H,H} = 2.4$), 7.89 (d, 1H, $^3J_{H,H} = 2.4$), 8.28 (d, 1H, $^3J_{H,H} = 2.4$). IR (CH_2C1_2): ν_{B-H}, 2495w; ν_{CO}, 1979s cm^{-1}.

*3.2. Synthesis of [TpRu(CO)(CNR)Br] (R = $PhCH_2$ (**3**), ^tBu (**4**)) and [TpRu(CO)(CNR)I] (R = $PhCH_2$ (**5**), ^tBu (**6**))*

These yellow compounds were prepared by using a similar procedure described below for the synthesis of compound **6**. *tert*-Butylisocyanide (0.093 g, 1.10 mmol) was added to a stirred solution of **2** (0.510 g, 1.00 mmol) in 30 ml of THF. The solution was then heated under reflux for 12 h. The volatiles were stripped off under vacuum. Recrystallization from CH_2Cl_2–MeOH gave 0.362 g of **6**. Yield 66%. $[TpRu(CO)(CNCH_2Ph)$-



Scheme 3.

Br] (**3**): Anal. Calc. for $C_{18}H_{17}BBrN_7ORu$: C, 40.10; H, 3.18; N, 18.19. Found: C, 39.70; H, 3.22; N, 17.88%. ^{1}H-NMR (CD_2Cl_2): δ 5.07 (s, 2H), 6.20 (t, 1H, $^3J_{H,H}$ = 2.3), 6.27 (m, 2H), 7.33 (m, 6H), 7.71 (m, 3H), 7.95 (m, 2H). IR (CH_2Cl_2): $\nu_{B–H}$, 2493; ν_{CN}, 2184; ν_{CO}, 1995s cm^{-1}. [TpRu(CO)(CN^{t}Bu)Br] (**4**): Anal. Calc. for $C_{15}H_{19}BBrN_7ORu$: C, 35.67; H, 3.79; N, 19.41. Found: C, 35.58; H, 3.85; N, 19.28%. ^{1}H-NMR ($CDCl_3$): δ 1.53 (s, 9H), 6.21 (br, 1H), 6.26 (br, 1H), 6.30 (br, 1H), 7.48 (br, 1H), 7.70 (m, 3H), 7.92 (br, 1H), 7.98 (br, 1H). IR (CH_2Cl_2): ν, 2495; ν_{CN}, 2172s; ν_{CO}, 1991s cm^{-1}. [TpRu(CO)(CNCH$_2$Ph)I] (**5**): Anal. Calc. for $C_{18}H_{17}BIN_7ORu$: C, 36.88; H, 2.92; N, 16.73. Found: C, 36.81; H, 2.95; N, 16.67%. ^{1}H-NMR (C_3H_6O-d_6): δ 5.33 (s, 2H), 6.27 (t, 1H, $^3J_{H,H}$ = 2.2), 6.30 (m, 2H), 7.37 (m, 3H), 7.55 (m, 2H), 7.76 (d, 1H, $^3J_{H,H}$ = 1.8), 7.85 (br, 3H), 7.89 (d, 1H, $^3J_{H,H}$ = 2.4), 8.04 (d, 1H, $^3J_{H,H}$ = 1.8), 8.07 (d, 1H, $^3J_{H,H}$ = 1.8). IR (CH_2Cl_2): $\nu_{B–H}$, 2492w; ν_{CN}, 2182s; ν_{CO}, 1993s cm^{-1}. [TpRu(CO)(CN^{t}Bu)I] (**6**): Anal. Calc. for $C_{15}H_{19}BIN_7ORu$: C, 32.63; H, 3.47; N, 17.76. Found: C, 32.26; H, 3.45; N, 17.57%. ^{1}H-NMR (C_3H_6O-d_6): δ 1.55 (s, 2H), 6.28 (t, 1H, $^3J_{H,H}$ = 2.2), 6.29 (t, 1H, $^3J_{H,H}$ = 2.2), 6.31 (t, 1H, $^3J_{H,H}$ = 2.2), 7.76 (d, 1H, $^3J_{H,H}$ = 1.6), 7.84 (d, 1H, $^3J_{H,H}$ = 2.4), 7.85 (d, 1H, $^3J_{H,H}$ = 2.4), 7.88 (d, 1H, $^3J_{H,H}$ = 2.0), 8.02 (d, 1H, $^3J_{H,H}$ = 1.6), 8.12 (d, 1H, $^3J_{H,H}$ = 2.0). IR (CH_2Cl_2): $\nu_{B–H}$, 2493w; ν_{CN}, 2168s; ν_{CO}, 1989s cm^{-1}.

*3.3. Preparation of [TpRu(CO)(η^2-S_2CNR_2)] (R′ = Me (**7**), Et (**8**))*

Compound **7** and **8** were prepared similarly by using the procedure described below for the synthesis of the yellow–green compound **7**. $Na^+S_2CNMe_2^-$ (0.082 g, 0.573 mmol) was added to a stirred solution of **2** (0.240 g, 0.481 mmol) in 30 ml of MeOH. The solution was then heated under reflux for 14 h. The volatiles were stripped off under vacuum. Recrystallization from CH_2Cl_2–MeOH gave 0.171 g. Yield 79%. [TpRu(CO)(η^2-S_2CNMe_2)] (**7**): yellow–green. Anal. Calc. for $C_{13}H_{16}BN_7ORuS_2$: C, 33.77; H, 3.48; N, 21.20. Found: C, 33.69; H, 3.45; N, 21.04%. ^{1}H-NMR (C_3H_6O-d_6): δ 3.36 (s, 6H), 6.25 (t, 2H, $^3J_{H,H}$ = 2.2), 6.29 (t, 1H, $^3J_{H,H}$ = 2.1), 7.63 (d, 2H, $^3J_{H,H}$ = 2.1), 7.88 (m, 4H). IR (CH_2Cl_2): $\nu_{B–H}$, 2487w; ν_{CO}, 1949s; ν_{CN}, 1501s cm^{-1}. [TpRu(CO)(η^2-S_2CNEt_2)] (**8**): pale green, yield 79%. Anal. Calc. for $C_{15}H_{20}BN_7ORuS_2$: C, 36.74; H, 4.11; N, 19.99. Found: C, 36.63; H, 4.03; N, 19.88%. ^{1}H-NMR (C_3H_6O-d_6): δ 1.33 (t, 6H, $^3J_{H,H}$ = 7.2), 3.84 (m, 4H), 6.25 (t, 2H, $^3J_{H,H}$ = 2.1), 6.31 (t, 2H, $^3J_{H,H}$ = 2.1), 7.62 (d, 2H, $^3J_{H,H}$ = 2.0), 7.88 (m, 4H). IR (CH_2Cl_2): $\nu_{B–H}$, 2489w; ν_{CO}, 1947s; ν_{CN}, 1501s cm^{-1}.

*3.4. Reaction of [TpRu(CO)(NCMe)Br] (**1**) with ^{i}PrSH and Et_3N*

Compound **1** (0.293 g, 0.63 mmol), ^{i}PrSH (ca. 0.5 ml, 5.22 mmol), Et_3N (ca. 0.5 ml, 3.59 mmol) and 1,2-dimethoxyethane (20 ml) were heated under reflux for 20 h. The solvent and volatiles were then removed under vacuum, and the residue was taken up in a minimum amount o f CH_2Cl_2. The products were separated by thin-layer chromatography using CH_2Cl_2–C_6H_{14} mixed solvents to give 2.6 mg of (*trans*, *anti*-1)-[$Tp_2Ru_2(CO)_2(\mu$-S^{i}Pr$)_2$] (**9**) (0.5%) and 109 mg of (*cis*, *syn*)-[$Tp_2Ru_2(CO)_2(\mu$-S^{i}Pr$)_2$] (**10**) (20.7%). (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**9**): yellow. Anal. Calc. for C$_{26}$H$_{34}$B$_2$N$_{12}$O$_2$RU$_2$S$_2$: C, 37.42; H, 4.11; N, 20.14. Found: C, 37.24; H, 3.93; N, 20.02%. ^{1}H-NMR (CDCl$_3$): δ 1.51 (d, 12H, $^3J_{\text{H,H}} = 6.8$), 4.20 (m, 2H), 6.17 (t, 2H), 6.18 (t, 2H), 6.29 (t, 2H), 7.59 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.60 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.66 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.67 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.73 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.79 (d, 2H, $^3J_{\text{H,H}} = 2.0$). IR (CH$_2$Cl$_2$): $\nu_{\text{B–H}}$, 2491w; ν_{CO}, 1962s cm^{-1}. (*cis*, *syn*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**10**): orange–yellow. Anal. Calc. for C$_{26}$H$_{34}$B$_2$N$_{12}$O$_2$Ru$_2$S$_2$: C, 37.42; H, 4.11; N, 20.14. Found: C, 37.14; H, 4.08; N, 20.07%. ^{1}H-NMR (CDCl$_3$): δ 0.50 (d, 12H, $^3J_{\text{H,H}} = 6.8$), 2.70 (m, 2H), 6.18 (t, 4H), 6.45 (t, 2H), 7.61 (d, 4H, $^3J_{\text{H,H}} = 2.4$), 7.82 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.88 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 8.92 (d, 2H, $^3J_{\text{H,H}} = 2.0$). IR: $\nu_{\text{B–H}}$, 2487w; ν_{CO}, 1981sh, 1968s cm^{-1} in CH$_2$Cl$_2$ and $\nu_{\text{B–H}}$, 2477w; ν_{CO}, 1989m, 1979s cm^{-1} in C$_6$H$_{14}$.

*3.5. Reaction of [TpRu(CO)(NCMe)I] (**2**) with ^{i}PrSH and Et$_3$N*

Compound **2** (0.301 g, 0.59 mmol), ^{i}PrSH (ca. 0.5 ml, 5.22 mmol), Et$_3$N (ca. 0.5 ml, 3.59 mmol) and 1,2-dimethoxyethane (20 ml) were heated under reflux for 2 h. The solvent and volatiles were then removed under vacuum, and the residue was taken up in a minimum amount of CH$_2$Cl$_2$. The products were separated by thin-layer chromatography using CH$_2$Cl$_2$–C$_6$H$_{14}$ mixed solvents to give 9.3 mg of (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**9**) (1.9%), 53.4 mg of (*cis*, *syn*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**10**) (10.8%), and 3.2 mg of (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-I)(μ-S^{i}Pr)] (**11**) (0.7%). (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-I)(μ-S^{i}Pr)] (**11**): yellow–brown. Anal. Calc. for C$_{23}$H$_{27}$B$_2$IN$_{12}$O$_2$Ru$_2$S: C, 31.17; H, 3.07; N, 18.96. Found: C, 31.02; H, 3.07; N, 18.87%. ^{1}H-NMR (CDCl$_3$): δ 0.89 (d, 6H, $^3J_{\text{H,H}} = 6.4$), 2.88 (m, 1H), 6.17 (t, 2H), 6.21 (t, 2H), 6.44 (t, 2H), 7.58 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.67 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.74 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.80 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.94 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 8.86 (d, 2H, $^3J_{\text{H,H}} = 2.0$). IR (CH$_2$Cl$_2$): $\nu_{\text{B–H}}$, 2489w; ν_{CO}, 1981s, 1949m cm^{-1}.

*3.6. Reaction of [TpRu(CO)(NCMe)Br] (**1**) with ^{t}BuSH and Et$_3$N*

Compound **1** (0.232 g, 0.50 mmol), ^{t}BuSH (ca. 0.5 ml, 4.40 mmol), Et$_3$N (ca. 0.5 ml, 3.59 mmol) and 1,2-dimethoxyethane (30 ml) were heated under reflux for 44 h. The solvent and volatiles were then removed under vacuum, and the residue was taken up in a minimum amount of CH$_2$Cl$_2$. The products were separated by thin-layer chromatography using CH$_2$Cl$_2$–C$_6$H$_{14}$ mixed solvents to give 0.3 mg of (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{t}Bu)$_2$] (**12**) (0.07%) and 11.1 mg of (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-Br)(μ-S^{t}Bu)$_2$] (**13**) (2.6%). (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{t}Bu)$_2$] (**12**): yellow. Anal. Calc. for C$_{28}$H$_{38}$B$_2$N$_{12}$O$_2$Ru$_2$S$_2$: C, 38.99; H, 4.44; N, 19.49. Found: C, 38.84; H, 4.43; N, 19.37%. ^{1}H-NMR (CDCl$_3$): δ 1.74 (s, 18H), 6.18 (m, 4H), 6.30 (t, 2H), 7.59 (m, 4H), 7.66 (m, 4H), 7.73 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.84 (d, 2H, $^3J_{\text{H,H}} = 2.0$). IR (CH$_2$Cl$_2$): $\nu_{\text{B–H}}$, 2489w; ν_{CO}, 1964s cm^{-1}. (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-Br)(μ-S^{t}Bu)$_2$] (**13**): orange–yellow. Anal. Calc. for C$_{24}$H$_{29}$B$_2$BrN$_{12}$O$_2$Ru$_2$S: C, 33.78; H, 3.43; N, 19.70. Found: C, 33.67; H, 3.43; N, 19.62%. ^{1}H-NMR (CDCl$_3$): δ 1.02 (s, 9H), 6.16 (t, 2H), 6.18 (t, 2H), 6.50 (t, 2H), 7.57 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.76 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.77 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.83 (d, 4H, $^3J_{\text{H,H}} = 2.0$), 7.92 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 9.07 (d, 2H, $^3J_{\text{H,H}} = 2.0$). IR (CH$_2$Cl$_2$): $\nu_{\text{B–H}}$, 2489w; ν_{CO}, 1976s, 1935m cm^{-1}.

*3.7. Reaction of [TpRu(CO)(NCMe)I] (**2**) with ^{t}BuSH and Et$_3$N*

Compound **2** (0.311 g, 0.61 mmol), ^{t}BuSH (ca. 0.5 ml, 4.40 mmol), Et$_3$N (ca. 0.5 ml, 3.59 mmol) and 1,2-dimethoxyethane (20 ml) were heated under reflux for 16 h. The solvent and volatiles were then removed under vacuum, and the residue was taken up in a minimum amount of CH$_2$Cl$_2$. The products were separated by thin-layer chromatography using CH$_2$Cl$_2$–C$_6$H$_{14}$ mixed solvents to give 1.0 mg of (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{t}Bu)$_2$] (**12**) (0.19%) and 48.7 mg of (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-I)(μ-S^{t}Bu)$_2$] (**14**) (8.9%). (*cis*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-I)(μ-S^{t}Bu)$_2$] (**14**): yellow–brown. Anal. Calc. for C$_{24}$H$_{29}$B$_2$IN$_{12}$O$_2$Ru$_2$S: C, 32.02; H, 3.25; N, 18.67. Found: C, 31.98; H, 3.23; N, 18.62%. ^{1}H-NMR (CDCl$_3$): δ 0.88 (s, 9H), 6.13 (t, 2H), 6.20 (t, 2H), 6.50 (t, 2H), 7.55 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.66 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.81 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 7.82 (d, 2H, $^3J_{\text{H,H}} = 2.4$), 7.99 (d, 2H, $^3J_{\text{H,H}} = 2.0$), 9.10 (d, 2H, $^3J_{\text{H,H}} = 2.0$). IR (C$_6$H$_{14}$): $\nu_{\text{B–H}}$, 2481w; ν_{CO}, 1985s, 1966s cm^{-1}.

*3.8. Reaction of [TpRu(CO)(NCMe)Br] (**1**) with ^{i}PrSH, ^{t}BuSH and Et$_3$N*

Compound **1** (0.262 g, 0.57 mmol), ^{i}PrSH (ca. 0.1 ml, 1.04 mmol), ^{t}BuSH (ca. 0.5 ml, 4.40 mmol), Et$_3$N (ca. 0.5 ml, 3.59 mmol) and 1,2-dimethoxyethane (15 ml) were heated under reflux for 25 h. The solvent and volatiles were then removed under vacuum, and the residue was taken up in a minimum amount of CH$_2$Cl$_2$. The products were separated by thin-layer chromatography using CH$_2$Cl$_2$–C$_6$H$_{14}$ mixed solvents to give 8.1 mg of (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**9**) (1.7%), 42.9 mg of (*cis*, *syn*)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{i}Pr)$_2$] (**10**) (9%), 4.1 mg of (*trans*, *anti*-1)-[Tp$_2$Ru$_2$(CO)$_2$(μ-S^{t}Bu)$_2$] (**12**) (0.8%), and 4.6 mg of (*cis*, *anti*-2)-[Tp$_2$Ru$_2$(CO)$_2$-(μ-S^{i}Pr)(μ-S^{t}Bu)] (**15**) (0.5%). (*cis*, *anti*-2)-[Tp$_2$Ru$_2$-(CO)$_2$(μ-S^{i}Pr)(μ-S^{t}Bu)] (**15**): orange–yellow. Anal. Calc.

Table 1
Crystal data

Compound	**8**	**9**·2CH$_2$Cl$_2$	**10**·3/2CH$_2$Cl$_2$	**12**	**14**	**15**·3/2CH$_2$Cl$_2$	**16**·1/2CH$_3$OH
Empirical formula	$C_{15}H_{10}BN_7ORuS_2$	$C_{28}H_{34}B_2Cl_4N_{12}O_2Ru_2S_2$	$C_{27}H_{36.5}B_2Cl_3N_{12}O_2Ru_2S_2$	$C_{28}H_{36}B_2N_{12}O_2Ru_2S_2$	$C_{24}H_{27}B_2IN_{12}O_2Ru_2S$	$C_{28.5}H_{39}B_2Cl_3N_{12}O_2Ru_2S_2$	$C_{23.5}H_{27}B_2IN_{12}O_{3.5}Ru_2S$
Formula weight	480.30	1000.35	955.41	860.57	898.30	975.95	916.29
Temperature (K)	295(2)	295(2)	293(2)	150(1)	295(2)	295(2)	295(2)
Space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Orthorhombic, $Pnnm$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Orthorhombic, $Pnnm$	Triclinic, $P\bar{1}$
a (Å)	12.1281(7)	9.2217(1)	13.0914(1)	10.0740(1)	16.163(2)	13.272(2)	9.6095(2)
b (Å)	10.6930(6)	9.4158(1)	16.2025(3)	11.4607(1)	12.329(1)	16.472(2)	15.8769(3)
c (Å)	15.8813(9)	11.9236(2)	18.3263(3)	17.4487(1)	17.812(2)	18.287(2)	22.9781(3)
α (°)	90	83.599(1)	90	80.775(1)	90	90	83.983(1)
β (°)	104.096(1)	86.249(1)	90	78.960(1)	98.909(2)	90	80.285(1)
γ (°)	90	80.852(1)	90	64.986(1)	90	90	75.537(1)
V (Å^3)	1997.6(2)	1014.58(2)	3887.3(1)	1784.66(3)	3506.6(6)	3997.8(7)	3338.7(1)
Z	4	1	4	2	4	4	4
D_{calc} (g cm^{-3})	1.597	1.637	1.633	1.601	1.702	1.621	1.823
μ (Mo–K$_\alpha$) (mm^{-1})	1.013	1.154	1.134	1.009	1.1842	1.105	1.940
F(000)	952	500	1918	868	1752	1964	1788
Crystal size (mm)	0.30 × 0.10 × 0.05	0.40 × 0.40 × 0.20	0.30 × 0.30 × 0.30	0.22 × 0.20 × 0.16	0.40 × 0.12 × 0.10	0.21 × 0.16 × 0.16	
Unit cell determination 2θ range (°)	3–57	3–55	3–56	2–55	3–57	3–57	2–53
(h, k, l) range	±15, ±13, ±21	±12, ±12, ±15	±16, ±21, ±22	±13, ±15, ±22	±21, ±15, ±22	±17, ±21, ±24	±12, ±19, ±28
No. of measured reflections	11 722	10 634	21 802	15 934	20 364	24 819	38 693
Observed reflections (N_o)	4453 ($>2\sigma$)	4576 ($>2\sigma$)	4465 ($>2\sigma$)	7918 ($>2\sigma$)	7755 ($>2\sigma$)	5058 ($>2\sigma$)	13 345 ($>2\sigma$)
R [a], R_w [a]	0.0292, 0.0650	0.0349, 0.0985	0.0525, 0.1258	0.0343, 0.0795	0.056, 0.1708	0.0502, 0.1192	0.0679, 0.1800
Refinement program	SHELXTL-PLUS	NRCVAX	SHELXTL-PLUS	NRCVAX	SHELXTL-PLUS	SHELXTL-PLUS	NRCVAX
No. of refined parameters (N_p)	244	235	243	462	398	249	814
Weighting scheme	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o) + 0.0007F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.0009F_o^2]^{-1}$	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o) + 0.00016F_o^2]^{-1}$
Goodness-of-fit [a]	0.944	1.045	1.121	1.034	1.068	1.018	1.056
$(\Delta\rho)_{max}$ (e Å^3)	0.381	1.278	1.610	1.652	3.828	0.976	1.762
$(\Delta\rho)_{min}$ (e Å^3)	−0.319	−0.818	−1.394	−0.811	−0.940	−0.977	–4.200

[a] $R = [\Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|]$. $R_w = [\Sigma \, \omega(|F_o| - |F_c|)^2/\Sigma \, \omega|F_o|^2]^{1/2}$. GOF $= [\Sigma \, \omega/F_o| - |F_c|^2/N_o - N_p]^{1/2}$.

for $C_{27}H_{36}B_2N_{12}O_2Ru_2S_2$: C, 38.22; H, 4.28; N, 19.81. Found: C, 38.06; H, 4.29; N, 19.77%. ^{1}H-NMR ($CDCl_3$): δ 1.80 (s, 9H), 1.37 (d, 6H, $^3J_{H,H} = 6.8$), 3.99 (m, 1H), 6.27 (t, 2H), 6.31 (t, 2H), 6.37 (t, 2H), 7.68 (d, 2H, $^3J_{H,H} = 2.0$), 7.69 (d, 2H, $^3J_{H,H} = 2.0$) 7.73 (d, 4H, $^3J_{H,H} = 2.4$), 7.75 (d, 2H, $^3J_{H,H} = 2.4$), 8.55 (d, 2H, $^3J_{H,H} = 2.0$). IR (C_6H_{14}): ν_{B-H}, 2481w; ν_{CO}, 1987s, 1979s cm^{-1}.

3.9. Reaction of (cis)-[$Tp_2Ru_2(CO)_2(\mu$-I)(μ-S^{i}Pr)] (**11**) with Me_3NO

A solution of complex **11** (8.9 mg, 0.010 mmol) in CH_2Cl_2 (10 ml) was added with $Me_3NO \cdot 2H_2O$ (51 mg, 0.46 mmol). The solution was stirred at r.t. for 1 h, and the solvent was removed under vacuum. Recrystallization from CH_2Cl_2–MeOH gave 6.1 mg of pure product **16**. Yield 68%. Anal. Calc. for $C_{23}H_{27}B_2IN_{12}O_3Ru_2S$: C, 30.62; H, 3.02; N, 18.63. Found: C, 30.59; H, 3.17; N, 18.54%. ^{1}H-NMR ($CDCl_3$): δ 0.89 (d, 6H, $^3J_{H,H} = 6.8$), 2.87 (m, 1H), 6.16 (t, 2H), 6.20 (t, 2H), 6.43 (t, 2H), 7.57 (d, 2H, $^3J_{H,H} = 2.0$), 7.63 (d, 2H, $^3J_{H,H} = 2.0$), 7.71 (d, dH, $^3J_{H,H} = 2.0$), 7.79 (d, 2H, $^3J_{H,H} = 2.0$), 7.92 (d, 2H, $^3J_{H,H} = 2.0$), 8.84 (d, 2H, $^3J_{H,H} = 2.0$). IR (CH_2Cl_2): ν_{B-H}, 2491w; ν_{CO}, 1979s, 1945m; ν_{SO}, 943s cm^{-1}.

3.10. Single-crystal X-ray diffraction studies

Suitable single crystals of **8**, **9**, **10**, **12**, **14**, **15**, and **16** were grown from CH_2Cl_2–MeOH or CH_2Cl_2–C_6H_{14} at r.t. and chosen for single crystal structure determinations. All the X-ray diffraction data were measured in frames with increasing ω (width of 0.3° per frame) and with the scan speed at 20.00 s/frame on a Siemens SMART-CCD instrument, equipped with a normal focus and 3 kW sealed-tube X-ray source. Empirical absorption corrections were carried out using SHELXTL-PC program for **8**, **10**, **14**, and **15**, and SADABS program for **9**, **12** and **16**. These three structures were solved by the heavy-atom method and refined by a full-matrix least-squares procedure using NRCVAX [12]. Structures **8**, **10**, **14**, and **15** were solved by direct methods and refined by a full-matrix least-squares procedure using SHELXTL-PLUS [13]. Neutral atom scattering factors for non-hydrogen atoms and the values for $\Delta f'$ and $\Delta f''$ described in each software [12,13] were used. The other essential details of single-crystal data measurement and refinement are listed in Table 1. In structure **10**, atom C(13) was found to contain 0.5 occupancy and both S(2)–C(13) and C(13)–C(14) bond lengths were fixed with 1.808 and 1.525 Å, respectively, to allow a satisfactory refinement. Likewise, the C(17)–Cl(3) bond length for one CH_2Cl_2 contained in structure **15** was also fixed with 1.89 Å. Several residual electron peaks with more than 1 e Å^{-3} were found with one peak close to atom Cl(2) in structure **9**, one close to atom S(2) in structure **10**, one close to atom Ru(1) in structure **12**, one close to atom S(1) in structure **14**, and one close to atom I(1) in structure **16**. The one close to S(1) in **14** has the largest value of 3.828 e Å^{-3} while there is a hole with the largest $(\Delta\rho)_{min}$ value of -4.200 e Å^{-3} close to I(1) in structure **16**. Apparently both positions of the S(1) atom in **14** and the I(1) atom in **16** are slightly disordered.

4. Conclusions

In this work, we have demonstrated that [TpRu(CO)(MeCN)X] (X = Br (**1**), I (**2**)), prepared readily from [$TpRu(CO)_2X$], can serve as a good starting material leading to a variety of substituted products, including [TpRu(CO)(CNR)X] (X = Br, R = $PhCH_2$ (**3**); X = Br, R = ^{t}Bu (**4**); X = I, R = $PhCH_2$ (**5**), X = I, R = ^{t}Bu (**6**)), [TpRu(CO)(η^2-S_2CNR_2)] (R = Me (**7**), Et (**8**)), (*cis*)-[$Tp_2Ru_2(CO)_2(\mu$-X)(μ-SR)] (X = I, R = ^{i}Pr (**11**); X = Br, R = ^{t}Bu (**13**); X = I, R = ^{t}Bu (**14**)), (*trans*, *anti*-1)-[$Tp_2Ru_2(CO)_2(\mu$-S^{i}Pr$)_2$] (**9**), (*cis*, *syn*)-[$Tp_2Ru_2(CO)_2(\mu$-S^{i}Pr$)_2$] (**10**), (*trans*, *anti*-1)-[$Tp_2Ru_2(CO)_2(\mu$-S^{t}Bu$)_2$] (**12**) and (*cis*, *anti*-2)-[$Tp_2Ru_2(CO)_2(\mu$-S^{i}Pr)(μ-S^{t}Bu)] (**15**). Compound **11** reacts with Me_3NO to form stereo- and chemospecifically the first diruthenium sulfenate, (*cis*)-[$Tp_2Ru_2(CO)_2(\mu$-I)(μ-S(O)^{i}Pr)] (**16**) with the S=O bond at the *endo* position with respect to carbonyls.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 173316, 173454, 173315, 173455, 173317, 173456, and 138612 for structures **8**, **9**, **10**, **12**, **14**, **15**, and **16**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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