4432 *Inorg. Chem.* **1997,** *36,* 4432−4437

Oxidation Reactions of Dithiocarbamate Complexes of Ruthenium(II)

Wa-Hung Leung,*,† Joyce L. C. Chim,† Hongwei Hou,† Tom S. M. Hun,†
Ian D. Williams,† and Wing-Tak Wong‡

Departments of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay,
Kowloon, Hong Kong, and University of Hong Kong, Pokfulam Road, Hong Kong

Received January 17, 1997⊗

The reaction of $Ru(Et_2dtc)_2(DMSO)_2$ (Et_2dtc = *N*,*N*-diethyldithiocarbamate; DMSO = dimethyl sulfoxide) with *t*-BuNC gave *trans*-$Ru(Et_2dtc)_2(CN\text{-}t\text{-}Bu)_2$, **1**. Complex **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.753(2)$ Å, $b = 11.583(2)$ Å, $c = 12.974(2)$ Å, and $\beta = 91.8(2)°$ for $Z = 2$. The crystal structure of **1** shows the trans disposition of the two isocyanides; the mean Ru−S and Ru−C distances are 2.409 and 1.977(2) Å, respectively. Treatment of $[Ru(diene)Cl_2]_n$ with $Na(Et_2dtc)$ afforded $Ru(Et_2dtc)_2(diene)$ (diene = bicyclo[2.2.1]-hepta-2,5-diene (NBD), **2**, 1,5-cyclooctadiene (COD), **3**). Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.316(1)$ Å, $b = 10.346(1)$ Å, $c = 15.123(2)$ Å, $\alpha = 103.69(2)°$, $\beta = 93.54(2)°$, and $\gamma = 100.61(2)°$ for Z = 2. The mean Ru−S and Ru−C distances in **2** are 2.416 and 2.137 Å, respectively. The reaction of *cis*-$Ru(Et_2dtc)_2(CO)_2$ with iodine gave the 2:1 molecular iodine complex *cis*-$Ru(Et_2dtc)_2(CO)_2\cdot{}^1/_2I_2$ **4**, which crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.347(2)$, $b = 22.227(2)$ Å, $c = 12.891(2)$ Å, and β =95.98 (2)° for $Z = 4$. The mean Ru−S and Ru−C and the I−I distances in complex **4** are 2.427, 1.903, and 2.745(1) Å, respectively. Treatment of $Ru(Et_2dtc)_2(DMSO)_2$ with I_2 gave the linear Ru(II)−Ru(III)−Ru(III) trimer $[Ru_3(Et_2dtc)_6(DMSO)_2](I_3)_2$, **5**, which crystallizes in the triclinic space group $P\bar{1}$ with $a = 14.125(3)$ Å, $b = 20.829(6)$ Å, $c = 13.658(3)$ Å, $\alpha = 97.57(2)°$, $\beta = 110.01(2)°$, and $\gamma = 71.25(2)°$ for $Z = 2$. The structure of complex **6** can be viewed as consisting of a $\{Ru_2^{III}(Et_2dtc)_4\}^{2+}$ core and a $\{Ru^{II}(Et_2dtc)_2(DMSO)_2\}$ moiety, which are linked together via the two dithiocarbamate sulfurs of the latter. While the two Ru(III) centers are connected by a Ru−Ru single bond (Ru−Ru = 2.826(2) Å), there is no direct interaction between the Ru(III) and Ru(II) centers. Oxidation of $Ru(Et_2dtc)_2L_2$ (L = PPh_3, *t*-BuNC) by I_2 gave the respective $[Ru(Et_2dtc)_2L_2]^+$ cations. The reaction of *cis*-$Ru(Et_2dtc)_2(PPh_3)_2$ with excess tosyl azide gave the diamagnetic Ru(IV) tetrazene complex $Ru(Et_2dtc)_2(Ts_2N_4)$, **7**. Complex **7** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.380(1)$ Å, $b = 11.322(1)$ Å, $c = 15.310(1)$ Å, $\alpha = 106.84(2)°$, $\beta = 106.87(2)°$, and $\gamma = 92.63(2)°$ for $Z = 2$. The Ru−S and Ru−N_α distances in **7** are 2.385 and 1.98 Å, respectively. The formal potentials of the Ru dithiocarbamate complexes were determined by cyclic voltammetry.

Introduction

Transition metal complexes of *N*,*N*-dialkyldithiocarbamates (R_2NCS_2) and related dithio ligands are of interest because of their resemblance to the active centers of metal−sulfur proteins which mediate redox reactions and electron transfer in the biological systems.[1] The recent crystallographic studies on the Fe−Mo cofactor of nitrogenase showed that the Fe/Mo/S active site is an Fe_7MoS_9 cluster.[2] However, the coordination mode of nitrogen and the mechanism by which the N≡N bond is split in the iron−sulfur active center of nitrogenase remain elusive. Owing to the periodic relationship between ruthenium and iron, the more subsitutionally inert ruthenium−thiolate complexes may serve as functional models of the iron−sulfur proteins. Additionally, there is an increasing interest in ruthenium−sulfur complexes due to their industrial applications in hydrodesulfurization (HDS) and related processes.[3] It has been shown that the ruthenium−sulfur HDS systems are far more active than the Mo−S systems in commerical use.[4] Remarkably Matsumoto and co-workers reported that $[Ru(Me_2dtc)(CO)(PPh_3)]_2(\mu\text{-}SPh)_2$ undergoes a reversible one-step four-electron redox reaction,[5] demonstrating that electron-rich Ru−dithocarbamate complexes are potentially useful for multielectron catalysis. Although dithiocarbamate complexes of ruthenium are well-known, the most widely studied are the coordinately saturated binary Ru(II) and Ru(III) complexes of the types $Ru(R_2dtc)_3$[6] and $[Ru_2(R_2dtc)_5]^+$.[7] Seven-coordinate $Ru(R_2dtc)_3X$ (X = Cl,[8] I_3[9]) and dimeric $[Ru(Me_2dtc)(CO)(PPh_3)(\mu\text{-}SPh)]_2(NO_3)_2$[5] are rare examples of Ru(IV) dithiocarbamates. In efforts to develop Ru−dithiocarbamate-based complexes for redox catalysis, we sought to investigate the oxidation chemistry of complexes of the type $Ru(Et_2dtc)_2L_2$, which contain a labile leaving ligand L. We report here the synthesis, oxidation reactions, and crystal structures of the $Ru(Et_2dtc)_2L_2$ complexes.

---

* To whom correspondence should be addressed. E-mail: chleung@usthk.ust.hk.

† The Hong Kong University of Science and Technology.

‡ The University of Hong Kong.

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1997.

(1) Burns, R. P.; McCullough, F. P.; McAuliffe, C. A. *Adv. Inorg. Nucl. Chem.* **1980**, *23*, 211.

(2) (a) Kim, J.; Rees, D. C. *Nature* **1992**, *257*, 1677. (b) Chan, M. K.; Kim J.; Rees; D. C. *Science* **1993**, *260*, 792.

(3) Stiefel, E. I. In *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K., Eds.; ACS Symposium Series No. 653; American Chemical Society: Washington, DC, **1996**; p 1 and references cited therein.

(4) For review, see for example: Chianelli, R. R.; Daage, M.; Ledoux, M. J. *Adv. Catal.* **1996**, *40*, 177.

(5) Kawano, M.; Uemura, H.; Watanabe, T.; Matsumoto, K. *J. Am. Chem. Soc.* **1993**, *115*, 2068.

(6) (a) Duffy, D. J.; Pignolet, L. H. *Inorg. Chem.* **1974**, *13*, 2045. (b) Pignolet, L. H. *Inorg. Chem.* **1974**, *13*, 2051.

(7) Mattson, B. M.; Heiman, J. R.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 564.

(8) Given, K. W.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 3153.

(9) Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1977**, *16*, 489.

S0020-1669(97)00053-0 CCC: $14.00

Experimental Section

General Considerations. Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. ^{1}H NMR spectra were obtained on a Bruker ALX 300 spectrometer. Chemical shifts (δ) are reported with reference to $SiMe_4$. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. Potentials were controlled with respect to a Ag^+−Ag reference electrode in acetonitrile but are reported with respect to the ferrocenium−ferrocene couple ($Cp_2Fe^{+/0}$) as measured in the same solution. Elemental analyses were performed by Medac Ltd., Brunel University, U.K.

All synthetic manipulations, except for those noted, were carried out by using standard Schlenk techniques under dry N_2. Solvents were purified by standard procedures and distilled prior to use. $[Ru(NBD)Cl_2]_n$ (NBD = norbornadiene or bicyclo[2.2.1]hepta-2,5-diene),[10] $[Ru(COD)Cl_2]_n$ (COD = 1,5-cyclooctadiene),[11] $[Ru(Et_2dtc)_2(DMSO)_2]$,[12] *cis*-$Ru(Et_2dtc)_2(PPh_3)_2$,[13] and TsN_3 (Ts = *p*-toluenesulfonyl)[14] were prepared by the literature methods.

Syntheses. Preparation of *trans*-Ru(Et$_2$dtc)$_2$(CN-*t*-Bu)$_2$ (1). To solution of $[Ru(Et_2dtc)_2(DMSO)_2]$ (0.15 g, 0.27 mmol) in toluene (20 mL) was added *t*-BuNC (0.1 mL), and the mixture was heated at reflux for 2 h. The solvent was pumped off, and the residue was extracted with hexane. Concentration (5 mL) and cooling at −10 °C afforded yellow crystals (yield: 0.10 g, 65%). ^{1}H NMR ($CDCl_3$): δ 1.20, 1.22, 1.24, 1.26 (t, 12H, CH$_2$C*H*$_3$), 1.45 (s, 18H, *t*-Bu), 3.44−4.00 (q, 8H, C*H*$_2$CH$_3$). IR (Nujol, cm^{-1}): 2098 ($\nu_{C\equiv N}$). Anal. Calcd for $RuC_{20}H_{36}N_4S_4$: C, 42.6; H, 6.8; N, 10.0. Found: C, 42.8; H, 7.0; N, 9.9.

Preparation of Ru(Et$_2$dtc)$_2$(NBD) (2). This was prepared by a modification of the literature method.[15] A mixture of $[Ru(NBD)Cl_2]_n$ (0.25 g, 0.90 mmol) and $Na(Et_2dtc)$ (0.43 g, 1.91 mol) in acetone (30 mL) was heated at reflux for 12 h. The solvent was pumped off, and the residue was extracted with CH_2Cl_2 and purified by column chromatography in air (alumina) with CH_2Cl_2 as eluant The yellow product was recrystallized from CH_2Cl_2/hexane (yield: 0.27 g, 60%). ^{1}H NMR ($CDCl_3$): δ 1.18, 1.30 (t, 12H, CH$_2$C*H*$_3$), 1.24 (s, 2H, CH$_2$ of NBD), 3.47−3.86 (m, 8H, C*H*$_2$CH$_3$), 3.72−3.86 (q, 4H, olefinic protons of NBD). MS (EI): *m*/*z* 489 (M^+). Anal. Calcd for $RuC_{17}H_{28}N_2S_2$: C, 41.7; H, 5.7; N, 5.7. Found: C, 42.0; H, 5.7; N, 5.7.

Preparation of Ru(Et$_2$dtc)$_2$(COD) (3). This was prepared as for complex **2** from $[Ru(COD)Cl_2]_n$ (0.15 g, 0.53 mmol) and $Na(Et_2dtc)$ (0.18 g, 1.06 mmol). Recrystallization from CH_2Cl_2/hexane afforded yellow crystals (yield: 0.08 g, 30%). ^{1}H NMR ($CDCl_3$): δ 1.19 (t, 6H, CH$_2$C*H*$_3$), 1.27 (t, 6H, CH$_2$C*H*$_3$), 1.70 (m, 2H, COD), 2.27(m, 2H, COD), 2.51 (m, 2H, COD), 2.58 (m, 2H, COD), 2.58 (m, 2H, COD), 3.07 (dt, 2H, olefinic protons of COD), 3.55 (dt, 2H, olefinic protons of COD), 3.75 (m, 8H, C*H*$_2$CH$_3$). Anal. Calcd for $RuC_{18}H_{32}N_4S_2$: C, 42.8; H, 6.3; N, 5.5. Found: C, 43.0; H, 6.4; N, 5.5.

Preparation of *cis*-Ru(Et$_2$dtc)$_2$(CO)$_2$·$^1/_2$I$_2$ (4). $Ru(Et_2dtc)_2(CO)_2$ was prepared by a modification of the literature method.[16] A mixture of $Na(Et_2dtc)$ (0.15 g, 0.88 mmol) and $[Ru(CO)_2Cl_2]_n$[17] (0.1 g, 0.44 mmol) in refluxing DMF (20 mL) was heated at reflux for 5 h. The volatile material was removed in vacuo, and the residue was purified by column chromatography (alumina). The product was eluted with CH_2Cl_2 as a yellow band. Recrystallization from ether/hexane gave an air-stable yellow solid (yield: 0.10 g, 50%). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 12H, C*H*$_3$), 3.61−3.82 (q, 8H, C*H*$_2$). MS (EI): *m*/*z* 454 (M^+), 398 (M^+ − 2CO). IR (Nujol, cm^{-1}): 2028, 1952 ($\nu_{C\equiv O}$).

To a solution of $Ru(Et_2dtc)_2(CO)_2$ (0.2 g, 0.44 mmol) in CH_2Cl_2 (20 mL) was added 1 equiv of I_2 (0.12 g, 0.44 mmol), and the mixture was stirred at room temperature overnight. The solvent was evaporated to dryness and the residue was washed with Et_2O. Recrystallization from CH_2Cl_2/hexane afforded dark red crystals (yield: 0.10 g, 40%). ^{1}H NMR ($CDCl_3$): δ 1.27, 1.32 (t, 12H, CH$_2$C*H*$_3$), 3.63−3.84 (q, 8H, C*H*$_2$CH$_3$). IR (Nujol, cm^{-1}): 2026, 1956. Anal. Calcd for $RuC_{12}H_{20}N_2S_2O_2I$: C, 24.8; H, 3.5; N, 4.8. Found: C, 24.7; H, 3.4; N, 3.6.

Preparation of [Ru$_3$(Et$_2$dtc)$_6$(DMSO)$_2$](I$_3$)$_2$ (5). To a solution of $Ru(Et_2dtc)_2(DMSO)_2$ (0.1 g, 0.18 mmol) in CH_2Cl_2 (20 mL) was added I_2 (0.064 g, 0.25 mmol), and the mixture was stirred at room temperature overnight. The solvent was evaporated to dryness, and the residue was washed with Et_2O. The product was recrystallized from CH_3CN/Et_2O as dark red crystals (yield: 0.08 g, 63%). ^{1}H NMR ($CDCl_3$): δ 1.19−1.49 (t, 36H, CH$_2$C*H*$_3$), 3.29 (s, 3H, *Me*$_2$SO), 3.41 (s, 3H, *Me*$_2$SO), 3.36−4.50 (m, 24H, C*H*$_2$CH$_3$). Anal. Calcd for $Ru_3C_{34}H_{72}N_6O_2S_{14}I_6$: C, 19.4; H, 3.4; N, 4.0. Found: C, 19.5; H, 3.5; N, 3.8.

Preparation of [Ru(Et$_2$dtc)$_2$(CN-*t*-Bu)$_2$](CF$_3$SO$_3$) (6). To a solution of complex **1** (0.1 g, 0.18 mmol) in CH_2Cl_2 (20 mL) was added 1 equiv of $AgCF_3SO_3$ (0.045 g, 0.18 mmol), and the mixture was stirred at room temperature overnight. The resulting orange solution was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2/hexane to give orange-yellow crystals (yield: 0.65 g, 50%). IR (Nujol, cm^{-1}): 2134 ($\nu_{C\equiv N}$). Anal. Calcd for $RuC_{21}H_{36}F_3N_4O_3S_5 \cdot H_2O$: C, 34.7; H, 5.2; N, 7.6. Found: C, 34.1; H, 5.3; N, 7.4.

Oxidation of *cis*-Ru(Et$_2$dtc)$_2$(PPh$_3$)$_2$. To a solution of *cis*-$Ru(Et_2dtc)_2(PPh_3)_2$ (0.1 g, 0.11 mmol) in CH_2Cl_2 (20 mL) was added I_2 (56 mg, 0.22 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was pumped off, and the residue was washed with hexane and recrystallized from CH_2Cl_2/Et_2O to give dark crystals (yield: 0.08 g). This paramagnetic product was identified as *trans*-$[Ru(Et_2dtc)_2(PPh_3)_2]^+$, presumably the I_3 salt, by UV/vis spectroscopy. The same cation was obtained for the oxidation of *cis*-$Ru(Et_2dtc)_2(PPh_3)_2$ with Ag(I) salts.

Reaction of Ru(Et$_2$dtc)$_2$(NBD) with I$_2$. To a solution of $Ru(Et_2dtc)_2(NBD)$ (50 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) was added I_2 (56 g, 0.22 mmol), and the mixture was stirred at room temperature for 2 h. Evaporation of the solvent and recrystallization from CH_2Cl_2/hexane afforded a dark paramagnetic solid, presumably the Ru(III) species $[Ru(Et_2dtc)_2(NBD)](I_3)$ (yield: 30 mg). The FAB mass spectrum shows the molecular ion assginable to $[Ru(Et_2dtc)_2(NBD)]^+$ [*m*/*z* 490 $(M + 1)^+$]. Anal. Calcd for $RuC_{17}H_{28}I_3N_2S_4$: C, 23.4; H, 3.2; N, 3.2. Found: C, 23.2; H, 3.2; N, 3.2.

Preparation of Ru(Et$_2$dtc)$_2$(Ts$_2$N$_4$) (7). To a solution of *cis*-$Ru(Et_2dtc)_2(PPh_3)_2$ (0.2 g, 0.22 mmol) in CH_2Cl_2 (20 mL) was added excess TsN_3 (0.20 g), and the mixture was stirred at room temperature for 1 day, during which the solution color changed gradually from yellow to dark red. The solvent was pumped off, and the residue was washed with ether. Recrystallization from CH_2Cl_2/ether gave dark crystals (yield: 0.06 g, 35%). The same compound was isolated in low yield by the reaction of $Ru(Et_2dtc)_2(DMSO)_2$ with TsN_3. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 12H, CH$_2$C*H*$_3$), 2.38 (s, 6H, *p*-CH$_3$), 3.67 (q, 8H, C*H*$_2$CH$_3$), 7.62 (d, 4H, phenyl). IR (Nujol, cm^{-1}): 1596 ($\nu_{N=N}$), 1170 ($\nu_{S=O}$). MS (FAB): *m*/*z* 766 (M^+). Anal. Calcd for $RuC_{24}H_{34}N_6O_4S_6$: C, 37.3; H, 4.5; N, 11.0. Found: C, 37.9; H, 4.5; N, 11.0%.

X-ray Crystallography. The details of crystal data collection and refinement parameters for $Ru(Et_2dtc)_2$(CN-*t*-Bu)$_2$ (**1**), $Ru(Et_2dtc)_2(NBD)$ (**2**), $Ru(Et_2dtc)_2(CO)_2 \cdot {}^1/_2 I_2$ (**4**), $[Ru_3(Et_2dtc)_6(DMSO)_2](I_3)_2$ (**6**), and $Ru(Et_2dtc)_2(Ts_2N_4)$ (**7**) are listed in Table 1. Diffraction data for complex **1** were collected on a Siemens P4 diffractometer, and those for complexes **2**, **4**, **6**, and **7** were collected on a Rigaku AFC7R diffractometer. A complete description of the details of the crystallographic methods is given in the Supporting Information. The data were corrected for Lorentz, polarization, and absorption effects. All structures were solved by direct methods and subsequently refined by full-matrix least-squares routines. Selected bond lengths and angles are collected in Tables 2−6.

Results and Discussion

Preparation of Ru(Et$_2$dtc)$_2$L$_2$. $Ru(Et_2dtc)_2(DMSO)_2$ was found to be a good starting material for the preparation of Ru-

---

(10) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178.

(11) Muller, J.; Fischer, E. O. *J. Organomet. Chem.* **1966**, *5*, 275.

(12) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(13) Critchow, P. B.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1367.

(14) Regitz, M.; Hocker, J.; Liedhegender, A. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 179.

(15) Powell, P. *J. Organomet. Chem.* **1974**, *65*, 89.

(16) Kingston, J. V.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1996**, *28*, 2709.

(17) Colton, F. A.; Farthing, R. H. *Aust. J. Chem.* **1971**, *24*, 903.

Table 1. Crystallographic Data for *trans*-Ru(Et_2dtc)$_2$(*t*-BuNC)$_2$ (**1**), Ru(Et_2dtc)$_2$(NBD) (**2**), Ru(Et_2dtc)$_2$(CO)$_2$·$^1/_2I_2$ (**4**), [Ru_3(Et_2dtc)$_6$(DMSO)$_2$](I_3)$_2$ (**6**), and Ru(Et_2dtc)$_2$(Ts_2N_4) (**7**)

	1	**2**	**4**	**6**	**7**
empirical formula	$C_{20}H_{36}N_4RuS_4$	$C_{17}H_{28}N_2RuS_4$	$C_{12}H_{20}N_2IRuS_4O_2$	$C_{34}H_{72}N_6I_6Ru_3S_{14}O_2$	$C_{24}H_{34}N_6O_4RuS_6$
fw	568.1	489.73	580.52	2110.46	764.00
a, Å	9.753(2)	7.316(1)	7.347(2)	14.125(3)	10.380(1)
b, Å	11.583(2)	10.346(1)	22.227(2)	20.829(6)	11.322(1)
c, Å	12.974(2)	15.123(2)	12.891(2)	13.658(3)	15.310(1)
α, deg		103.69(2)		97.57(2)	106.84(2)
β, deg	99.18(2)	93.54(2)	95.98(2)	110.01(2)	106.87(2)
γ, deg		100.61(2)		71.25(2)	92.63(2)
V, $Å^3$	1446.9(4)	1086.5(3)	2093.8(8)	3574(1)	1631.3(4)
Z	2	2	4	2	2
crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, °C	−75	23	23	23	0
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.290	1.497	1.841	1.961	1.555
μ, cm^{-1}	8.43	11.08	26.28	36.59	9.04
R^a	0.026	0.027	0.031	0.061	0.047
$R_w{}^b$	0.030	0.035	0.033	0.057	0.089
F(000)	584	504	1132	2016	784
GoF^c	1.33	3.06	1.70	2.95	2.97

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w^2(|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$. [c] $\text{GoF} = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

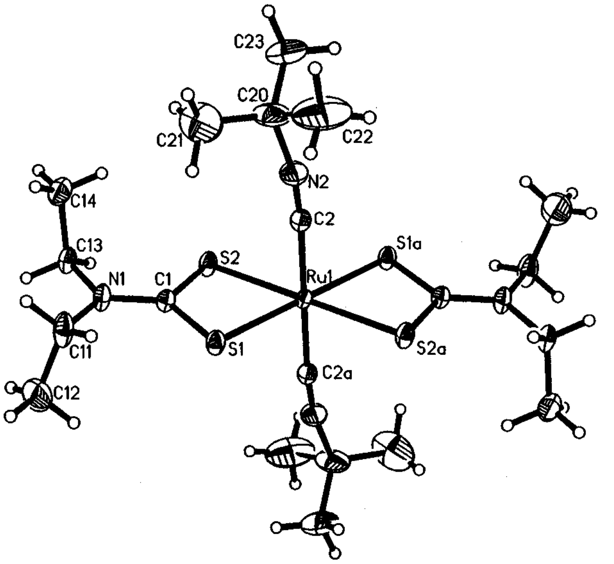


Figure 1. Perspective view of *trans*-Ru(Et_2dtc)$_2$(CN-*t*-Bu)$_2$, **1**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-Ru(Et_2dtc)$_2$(*t*-BuNC)$_2$

Ru−S(1)	2.420(2)	Ru−S(2)	2.398(1)
Ru−C(2)	1.977(2)	C(1)−N(1)	1.335(2)
S(1)−Ru−S(2)	72.0(1)	S(1)−Ru−C(2)	87.7(1)
S(2)−Ru−C(2)	87.1(1)	S(1)−Ru−S(1)a	180.0(1)
S(2)−Ru−S(2)a	180.0(1)	C(2)−Ru−S(1)a	92.3(1)
C(2)−Ru−C(2)a	180.1(1)		
S(1)−Ru−N(1)	83.5(1)	S(1)−Ru−C(1)	106.1(2)
S(1)−Ru−C(4)	90.3(2)		

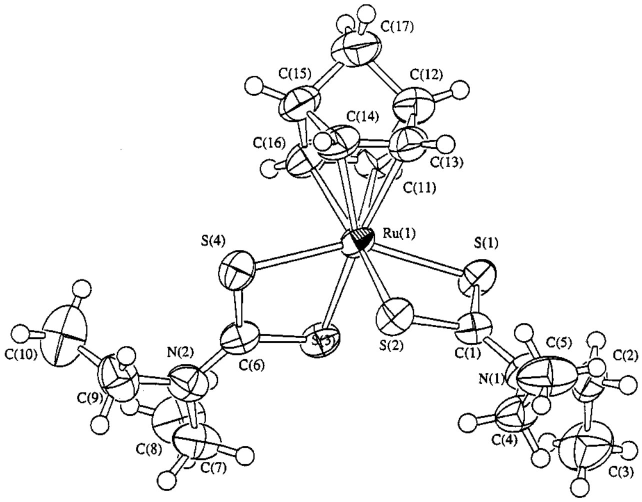


Figure 2. Perspective view of Ru(Et_2dtc)$_2$(NBD), **2**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Ru(Et_2dtc)$_2$(NBD)

Ru(1)−S(1)	2.415(1)	Ru(1)−S(2)	2.416(1)
Ru(1)−S(3)	2.413(1)	Ru(1)−S(4)	2.420(1)
Ru(1)−C(11)	2.187(4)	Ru(1)−C(13)	2.183(4)
Ru(1)−C(14)	2.179(4)	Ru(1)−C(16)	2.169(4)
C(13)−C(14)	1.386(6)	C(11)−C(16)	1.395(6)
S(1)−Ru(1)−S(2)	71.90(3)	S(1)−Ru(1)−S(3)	86.85(4)
S(1)−Ru(1)−S(4)	149.89(4)	S(1)−Ru(1)−C(11)	85.1(1)
S(1)−Ru(1)−C(13)	83.7(1)	S(1)−Ru(1)−C(14)	120.1(1)
S(1)-Ru(1)-C(16)	122.1(1)	C(11)-Ru(1)-C(13)	65.1(2)
C(14)-Ru(1)-C(16)	65.8(2)	C(11)-Ru(1)-C(16)	37.4(2)
C(11)-Ru(1)-C(14)	77.8(2)		

(II) dithiocarbamate complexes of the type Ru(Et_2dtc)$_2L_2$, where L is a neutral ligand such as phosphine or isocyanide. For example, reaction of Ru(Et_2dtc)$_2$(DMSO)$_2$ with *t*-BuNC afforded *trans*-Ru(Et_2dtc)$_2$(*t*-BuNC)$_2$, **1**, isolated as air-stable yellow crystals. The structure of *trans*-[Ru(Et_2dtc)$_2$(*t*-BuNC)$_2$] was established by X-ray crystallography. Figure 1 shows a perspective view of the molecule; selected bond lengths and angles are given in Table 2. In contrast to the structure of *cis*-Ru(Et_2dtc)$_2$(PPh_3)$_2$, the two isocyanides in **1** are *trans* to each other, presumably because PPh_3 is a stronger π-acid ligand and prefers cis disposition in order to minimize competition for Ru d_π orbitals. The mean Ru−C and Ru−S bond distances are ca. 1.977 and 2.40 Å, respectively. The reaction of Ru(Et_2dtc)$_2$(DMSO)$_2$ with pyridine (py) was found to be slow and gave Ru(Et_2dtc)$_2$(py)$_2$ in low yield. Reaction of Ru(Et_2dtc)$_2$(DMSO)$_2$ with 4,4′-bipyridine led to isolation of an intractable blue material, presumably a polymer, which has yet to be characterized.

The diene complexes Ru(Et_2dtc)$_2$(diene) were prepared from [Ru(diene)Cl_2]$_n$ (diene = NBD (**2**), COD (**3**)) and Na(Et_2dtc) as previously reported.[15] The solid-state structure of **2** was determined and is shown in Figure 2; selected bond lengths and angles are given in Table 3. The mean Ru−S and Ru−C distances are ca. 2.16 and 2.180 Å, respectively. The olefinic C−C distance in **2** of ca. 1.391 Å is longer than that in the free ligand (1.35 Å) and comparable to those for normal Ru(II)−

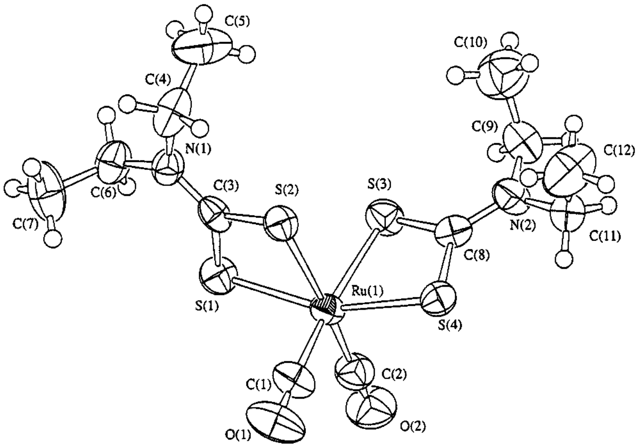


Figure 3. Perspective view of the $Ru(Et_2dtc)_2(CO)_2$ moiety of **4**.

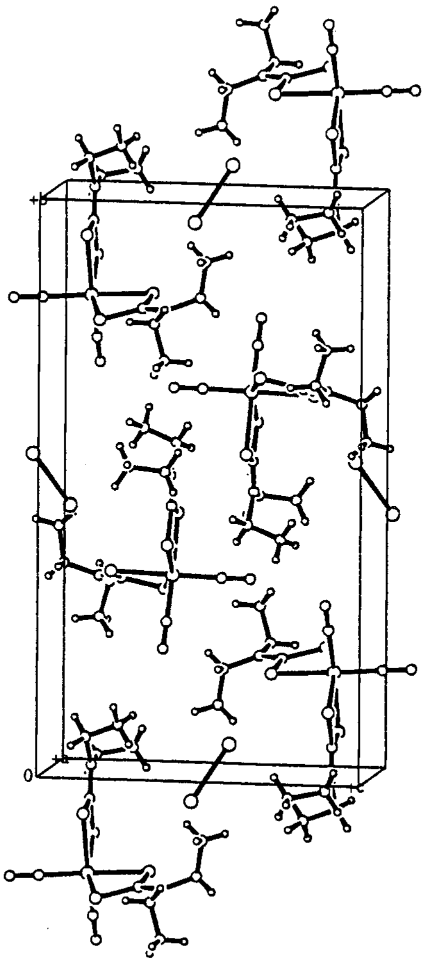


Figure 4. Packing diagram for $Ru(Et_2dtc)_2(CO)2\cdot{}^1/_2I_2$ **4**.

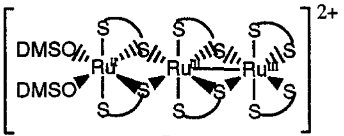
NBD π complexes (e.g. 1.386(6) Å for $RuCl_2(NBD)(C_6H_5NH_2)$[18]), indicative of Ru-to-olefin back-bonding in **2**.

Oxidation. In attempts to prepare the higher valent Ru dithiocarbamate complexes, the oxidation reactions of $Ru(Et_2dtc)_2L_2$ with iodine were studied. Treatment of $Ru(Et_2dtc)_2(CO)_2$ with stoichiometric I_2 afforded the 2:1 molecular iodine complex $Ru(Et_2dtc)_2(CO)_2\cdot{}^1/_2I_2$, **4**. No oxidation of $Ru(Et_2dtc)_2(CO)_2$ occurs, apparently because the Ru(II) state is strongly stabilized by the π-acid ligand CO. Figure 3 shows a perspective view of the *cis*-$Ru(Et_2dtc)_2(CO)_2$ moiety, and Figure 4 shows the packing diagram for **4**. Selected bond lengths and angles are listed in Table 4. The geometry around Ru is octahedral with the two cis-disposed carbonyls. The Ru−C distance of 1.903 Å in **4** is longer than those in $Ru_2(Et_2dtc)_4(CO)_2$ (1.79 Å)[19] and $Ru_3(Et_2dtc)_4(CO)_3Cl_2$ (1.63−1.69 Å).[20] This may be attributed to the weaker Ru-to-C back-bonding in the dicarbonyl complex **4** compared with the latter two complexes, which contain only one carbonyl per Ru. The S−I separation of ca. 3.7 Å indicates the absence of direct S−I interaction in **4**. In addition, the I−I distance in **4** of 2.745 Å is more similar to that in free I_2 (2.67 Å[21]) than to those in molecular iodine complexes [e.g. 3.147(1) Å in ethylenethiourea−$2(I_2)$],[22] suggesting that there is little charge transfer between the $Ru(Et_2dtc)_2(CO)_2$ and the iodine moieties. Accordingly, the C≡O stretching frequencies for **4** (2026 and 1956 cm^{-1}) are virtually identical to those for $Ru(Et_2dtc)_2(CO)_2$ (2028 and 1952 cm^{-1}).

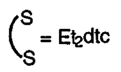
Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Ru(Et_2dtc)_2(CO)_2\cdot{}^1/_2I_2$

I(1)−I(1)′	2.745(1)	Ru(1)−S(1)	2.418(2)
Ru(1)−S(2)	2.445(2)	Ru(1)−S(3)	2.444(2)
Ru(1)−S(4)	2.402(2)	Ru(1)−C(1)	1.896(10)
Ru(1)−C(2)	1.910(2)	O(1)−C(1)	1.128(10)
O(2)−C(2)	1.115(10)		
S(1)−Ru(1)−S(2)	72.15(7)	S(1)−Ru(1)−S(3)	92.30(8)
S(1)−Ru(1)−S(4)	159.32(8)	S(1)−Ru(1)−C(1)	95.7(3)
S(1)−Ru(1)−C(2)	100.3(3)	S(2)−Ru(1)−S(3)	88.86(8)
S(2)−Ru(1)−S(4)	93.09(8)	S(2)−Ru(1)−C(1)	90.3(3)
S(2)−Ru(1)−C(2)	172.1(3)	S(3)−Ru(1)−S(4)	72.54(8)
S(3)−Ru(1)−C(1)	171.3(3)	S(3)−Ru(1)−C(2)	89.2(3)
S(4)−Ru(1)−C(1)	98.9(3)	S(4)−Ru(1)−C(2)	93.6(3)
C(1)−Ru(1)−C(2)	92.7(4)	Ru(1)−C(1)−O(1)	178.0(9)
Ru(1)−C(2)−O(2)	178.8(9)		

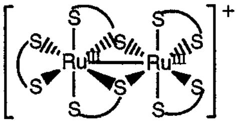
Interestingly, treatment of $Ru(Et_2dtc)_2(DMSO)_2$ with a stoichiometric amount of I_2 gave the linear trimeric complex $[Ru_3(Et_2dtc)_6(DMSO)_2](I_3)_2$, **5**, the structure of which was confirmed by an X-ray diffraction study. Figure 5 shows a perspective view of the cation $[Ru_3(Et_2dtc)_6(DMSO)_2]^{2+}$; selected bond lengths and angles are given in Table 5. The cation can be viewed as consisting of a $\{Ru_2(Et_2dtc)_4\}^{2+}$ core and a *cis*-$Ru(Et_2dtc)_2(DMSO)_2$ unit, which are linked together via the two dithiocarbamate sulfurs of the latter.



5



The bonding mode of the dithiocarbamates in the $\{Ru_2(Et_2dtc)_4\}^{2+}$ core is reminiscent of that for the reported monocation α-$[Ru_2(Me_2dtc)_5]^+$ (**I**).[23]



I

---

[18] Manoli, J.-M.; Gaughan, A. P., Jr.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *72*, 247.

[19] Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 2418.

[20] Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 2422.

[21] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 574.

[22] Herbstein, F. H; Schwotzer, W. *J. Am. Chem. Soc.* **1984**, *106*, 2367.

[23] Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 2410.

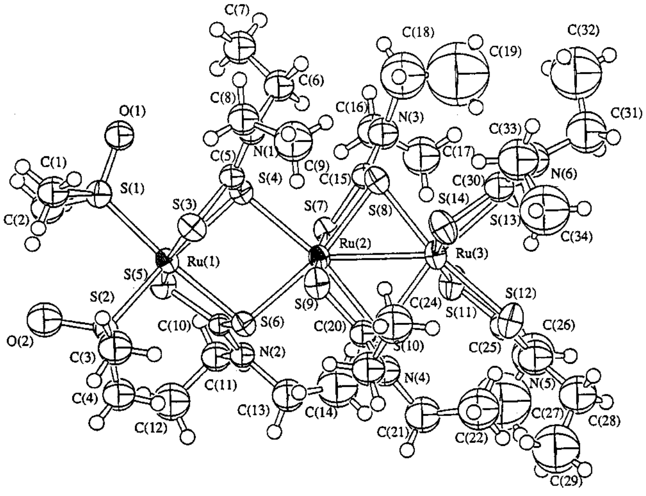


Figure 5. Perspective view of $[Ru_3(Et_2dtc)_6(DMSO)_2]^{2+}$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Ru_3(Et_2dtc)_6(DMSO)_2]^{2+}$

Ru(1)−S(1)	2.287(4)	Ru(1)−S(2)	2.261(4)
Ru(1)−S(3)	2.411(4)	Ru(1)−S(4)	2.429(4)
Ru(1)−S(5)	2.371(4)	Ru(1)−S(6)	2.424(4)
Ru(2)−Ru(3)	2.826(2)	Ru(2)−S(4)	2.476(4)
Ru(2)−S(6)	2.426(4)	Ru(2)−S(7)	2.418(4)
Ru(2)−S(8)	2.313(4)	Ru(2)−S(9)	2.411(4)
Ru(2)−S(10)	2.310(4)	Ru(3)−S(8)	2.301(4)
Ru(3)−S(10)	2.309(4)	Ru(3)−S(11)	2.408(4)
Ru(3)−S(12)	2.393(4)	Ru(3)−S(13)	2.398(4)
Ru(3)−S(14)	2.406(4)		
S(1)−Ru(1)−S(2)	93.6(1)	S(1)−Ru(1)−S(3)	83.3(1)
S(1)−Ru(1)−S(4)	92.1(1)	S(1)−Ru(1)−S(5)	96.2(1)
S(1)−Ru(1)−S(6)	167.0(1)	S(2)−Ru(1)−S(3)	99.0(1)
S(2)−Ru(1)−S(4)	169.8(1)	S(2)−Ru(1)−S(5)	93.2(1)
S(2)−Ru(1)−S(6)	94.5(1)	S(3)−Ru(1)−S(4)	72.7(1)
S(3)−Ru(1)−S(5)	166.7(1)	S(3)−Ru(1)−S(6)	100.5(1)
S(4)−Ru(1)−S(5)	94.6(1)	S(4)−Ru(1)−S(6)	81.6(1)
S(5)−Ru(1)−S(6)	73.2(1)	Ru(3)−Ru(2)−S(4)	148.95(9)
Ru(3)−Ru(2)−S(6)	140.5(1)	Ru(3)−Ru(2)−S(7)	87.95(9)
Ru(3)−Ru(2)−S(8)	52.0(1)	Ru(3)−Ru(2)−S(9)	89.4(1)
Ru(3)−Ru(2)−S(10)	52.3(1)	S(4)−Ru(2)−S(6)	80.6(1)
S(4)−Ru(2)−S(7)	83.6(1)	S(4)−Ru(2)−S(8)	87.1(1)
S(4)−Ru(2)−S(9)	98.1(1)	S(4)−Ru(2)−S(10)	167.3(1)
S(6)−Ru(2)−S(7)	99.6(1)	S(6)−Ru(2)−S(8)	166.8(1)
S(6)−Ru(2)−S(9)	82.7(1)	S(6)−Ru(2)−S(10)	88.5(1)
S(7)−Ru(2)−S(8)	74.3(1)	S(7)−Ru(2)−S(9)	177.3(1)
S(7)−Ru(2)−S(10)	104.9(1)	S(8)−Ru(2)−S(9)	103.7(1)
S(8)−Ru(2)−S(10)	104.3(1)	S(9)−Ru(2)−S(10)	52.31(9)
Ru(2)−Ru(3)−S(8)	104.3(1)	Ru(2)−Ru(3)−S(10)	52.31(9)
Ru(2)−Ru(3)−S(11)	97.1(1)	Ru(2)−Ru(3)−S(12)	137.5(1)
Ru(2)−Ru(3)−S(13)	139.8(1)	Ru(2)−Ru(3)−S(14)	96.8(1)
S(8)−Ru(3)−S(10)	104.7(1)	S(8)−Ru(3)−S(11)	104.7(1)
S(8)−Ru(3)−S(12)	169.39(1)	S(8)−Ru(3)−S(13)	87.6(1)
S(8)−Ru(3)−S(14)	84.2(1)	S(10)−Ru(3)−S(11)	85.8(1)
S(10)−Ru(3)−S(12)	85.5(1)	S(10)−Ru(3)−S(13)	166.3(2)
S(10)−Ru(3)−S(14)	102.4(1)	S(11)−Ru(3)−S(12)	72.3(1)
S(11)−Ru(3)−S(13)	97.0(1)	S(11)−Ru(3)−S(14)	166.2(1)
S(12)−Ru(3)−S(13)	82.6(1)	S(12)−Ru(3)−S(14)	97.0(1)
S(13)−Ru(3)−S(14)	72.4(1)		

The oxidation states of Ru(1), Ru(2), and Ru(3) are assigned as II, III, and III, respectively. The Ru(2)−Ru(3) distance of 2.826(2) Å indicates that there is a single bond between Ru(2) and Ru(3), which results in the diamagnetism of complex **6**. The Ru−Ru bond length is, however, is considerably longer than that for α-$[Ru_2(Me_2dtc)_5]^+$ (2.401 Å).[23] On the other hand, there is no direct metal−metal interaction between Ru(1) and Ru(2). The mean Ru(1)−S(DMSO) distance of 2.274 Å is similar to those for $[Ru(DMSO)_6]^{2+}$ (2.259 Å).[24] The Ru−S(8) and Ru−S(10) distances (2.301−2.311 Å) are shorter than other Ru−S distances (2.393−2.418 Å) for Ru(2) and Ru(3) apparently because of the single bond between Ru(2) and Ru(3).

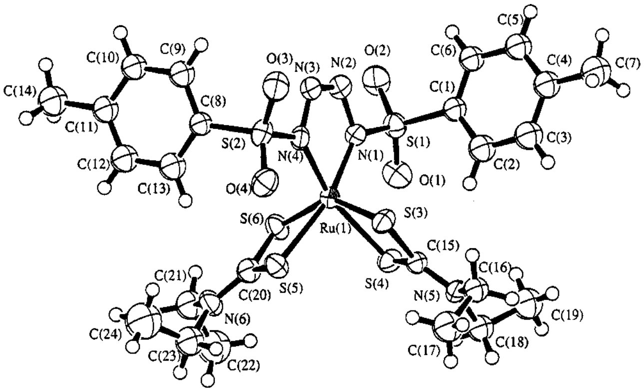
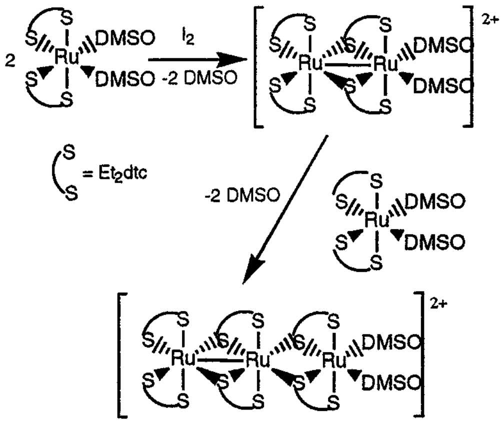


Figure 6. Perspective view of $Ru(Et_2dtc)_2(Ts_2N_4)$, **7**.

Scheme 1



The mechanism for the formation of trimer **6** is not clear but possibly involves the coupling of the dimeric Ru(III)−Ru(III) intermediate $\{Ru_2(Et_2dtc)_4\}^{2+}$ with the starting $Ru(Et_2dtc)_2(DMSO)_2$ (Scheme 1).

Attempts to synthesize the trimeric Ru(III)−Ru(III)−Ru(III) complex by oxidation of **6** with one-electron oxidants such as Ag(I) and Ce(IV) salts led to isolation of red oils, which do not crystallize. Oxidation of $Ru(Et_2dtc)_2(DMSO)_2$ with excess I_2 gave **6** as the only crystalline product.

Reaction of $Ru(Et_2dtc)_2(CN\text{-}t\text{-}Bu)_2$ with $AgCF_3SO_3$ or iodine gave the cation $[Ru(Et_2dtc)_2(CN\text{-}t\text{-}Bu)_2]^+$ (**6**), isolated as the triflate salt. The $\nu_{C\equiv N}$ for **6** (2134 cm^{-1}) was found at higher frequency than that for the Ru(II) congener (2098 cm^{-1}), suggesting that the Ru-to-C back-bonding is weakened on oxidation. Treatment of *cis*-$Ru(Et_2dtc)_2(PPh_3)_2$ and $Ru(Et_2dtc)_2(NBD)$ with Ag(I) or iodine afforded the respective Ru(III) cations $[Ru(Et_2dtc)_2(PPh_3)_2]^+$ [25] and $[Ru(Et_2dtc)_2(NBD)]^+$.

Oxidative Addition Reactions with Azides. Oxidative addition of *cis*-$[Ru(Et_2dtc)_2(PPh_3)_2]$ with tosyl azide gave the novel Ru(IV) ditosyltetrazene complex $Ru(Et_2dtc)_2(Ts_2N_4)$, **7**. $Ru(Et_2dtc)_2(DMSO)_2$ reacted with TsN_3 similarly to give **7** in lower yield. The solid state structure of **7** has been established by X-ray crystallography. Figure 6 shows a perspective view of the molecule, selected bond lengths and angles are given in Table 6. The geometry around Ru is best described as distorted trigonal prismatic with two dithiocarbamate sulfurs and one α

---

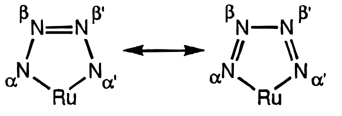
(24) Meno, M.; Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1543.

(25) Davies, A. R.; Einstein, F. W. B.; Farrell, N. P.; James, B. R.; McMillan, R. S. *Inorg. Chem.* **1978**, *17*, 1965.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $Ru(Et_2dtc)_2(Ts_2N_4)$

Ru(1)−S(1)	2.348(4)	Ru(1)−S(4)	2.416(4)
Ru(1)−S(5)	2.413(4)	Ru(1)−S(6)	2.362(4)
Ru(1)−N(1)	1.99(1)	Ru(1)−N(4)	1.97(1)
N(1)−N(2)	1.362(2)	N(2)−N(3)	1.28(2)
N(3)−N(4)	1.37(2)		
S(3)−Ru(1)−S(4)	72.4(1)	S(3)−Ru(1)−S(5)	83.4(1)
S(3)−Ru(1)−S(6)	146.0(1)	S(3)−Ru(1)−N(1)	111.5(4)
S(3)−Ru(1)−N(4)	94.7(4)	S(4)−Ru(1)−S(5)	90.7(1)
S(4)−Ru(1)−S(6)	84.3(1)	S(4)−Ru(1)−N(1)	99.1(3)
S(4)−Ru(1)−N(4)	162.9(4)	S(5)−Ru(1)−S(6)	72.2(1)
S(5)−Ru(1)−N(1)	164.0(3)	S(5)−Ru(1)−N(4)	99.1(4)
S(6)−Ru(1)−N(1)	96.1(4)	S(6)−Ru(1)−N(4)	112.0(4)
N(1)−Ru(1)−N(4)	74.8(5)	Ru(1)−N(1)−N(2)	107.9(9)
N(1)−N(2)−N(3)	114(1)	N(2)−N(3)−N(4)	114(1)
Ru(1)−N(4)−N(3)	118.5(9)		

Scheme 2



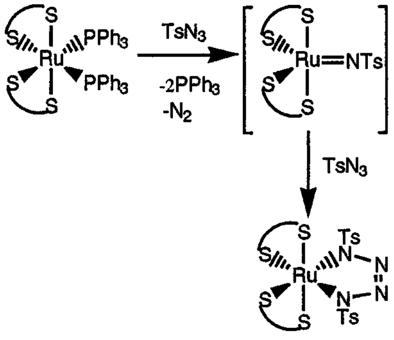
II **III**

nitrogen at the corners of each trigonal face. The $N_\alpha-N_\beta$ and $N_\beta-N_{\beta'}$ distances of 1.37 and 1.28(2) Å suggest that the tetraaza ligand is in the dianionic 2-ene form **II** rather than the neutral 1,3-diene form **III** (Scheme 2).

The $Ru-N_\alpha$ distances [1.99(1) and 1.97(1) Å] for complex **7** are comparable to the Ru−N(amide) distances in Ru^{IV}(chbae)-(PPh_3)(py) [1.987−2.044(5) Å; H_4(chbae) = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane; py = pyridine][26] but are longer than those in $Ru^{IV}(bipy)(NHCMe_2CMe_2NH)_2$ (1.856 Å; bipy = 2,2′-bipyridine).[27] Interestingly, the $Ru-N_\alpha$ distances in this formally Ru(IV) tetrazene complex are slightly longer than those in the divalent analogue (η^6-cymen)Ru[N(2,4,6-*t*-$Bu_3C_6H_2$)N_3-(mes)] (1.946(3) and 1.967 Å; mes = 2-mesityl).[28] Complex **7** is diamagnetic with a well-resolved NMR spectrum, indicative of the $(d_{yz})^2(d_{xz})^2$ ground-state electron configuration. The IR spectrum shows an absorption at 1596 cm^{-1}, which is tentatively assigned as the N═N stretch. It might be noted that mono-nuclear Ru(IV) dithiocarbamate complexes are rather rare. The only structurally characterized examples are the pentagonal bipyramidal complexes $Ru(Et_3dtc)_3X$ (X = Cl^8 and $I_3{}^9$), which are also diamagnetic.

Cycloaddition of a metal−imido moiety to azides to give tetrazene complexes is not without precedence. Recently, Wilkinson and co-workers isolated a Ru(II) tetrazene complex from the reaction of a Ru(II)−imido moiety with an aryl azide.[28] In this connection, we believe that complex **7** was formed via 1,3-dipolar cycloaddition of the unisolated Ru(IV)−tosylimido intermediate to TsN_3 (Scheme 3).

Scheme 3



7

Attempts to intercept the Ru(IV) nitrene intermediate by olefins were not successful. In contrast to the case of tosyl azide, there was no observable reaction of $Ru(Et_2dtc)_2(PPh_3)_2$ with 1-azidoadamantane. Reaction of $Ru(Et_2dtc)_2(DMSO)_2$ with Me_3SiN_3 gave a paramagnetic complex which shows $\nu_{N\equiv N}$ at 2200 cm^{-1}, suggestive of the formation of the Ru(III) azide complex $Ru(Et_2dtc)_2N_3$.

Table 7. Reduction Potentials ($E°$) for the Ru−Dithiocarbamate Complexes

	$E°$, V (vs $Cp_2Fe^{+/0}$)[a]	
complex	oxidn	redn
$Ru(Et_2dtc)_2(DMSO)_2$	0.35[b]	
$Ru(Et_2dtc)_2(t\text{-}BuNC)_2$	−0.07 (100)	
$Ru(Et_2dtc)_2(NBD)$	0.04 (104)	
$[Ru_3(Et_2dtc)_6(DMSO)_2]^{2+}$	0.19 (100)	−0.70[b]
$Ru(Et_2dtc)_2(Ts_2N_4)$	0.52 (90)	−0.64 (90)

[a] Potentials measured at a glassy carbon electrode in 0.1 M [n-$Bu_4N]PF_6$/ CH_2Cl_2; scan rate = 100 mV s^{-1}; ΔE_p values (mV) are given in parentheses. [b] Irreversible.

Electrochemistry. The formal potentials of the Ru dithiocarbamate complexes have been determined by cyclic voltammetry and are summarized in Table 7. The cyclic voltammograms of *trans*-$Ru(Et_2dtc)_2$(CN-*t*-Bu)$_2$ and $Ru(Et_2dtc)_2(NBD)$ exhibit reversible oxidation couples at −0.07 and 0.04 V vs $Cp_2Fe^{+/0}$, respectively, which are tentatively assigned as the Ru(III/II) couples. These Ru(III/II) potentials are comparable to that for *cis*-$Ru(Et_2dtc)_2(PPh_3)_2$ (0.23 V vs SCE).[24] The oxidation of $Ru(Et_2dtc)_2(DMSO)_2$ occurs at 0.35 V and is irreversible. This suggests that the ability to stabilize the Ru(II) state decreases in the order DMSO > *t*-BuNC ∼ NBD > PPh_3.

The cyclic voltammogram of the trimer **6** displays a reversible oxidation couple at 0.19 V, tentatively assigned as the Ru(III,III,III)/Ru(II,III,III) couple, along with an irreversible wave at −0.70 V. Although the Ru(III,III,III)/Ru(II,III,III) couple is reversible on the cyclic voltammetric time scale, attempts to isolate the oxidation product by reacting **6** with stoichiometric Ag(I) or Ce(IV) were unsuccessful. The tetrazene complex **7** exhibits a reveresible couple at 0.52 V vs $Cp_2Fe^{+/0}$, which possibly is a ligand-centered oxidation.

Acknowledgment. We thank the Hong Kong University of Science and Technology and the Croucher Foundation for support.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**, **2**, **4**, **6**, and **7** are available on the Internet only. Access information is given on any current masthead page.

IC970053Q

---

(26) Che, C.-M.; Cheng, W.-K.; Leung, W.-H.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1987**, 418.

(27) Chiu, W.-H.; Peng, S.-M.; Che, C.-M. *Inorg. Chem.* **1996**, *35*, 3369.

(28) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 3771.