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# Heterobimetallic µ-nitrido complexes containing ruthenium(II) dithiocarbamate

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#### Abstract

Interaction of [Ru(Co)H(Et<sub>2</sub>dtc)with triflic acid (HOTf) afforded [Ru(Co)H(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(OTf) (1), which has been characterized by X-ray crystallography. The Ru–C, Ru–O, average Ru–S and average Ru–P distances in 1 are 1.811(5), 2.216(3), 2.433 and 2.423 Å, respectively. Reaction of 1 with amines L results in the formation of adducts *trans*-[Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>L](OTf) (L = N<sub>2</sub>H<sub>4</sub> (2) and NH<sub>2</sub>OH (3)). The Ru–C, Ru–N, average Ru–S and average Ru–P distance in 3 are 1.85(1), 2.179(8), 2.433 and 2.393, respectively; the Ru–N–O angle being 119.7(5)°. Treatment of 1 with [N<sup>n</sup>Bu<sub>4</sub>][OsN(C<sub>7</sub>H<sub>6</sub>S<sub>2</sub>)<sub>2</sub>] ([C<sub>7</sub>H<sub>6</sub>S<sub>2</sub>]<sup>2</sup> – = 3,4-toluenedithiolate(2 – )), and [ReN(Et<sub>2</sub>dtc)<sub>2</sub>] (Et<sub>2</sub>dtc = *N*,*N*-diethyldithiocarbamate) gave the corresponding µ-nitrido complexes [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(NOsO<sub>3</sub>)] (4), [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>{NOs(C<sub>7</sub>H<sub>6</sub>S<sub>2</sub>)<sub>2</sub>] (5) and [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>{NRe(Et<sub>2</sub>dtc)<sub>2</sub>}] (6). The structures of complexes 4–6 have been established by X-ray crystallography. The Os–N and Ru–N distances and Os–N–Ru angle in 4 are 1.719(7) and 2.075(7) Å, and 155.1(4)°, respectively. The Os–N and Ru–N distances and Os–N–Ru angle in 5 are 1.680(6) and 2.068(6) Å, and 166.2(3)°, respectively. The Re–N and Ru–N distances, and Re–N–Ru angle for 6 are 1.670(3) and 2.108(3) Å, and 170.9(2)°, respectively. The bond lengths and angles for these µ-nitrido complexes are indicative of asymmetric bridging mode of nitride, i.e. M≡N → Ru(II) (M = Os(VIII), Os(VI), Re(V)). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Ruthenium complexes; Nitrido complexes; Heterobimetallic complexes

# 1. Introduction

 $\mu$ -Nitrido-bridged dimetallic complexes are of interest because they are believed to play important roles in metal-centered nitrogen atom transfer reactions [1–4]. Previously we reported that  $\mu$ -nitrido osmium complexes can be prepared conveniently by metathesis of anionic nitrido-osmium(VII) or nitrido-osmium(VI) complexes with appropriate metal triflates including d<sup>10</sup>-configured [Au(PPh<sub>3</sub>)(OTf)] and d<sup>8</sup>-configured [Pt(PR<sub>3</sub>)<sub>2</sub>(OTf)<sub>2</sub>], [Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>(OTf)] [5,6] and d<sup>6</sup>configured [Ru(OEP)(NO)(OTf)] (OTf = triflate; H<sub>2</sub>OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin) [7]. The bonding in these osmium u-nitrido complexes containing d<sup>10</sup>- and d<sup>8</sup>-configured M are best described as  $Os=N \rightarrow M$ , consisting of Os=N triple bond and OsN-M donor-acceptor type interaction [5], whereas Ru-N multiple bond character was also noted in [Ru(OEP)(NO)(NOsO<sub>3</sub>)] [7]. To further probe the influence of M on the bonding mode in OsNM complexes, we set out to prepare bimetallic nitrido complexes containing other Ru(II) fragments. [Ru(CO)(Et<sub>2</sub>dtc)- $(PPh_3)_2(OTf)$ ] (Et<sub>2</sub>dtc = N,N-diethyldithiocarbamate) is chosen to be a nitride acceptor because the  $[Ru(CO)(R_2dtc)(PPh_3)_n]$  cores (R = Me or Et; n = 1 or 2) are known to form stable complexes with  $\pi$ -donor ligands such as thiophenolate, polysulfides [8] and Ndonor ligands such as amines [9] and tosylamide [10]. We here report the reactions of [Ru(CO)(Et<sub>2</sub>dtc)-

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 $(PPh_3)_2(OTf)$ ] with hydrazine, hydroxylamine and metal nitrides and the isolation of the respective Ru(II) amine and  $\mu$ -nitrido complexes.

#### 2. Experimental

#### 2.1. General

All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were purified and distilled prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer. Chemical shifts ( $\delta$ , ppm) were reported with reference to SiMe<sub>4</sub> (<sup>1</sup>H) and H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer. Mass spectra were obtained on a Finnigan TSO-7000 spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes are glassy carbon and Ag-AgNO<sub>3</sub> (0.1 M in acetonitrile) electrodes, respectively. Potentials were reported with reference to the ferrocenium-ferrocene couple. Elemental analyses were performed by Medac Ltd, Surrey, UK.

The compounds [Ru(CO)(H)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>] [11], [N<sup>n</sup>Bu<sub>4</sub>][OsO<sub>3</sub>N] [12], [N<sup>n</sup>Bu<sub>4</sub>][OsN(C<sub>7</sub>H<sub>6</sub>S<sub>2</sub>)<sub>2</sub>] ([C<sub>7</sub>H<sub>6</sub>S<sub>2</sub>]<sup>2-</sup> = 3,4-toluenedithiolate(2 - )] [6,13] and [ReN(Et<sub>2</sub>dtc)<sub>2</sub>] [14] were synthesized according to the literature methods. The hydrogen atom labelling scheme for C<sub>7</sub>H<sub>6</sub>S<sub>2</sub><sup>2-</sup> is shown below.



#### 2.2. Synthesis

#### 2.2.1. $[Ru(CO)(Et_2dtc)(PPh_3)_2(OTf)]$ (1)

To a solution of  $[Ru(CO)(H)(Et_2dtc)(PPh_3)_2]$  (0.10 g, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added excess triflic acid (0.2 ml of a 1 M solution in CH<sub>2</sub>Cl<sub>2</sub>) at 0°C. The reaction mixture was warmed to room temperature and was stirred overnight. The solvent was then pumped off and the residue was washed with Et<sub>2</sub>O. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexane afforded pale yellow crystals. Yield: 0.023 g (20%). *Anal.* Calc. for C<sub>43</sub>H<sub>40</sub>F<sub>3</sub>NO<sub>4</sub>P<sub>2</sub>RuS<sub>3</sub>: C, 54.3; H, 4.2; N, 1.5. Found: C, 54.6; H, 4.3; N, 1.5%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.20 (t, 6H, CH<sub>2</sub>CH<sub>3</sub>), 3.65 (q, 4H, CH<sub>2</sub>CH<sub>3</sub>), 7.24 – 7.37 (m, 30H, phenyl H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  38.24 (s). IR (Nujol):  $\nu$ (cm<sup>-1</sup>), 1950 [ $\nu$ (C=O)]; 1032, 1232, 1324 [ $\nu$ (S=O)].

# 2.2.2. $[Ru(CO)(Et_2dtc)(PPh_3)_2(NH_2NH_2)](OTf)$ (2)

To a solution of **1** (0.10 g, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added hydrazine hydrate (0.1 ml) and the reaction mixture was stirred at room temperature for 1 h. The solvent was then pumped off and the residue was washed with Et<sub>2</sub>O. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O afforded yellow crystals. Yield: 0.08 g (75%). *Anal.* Calc. for C<sub>43</sub>H<sub>44</sub>F<sub>3</sub>N<sub>3</sub>O<sub>4</sub>P<sub>2</sub>RuS<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 49.5; H, 4.3; N, 3.9. Found: C, 48.9; H, 4.5; N, 3.7%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.20 (t, 6H, CH<sub>2</sub>CH<sub>3</sub>), 3.47–3.78 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 3.42 (s br, 2H, N<sub>2</sub>H<sub>4</sub>), 7.27–7.46 (m, 30H, phenyl H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  38.76. IR (Nujol):  $\nu$ (cm<sup>-1</sup>), 1976 [ $\nu$ (C=O)]; 3335, 3315 [ $\nu$ (NH<sub>2</sub>)].

# 2.2.3. $[Ru(CO)(Et_2dtc)(PPh_3)_2(NH_2OH)](OTf)$ (3)

To a solution of **1** (0.06 g, 0.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added 1 equiv. of hydroxylamine and the reaction mixture was stirred at room temperature for 2 h. The solvent was pumped off and the residue was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-hexane to afford yellow crystals. Yield: 0.05 g, 85%. *Anal.* Calc. for C<sub>43</sub>H<sub>43</sub>F<sub>3</sub>-N<sub>2</sub>O<sub>5</sub>P<sub>2</sub>RuS<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 49.4; H, 4.2; N, 2.6. Found: C, 49.3; H, 4.1; N, 2.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.16 (t, 6H, CH<sub>2</sub>CH<sub>3</sub>), 3.62 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 6.14 (s br, 2H, NH<sub>2</sub>), 6.99 (s br, 1H, OH), 7.28–7.40 (m, 30H, phenyl H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  38.73. IR (Nujol):  $\nu$ (cm<sup>-1</sup>), 1976 [ $\nu$ (C  $\equiv$  O)]; 3260 [ $\nu$ (NH<sub>2</sub>)]; 3500 br [ $\nu$ (OH)].

# 2.2.4. [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(NOsO<sub>3</sub>)] (4)

To a solution of **1** (0.10 g, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added 1 equiv. of [N<sup>n</sup>Bu<sub>4</sub>][NOsO<sub>3</sub>] (0.05 g, 0.11 mmol). The reaction mixture was stirred at room temperature for 1 h. The solvent was then pumped off in vacuo, and the orange residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane to afford dark orange crystals. Yield: 0.07 g (60%) *Anal*. Calc. for C<sub>42</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>OsP<sub>2</sub>RuS<sub>2</sub>: C, 48.5; H, 3.9; N, 2.6. Found: C, 47.9; H, 3.8; N, 2.7%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.24 (t, 6H, CH<sub>3</sub>CH<sub>2</sub>), 3.60 (q, 4H, CH<sub>3</sub>CH<sub>2</sub>), 7.29–7.36 (m, 30H, phenyl H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  39.22 (s) IR (Nujol):  $\nu$ (cm<sup>-1</sup>), 882, 902 [ $\nu$ (Os=O)], 1092 [ $\nu$ (Os=N)], 1970 [ $\nu$ (C=O)].

# 2.2.5. $[Ru(CO)(Et_2dtc)(PPh_3)_2\{NOs(C_7H_6S_2)_2\}]$ (5)

To a solution of **1** (0.093 g, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added 1 equiv. of  $[N^nBu_4][OsN(C_7H_6S_2)_2]$  (0.075 g, 0.1 mmol) and the mixture was stirred at room temperature for 2 h. The solvent was pumped off and the dark residue washed with hexane and Et<sub>2</sub>O. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexane afforded dark yellow crystals. Yield: 0.065 g (50%). *Anal.* Calc. for C<sub>56</sub>H<sub>52</sub>N<sub>2</sub>OOsP<sub>2</sub>RuS<sub>6</sub>: C, 51.1; H, 4.1; N, 2.1. Found: C, 51.0; H, 4.0; N, 2.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.33 (overlapping t, 6H, CH<sub>3</sub>), 2.35 (s, 6H, CH<sub>3</sub> of C<sub>7</sub>H<sub>6</sub>S<sub>2</sub>), 3.47–3.66 (m, 4H, CH<sub>2</sub>), 6.74 (d, J = 7.9 Hz, 2H, H<sub>b</sub>),

7.42 (s, 2H, H<sub>c</sub>), 7.50 (d, J = 7.9 Hz, 2H, H<sub>a</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  33.45 (s). IR (Nujol):  $v(\text{cm}^{-1})$ , 1974 [v(CO)].

# 2.2.6. $[Ru(CO)(Et_2dtc)(PPh_3)_2\{NRe(Et_2dtc)_2\}](OTf)$ (6)

To a solution of **1** (0.10 g, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was added 1 equiv. of [ReN(Et<sub>2</sub>dtc)<sub>2</sub>] (0.05 g, 0.11 mmol). The yellow reaction mixture was stirred at room temperature overnight. The solvent was then pumped off in vacuo, and the yellow residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane to afford yellow crystals, which were suitable for X-ray diffraction study. Yield: 0.06 g (38%). *Anal.* Calc. for C<sub>53</sub>H<sub>60</sub>F<sub>3</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>ReRuS<sub>7</sub>: C, 44.0; H, 4.2; N, 3.9. Found: C, 42.7; H, 4.1; N, 3.8%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.25–1.40 (m, 18H, CH<sub>3</sub>CH<sub>2</sub>), 3.63 – 3.92 (m, 12H, CH<sub>3</sub>CH<sub>2</sub>), 7.20–7.43 (m, 30H, phenyl H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  35.47 (s). IR (Nujol):  $\nu$ (cm<sup>-1</sup>), 1970 [ $\nu$ (CO)].

# 2.3. X-ray crystallography

A summary of pertinent crystal data and experimental details for complexes 1, 3, 4, 5 and 6 are listed in Table 1. Intensity data were collected on a Siemens P4 diffractometer (for 1, 4, 5 and 6) and a MAR research image-plate diffractometer (for 3) at room temperature using the graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ 0.71073 Å). The absorption corrections for complexes 1 and 4–6 are semi-empirical based on psi-scan data. For complex 3, an approximation to absorption correction by inter-image scaling was also applied. The large residual maximum (+2.9 e Å<sup>-3</sup>) and minimum (-3.0 e  $Å^{-3}$ ) electron density in compound 4 are 0.92 and 0.79 Å from the Os atom, respectively. No peaks of chemical significance remain in the structure. All the structures were solved by direct methods and refined by full-matrix least-squares procedures. Calculations were performed using the SHELXL [15] (for complexes 1 and **4–6**) and TEXSAN (for complex **3**) [16] crystallographic packages. The disorder of the coordinated triflate in 1 appears to be 90:10. Whilst a discernible peak may be found for S(3A), which has similar geometry to O(2)and O(3), the 10% occupancy peaks for the rest of group are too small to be modelled. The presence of the disorder thus increases the thermal parameters of the remaining atoms of the group since they must still be refined with full occupancy factors. For 5, the disorder for the methyl group in the toluenedithiolate ligands is not constrained to be 50:50 by crystallographic symmetry. The ring C(77) position has 60:40 disorder and C(87) 55:45. This was modelled by holding the two thermal parameters equivalent and refining the site occupancy. The site occupancies were then rounded off and fixed, and separate isotropic thermal parameters refined (all U's are in the range of 0.13-0.14). The C(77) and C(87) groups of the neighbouring molecules are not in contact, so the two disorders were treated independently. The disorder for the phenyl groups in 6

Table 1

Crystal data and experimental details for  $[Ru(CO)(Et_2dtc)(PPh_3)(OTf)]$  (1),  $[Ru(CO)(Et_2dtc)(PPh_3)_2(NH2OH)](OTf)$  (3),  $[Ru(CO)(Et_2dtc)(PPh_3)_2(NOsO_3)]$  (4),  $[Ru(CO)(Et_2dtc)(PPh_3)_2\{NOs(C_7H_6S_2)\}]$  (5) and  $[Ru(CO)(Et_2dtc)(PPh_3)_2\{NRe(Et_2dtc)_2\}](OTf)$  (6)

	1	3	4	5	6
Empirical formula	$C_{43}H_{40}F_3NO_4P_2RuS_3$	$C_{43}H_{43}F_3N_2O_5P_2RuS_3$	$C_{42}H_{40}N_2O_4OsP_2S_2Ru$	$C_{56}H_{52}N_2OOsP_2RuS_6$	$\mathrm{C}_{53}\mathrm{H}_{60}\mathrm{F}_{3}\mathrm{N}_{4}\mathrm{O}_{4}\mathrm{P}_{2}\mathrm{ReRuS}_{7}$
Formula weight	950.95	984.02	1054.09	1314.57	1447.68
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
a (Å)	10.372(4)	11.348(1)	10.373(1)	13.217(1)	11.4980(1)
b (Å)	23.670(9)	14.773(1)	22.949(1)	22.028(2)	16.286(2)
<i>c</i> (Å)	17.785(6)	16.395(1)	17.521(1)	19.985(2)	16.320(3)
α (°)		106.36(2)			92.270(1)
β (°)	90.26(2)	101.57(2)	90.330(1)	107.49(1)	93.450(1)
γ (°)		102.84(2)			97.140(1)
V (Å <sup>3</sup> )	4366(3)	2467.5(7)	4170.8(5)	5549.5(9)	3023.4(7)
Space group	$P2_1/n$ (no. 14)	<i>P</i> 1 (no. 2)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	<i>P</i> 1 (no. 2)
Ζ	4	2	4	4	2
$D_{\rm calc}~({\rm g~cm^{-3}})$	1.447	1.324	1.679	1.573	1.590
Temperature (K)	293	298	293	293	293
F(000)	1944	1008	2080	2624	1452
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	6.3	5.62	36.25	28.33	25.99
Total reflections	10 504	8578	10 371	9908	14 341
Independent reflections	8546 ( $R_{\rm int} = 0.0481$ )		8460 $(R_{\rm int} = 0.0312)$	9448 ( $R_{\rm int} = 0.0443$ )	13 677 $(R_{\rm int} = 0.0315)$
Observed reflections		7334 $[I > 1.5\sigma(I)]$			
$R_1 (F_o > 2\sigma(F_o))$	0.0489	0.090	0.0666	0.0503	0.0353
$wR_2$ (all data)	0.1345	0.144 <sup>a</sup>	0.1905	0.1113	0.0951
Goodness-of-fit	1.020	5.39	1.067	1.018	0.999

<sup>a</sup>  $R_w$  refined on F.



Fig. 1. Perspective view of  $[Ru(CO)(Et_2dtc)(PPh_3)_2(OTf)]$  (1). Phenyl rings of PPh<sub>3</sub> are omitted for clarity

Table 2

Selected	bond	lengths	(Å)	and	angles	(°)	for	trans-[Ru(CO)-
(Et <sub>2</sub> dtc)(I	PPh <sub>3</sub> ) <sub>2</sub> (	OTf)] (1)						

Ru–P(1)	2.441(1)	Ru–P(2)	2.404(1)
Ru-S(1)	2.431(2)	Ru-S(2)	2.434(2)
Ru–O(2)	2.216(3)	Ru-C(1)	1.811(5)
O(1)–C(1)	1.153(5)		
P(1)-Ru-P(2)	102.4(1)	P(1)-Ru-S(1)	93.5(1)
P(2)-Ru-S(1)	164.2(1)	P(1)-Ru-S(2)	165.6(1)
P(2)-Ru-S(2)	92.1(1)	S(1)-Ru-S(2)	72.1(1)
P(1)-Ru-O(2)	93.1(1)	P(2)-Ru-O(2)	88.7(1)
S(1)-Ru-O(2)	90.4(1)	S(2)-Ru-O(2)	87.5(1)
P(1)-Ru-C(1)	91.0(1)	P(2)-Ru-C(1)	93.5(2)
S(1)-Ru-C(1)	86.1(2)	S(2)-Ru-C(1)	87.7(1)
Ru–C(1)–O(1)	175.5(4)		

is difficult to model but appears to be 80:20. A figure showing the disorder is added to the supplementary material.

#### 3. Results and discussion

#### 3.1. Synthesis of [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(OTf)]

The triflate compound  $[Ru(CO)(Et_2dtc)(PPh_3)_2(OTf)]$ (1) was made in high yield by reaction of triflic acid with  $[Ru(CO)(Et_2dtc)(PPh_3)_2(H)]$ , isolated as air-stable cream coloured crystals Eq. (1)

[Ru(CO)(H)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>] + HOTf

$$\rightarrow [\operatorname{Ru}(\operatorname{CO})(\operatorname{Et_2dtc})(\operatorname{PPh_3})_2(\operatorname{OTf})] + \operatorname{H_2}$$
(1)

The v(CO) for 1 occurs at 1950 cm<sup>-1</sup>, which is considerably lower than that for the starting hydride

compound, indicating that the coordinated triflate is a rather weak donor ligand. Fig. 1 shows the molecular structure of 1; selected bond lengths and angles are listed in Table 2. The geometry around Ru is pseudo-octahedral with the triflate *trans* to the carbonyl. This structure is different from that for a related compound [Ru(SH)(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>], in which the HS<sup>-</sup> and CO ligands are mutually *cis* and the two PPh<sub>3</sub> mutually *trans* [17]. The average Ru–P distance in 1 (2.423 Å) is slightly longer than that in [Ru(SH)(CO)(Et<sub>2</sub>dtc)-(PPh<sub>3</sub>)<sub>2</sub>] (2.381 Å) [17]. The average Ru–S distance of 2.433 Å is typical for Ru(II) dithiocarbamte complexes [9,10].

# 3.2. Amine adducts of 1

Complex 1 was found to react with N-donor ligands to give the corresponding adducts of Ru(II) dithiocarbamate (Scheme 1).

Thus, treatment of **1** with hydrazine hydrate afforded the hydrazine adduct  $[Ru(CO)(Et_2dtc)(PPh_3)_2-(N_2H_4)](OTf)$  (**2**). The IR spectrum for **2** shows v(N-H)at 3315 and 3335 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of **2** shows two broad singlets at  $\delta$  3.42 and 4.48, assignable to the amino protons. The IR v(CO) for **2** of 1976 cm<sup>-1</sup> is higher than that for **1** due to cationic nature of the complex.

Similarly, reaction of 1 with hydroxylamine hydrate afforded the Ru(II) hydroxylamine adduct [Ru(CO)-(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(NH<sub>2</sub>OH)](OTf) (3). The IR spectrum of 3 shows v(NH) at 3260 along with v(OH) at 3500 cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectrum of **3**, the amino and hydroxyl protons appear as broad singlets at  $\delta$  6.14 and 6.99, respectively. The structure of 3 has been unambiguously established by X-ray crystallography. Fig. 2 shows a diagram of the molecule; selected bond lengths and angles are given in Table 3. The geometry around Ru is distorted octahedral with the hydroxylamine *trans* to CO. The average Ru-S, average Ru-P and Ru-C distances (2.433, 2.393, and 1.85(1) Å, respectively) are similar to those in 1. The Ru-N distance of 2.179(8) Å is slightly shorter than those in {[Ru(Me<sub>2</sub>dtc)(CO)- $(PPh_3)_2(\mu-S_4)(\mu-N_2H_4)$  (2.222(8) and 2.228(8) Å) [9]. The N-O distance of 1.45(1) Å is similar to that in  $[Re(CO)_3(PPh_3)_2(NH_2OH)](OTf)$  (1.422(5) Å) [18]. The Ru-N-O angle of 119.7(5)° is larger than the ideal tetrahedral value (109.5°). A similar bond angle has been found for  $[Re(CO)_3(PPh_3)_2(NH_2OH)](OTf)$  $(\text{Re-N-O angle} = 116.4(3)^{\circ})$  [18].

# 3.3. Heterobimetallic nitrido complexes with Ru dithiocarbamate

Complex 1 was also found to react with metal nitrides to give binuclear nitrido complexes. Thus, treatment of 1 with  $[N^nBu_4][OsO_3N]$  afforded the

Ru(II)NOs(VIII) complex [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>-(NOsO<sub>3</sub>)] (4). Like the reported MNOs(VIII) [M = Au(I), Pt(II), Ir(I)] complexes [5,6], the v(Os = O) for 4 (882 and 902 cm<sup>-1</sup>) are higher than those for [OsO<sub>3</sub>N]<sup>-</sup> (858 and 890 cm<sup>-1</sup>) [12], suggesting that the Os=O bonds are strengthened on formation of nitride bridge. The  $v_{as}(Os=N-Ru)$  was found at 1070 cm<sup>-1</sup>, which is higher than that for  $[OsO_3N]^-$  (1023 cm<sup>-1</sup>) [12]. The structure of **4** has been unambiguously established by X-ray crystallography. Fig. 3 shows a perspective view of the molecule; selected bond lengths and angles are listed in Table 4. The geometry around Ru is pseduo-octahedral with the [NOsO<sub>3</sub>] group *trans* to the carbonyl. The Os–N and average Os–O distances for **4** 



 $\label{eq:response} \begin{array}{l} \mbox{Reagents and conditions: (i) HOTf, CH_2Cl_2, 0^{\circ}C, (ii) L, CH_2Cl_2, RT, (iii) [^nBu_4N][OsO_3N] \\ \mbox{CH}_2Cl_2, RT (iv) [^nBu_4N][OsN(C_7H_6S_2)_2], CH_2Cl_2, RT (v) [ReN(Et_2dtc)_2], CH_2Cl_2, RT \\ \end{array}$ 

Scheme 1.



Fig. 2. Perspective view of [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(NH<sub>2</sub>OH)](OTf) (3).

Table 3 Selected bond lengths (Å) and angles (°) for *trans*-[Ru(CO(Et<sub>2</sub>dtc)-(PPh<sub>3</sub>)<sub>2</sub>)(NH<sub>2</sub>OH)](OTf) (**3**)

Ru(1)–S(1)	2.434(3)	Ru(1)–S(2)	2.431(3)
Ru(1) - P(1)	2.403(2)	Ru(1) - P(2)	2.382(2)
Ru(1)–N(1)	2.179(8)	Ru(1)-C(1)	1.85(1)
C(1)–O(1)	1.15(1)	N(1)–O(2)	1.45(1)
S(1)-Ru(1)-S(2)	72.21(9)	S(1)-Ru(1)-P(1)	90.72(8)
S(1)-Ru(1)-P(2)	163.68(9)	S(1)-Ru(1)-N(1)	85.3(2)
S(1)-Ru(1)-C(1)	90.5(3)	S(2)-Ru(1)-P(1)	162.82(9)
S(2)-Ru(1)-P(2)	91.48(9)	S(2)-Ru(1)-N(1)	80.6(2)
S(2)-Ru(1)-C(1)	91.9(3)	P(1)-Ru(1)-P(2)	105.56(9)
P(1)-Ru(1)-N(1)	96.4(2)	P(1)-Ru(1)-C(1)	90.1(3)
P(2)-Ru(1)-N(1)	91.8(2)	P(2)-Ru(1)-C(1)	90.5(3)
N(1)-Ru(1)-C(1)	172.3(4)	Ru(1)-N(1)-O(2)	119.7(5)
Ru(1)-C(1)-O(1)	176.0(10)		

(1.719(7) and 1.682 Å, respectively) are similar to those in [Au(PPh<sub>3</sub>)(NOsO<sub>3</sub>)] [5]. The Ru-N distance for 4 of 2.075(7) Å is comparable to that in 3 but considerably longer than those for typical µ-nitridoruthenium complexes, e.g.  $K_3[Ru_2NCl_8(H_2O)_2]$  (1.718(3) Å) [19],  $[Ru_2N(en)_5]Cl_5$  (en = 1,2-diaminoethane, 1.742(1) Å) [20],  $[Ru_2N(bpy)_2Cl_5(H_2O)]$ (bpy = 2, 2'-bipyridine,1.744(2) Å), and  $(H_5O_2)[Ru_2N(bpy)_2Cl_6]$  (1.734(4) Å) [21], which contain symmetric Ru=N=Ru bridges. The Ru-N-Os linkage in 4 is slightly bent with an angle of 155.1(4)°, which is larger than that for [Ru(OEP)- $(NO)(NOsO_3)$ ] (138.4(8)°) [7]. These structural data are indicative of the Os=N-Ru bonding mode, consisting of an Os=N triple bond and  $OsN \rightarrow Ru$  dative bond. This bonding picture is in agreement with IR data: the v(CO) for 4 (1970 cm<sup>-1</sup>) is higher than that for the amide complex  $[Ru(CO)(Et_2dtc)(PPh_3)_2(NTs)]$  (Ts = tosyl, 1936 cm<sup>-1</sup>) [10] but similar to those for 2 and 3.

Table 4

Selected bond lengths (Å) and angles (°) for  $[Ru(CO)(Et_2dtc)-(PPh_3)_2(NOsO_3)]$  (4)

Os(1)-O(2)	1.712(10)	Os(1)–O(3)	1.661(13)
Os(1)–O(4)	1.675(13)	Os(1)-N(1)	1.719(7)
Ru(1) - P(1)	2.383(2)	Ru(1) - P(2)	2.382(2)
Ru(1)-S(1)	2.433(3)	Ru(1)-S(2)	2.424(3)
Ru(1)-N(1)	2.075(7)	Ru(1)-C(1)	1.849(9)
O(1)–C(1)	1.135(12)		
O(2)–Os(1)–O(3)	112.1(6)	O(2)–Os(1)–O(4)	104.8(7)
O(3) - Os(1) - O(4)	112.3(8)	O(2)-Os(1)-N(1)	109.2(4)
O(3)-Os(1)-N(1)	109.3(5)	O(4) - Os(1) - N(1)	109.0(5)
P(1)-Ru(1)-P(2)	102.3(1)	P(1)-Ru(1)-S(1)	165.6(1)
P(2)-Ru(1)-S(1)	92.0(1)	P(1)-Ru(1)-S(2)	93.6(1)
P(2)-Ru(1)-S(2)	164.0(1)	S(1)-Ru(1)-S(2)	72.1(1)
P(1)-Ru(1)-N(1)	91.0(2)	P(2)-Ru(1)-N(1)	94.4(2)
S(1)-Ru(1)-N(1)	87.2(2)	S(2)-Ru(1)-N(1)	85.7(2)
P(1)-Ru(1)-C(1)	92.6(3)	P(2)-Ru(1)-C(1)	92.3(3)
S(1)-Ru(1)-C(1)	87.5(3)	S(2)-Ru(1)-C(1)	86.5(3)
N(1)-Ru(1)-C(1)	171.6(4)	Os(1)-N(1)-Ru(1)	155.1(4)
Ru(1)-C(1)-O(1)	171.2(9)		

Like  $[Au(PPh_3)(NOsO_3)]$  [5] and  $[Ru(NO)(OEP)-(NOsO_3)]$  [7], no reactions between **4** and alkenes such as styrene were observed.

Treatment of **1** with  $[N^nBu_4][OsN(C_7H_6S_2)_2]$  afforded the Ru(II)NOs(VI) complex  $[Ru(CO)(Et_2dtc)-(PPh_3)_2\{NOs(C_7H_6S_2)_2\}]$  **5**. The molecular structure of **5** is shown in Fig. 4; selected bond lengths and angles are listed in Table 5. The geometry around Os is distorted square pyramidal with Os situated at ca. 0.70 Å above the S<sub>4</sub> plane. The Os-to-S<sub>4</sub> plane displacement for **5** is similar to that for a related Os-Ir bimetallic complex  $[Ir(CO)(PPh_3)_2\{NOs(C_7H_6S_2)_2\}]$  (0.69 Å) [6]. The Os-N [1.680(6) Å] and average Os-S (2.305 Å) distances and average N-Os-S angle (107.6°) are simi-



Fig. 3. Perspective view of [Ru(CO)(Et<sub>2</sub>dtc)(PPh<sub>3</sub>)<sub>2</sub>(NOsO<sub>3</sub>)] (4). Phenyl rings of PPh<sub>3</sub> are omitted for clarity.



Fig. 4. Perspective view of  $[Ru(CO)(Et_2dtc)(PPh_3)_2\{NOs(C_7H_6S_2)_2\}]$  (5). Phenyl rings of PPh<sub>3</sub> are omitted for clarity.

lar to those for  $[OsN(C_6H_4S_2)_2]^-$  (1.65 and 2.323 Å and 107.2°, respectively) [13], suggesting that the Os=N triple bond in [OsN(C<sub>6</sub>H<sub>4</sub>S<sub>2</sub>)<sub>2</sub>]<sup>-</sup> is not significantly perturbed on coordination to Ru. The long Ru-N distance (2.068(6) Å) together with the approximately linear Os-N-Ru linkage (166.2(3)°) indicate that the interaction between Ru and nitride in 5 is also of donor acceptor type. Accordingly, the IR CO stretching mode occurs at a quite high energy (1974  $\text{cm}^{-1}$ ). The  $v_{as}$ (Os=N-Ru) was not assigned due to the presence of ligand bands in the 1000–1200 cm<sup>-1</sup> region. The cyclic voltammogram of 5 in CH<sub>2</sub>Cl<sub>2</sub> features a reversible couple  $(i_a/i_c \sim 1 \text{ and scan-rate independent})$  at ca. 0.38 V versus ferrocenium-ferrocene, which is tentatively assigned as the Os(VII)-Os(VI) couple. The Os(-VII)-Os(VI) potential for 5 is identical with that for  $[OsN(C_7H_6S_2)_2]^-$  [6], indicating that there is no electronic communication between Ru and Os in 5.

The dimetallic Ru(II)NRe(V) complex {Ru(CO)- $(Et_2dtc)(PPh_3)_2[NRe(Et_2dtc)_2]$  (OTf) (6) was prepared similarly from 1 and [ReN(Et<sub>2</sub>dtc)<sub>2</sub>]. Fig. 5 shows a perspective view of the cation  $\{Ru(CO)(Et_2dtc)\}$  $(PPh_3)_2[NRe(Et_2dtc)_2]$ <sup>+</sup>; selected bond lengths and angles are listed in Table 6. The geometry around Re is distorted square pyramidal with Re-to-S<sub>4</sub> plane displacement of 0.71 Å. The average Ru-P, Ru-S, Ru-C and Ru–N distances in 6 are similar to those for 5. The Re-N and average Re-S distances (1.670(3) and 2.381 Å) are comparable to those for  $[ReN(Et_2dtc)_2]$  (1.656(8) and 2.388 Å, respectively) [22]. The relatively long Ru–N bond (2.108(3) Å) and essentially linear Ru-N-Re linkage (170.9(2)°) is indicative of the formulation of ReN $\rightarrow$ Ru. Accordingly, a high IR CO stretching frequency (1970 cm<sup>-1</sup>) was observed for **6**. In summary, we have isolated a series of binuclear

nitrido complexes containing the  $[Ru(CO)(Et_2dtc)-(PPh_3)_2]$  moiety. The crystal structures for these  $\mu$ -nitrido-Ru(II) complexes suggest asymmetric bridging mode of nitride, i.e.  $M \equiv N \rightarrow Ru$ . On the basis of the IR CO stretching frequencies, there is no evidence for nitride-to-Ru  $\pi$  interaction in these complexes. The donor strength of the bridging nitride ligand in this binuclear complex was found to be similar to that for hydrazine or hydroxylamine. The Ru–N–M linkage in these complexes are roughly linear (Ru–N–M angle ranging from 155.1(4) to 170.9(2)°). The slight bending of Ru–N–M may be due to steric reasons and/or electron factors, which have yet to be explored.

Table 5 Selected bond	lengths and	angles for	$(\mathbf{P}_{\mathbf{u}}(\mathbf{CO})(\mathbf{Et} dt_{\mathbf{c}}))$
$(PPh_3)_2[NOs(C_7H_6S)]$	$S_{2}_{2}_{2}]$ (5)	angles 101	
Os(1)-N(1)	1.680(6)	Os(1)–S(4)	2.303(2)
Os(1)–S(3)	2.304(3)	Os(1)–S(2)	2.306(2)
Os(1)–S(1)	2.307(3)	Ru(1)-C(1)	1.855(8)
Ru(1)-N(1)	2.068(6)	Ru(1) - P(1)	2.381(2)
Ru(1) - P(2)	2.383(2)	Ru(1)-S(5)	2.427(2)
Ru(1)-S(6)	2.430(2)	C(1)–O(1)	1.131(8)
N(1)-Os(1)-S(4)	107.1(2)	N(1)-Os(1)-S(3)	108.2(2)
S(4)–Os(1)–S(3)	85.74(11)	N(1)-Os(1)-S(2)	109.1(2)
S(4)–Os(1)–S(2)	143.71(9)	S(3)–Os(1)–S(2)	83.35(11)
N(1)–Os(1)–S(1)	105.9(2)	S(4) - Os(1) - S(1)	84.30(10)
S(3) - Os(1) - S(1)	145.96(9)	S(2) - Os(1) - S(1)	85.69(11)
C(1)-Ru(1)-N(1)	169.2(3)	C(1)-Ru(1)-P(1)	91.0(2)
N(1)-Ru(1)-P(1)	92.19(16)	C(1)-Ru(1)-P(2)	93.9(2)
N(1)-Ru(1)-P(2)	95.62(16)	P(1)-Ru(1)-P(2)	100.34(7)
C(1)-Ru(1)-S(5)	84.1(2)	N(1)-Ru(1)-S(5)	85.43(16)
P(1)-Ru(1)-S(5)	94.37(8)	P(2)-Ru(1)-S(5)	165.20(8)
C(1)-Ru(1)-S(6)	87.5(2)	N(1)-Ru(1)-S(6)	86.86(16)
P(1)-Ru(1)-S(6)	166.13(8)	P(2)-Ru(1)-S(6)	93.53(8)
S(5)-Ru(1)-S(6)	71.77(8)	O(1)-C(1)-Ru(1)	171.9(7)
Os(1)–N(1)–Ru(1)	166.2(3)		



Fig. 5. Perspective view of the cation  $[Ru(CO)(Et_2dtc)(PPh_3)_2\{NRe(Et_2dtc)_2\}]^+$ . Phenyl rings of PPh<sub>3</sub> are omitted for clarity. C(92) and C(94) are hidden by the toluenedithiolate ligands.

Table 6 Selected bond lengths (Å) and angles (°) for  $\{Ru(CO)(Et_2dtc)-(PPh_3)_2[NRe(Et_2dtc)_2]\}(OTf)$  (6)

Re–S(1)	2.378(1)	Re–S(2)	2.385(1)
Re-S(3)	2.383(1)	Re-S(4)	2.378(1)
Re-N(4)	1.670(3)	Ru-S(5)	2.431(1)
Ru–S(6)	2.418(1)	Ru-P(1)	2.394(1)
Ru-C(1)	1.852(4)	Ru-N(4)	2.108(3)
O(1)–C(1)	1.145(1)		
S(1)-Re-S(2)	73.4(1)	S(1)-Re-S(3)	96.0(1)
S(2)-Re-S(3)	145.4(1)	S(1)-Re- $S(4)$	145.8(1)
S(2)-Re-S(4)	97.1(1)	S(3)-Re-S(4)	73.0(1)
S(1)-Re-N(4)	106.7(1)	S(2)-Re-N(4)	107.3(1)
S(3)-Re-N(4)	107.3(1)	S(4)-Re-N(4)	107.4(1)
S(5)–Ru–S(6)	72.1(1)	S(5)-Ru-P(1)	159.2(1)
S(6) - Ru - P(1)	87.3(1)	S(5)-Ru-P(2)	92.5(1)
S(5)-Ru-N(4)	88.0(1)	P(1)-Ru-P(2)	108.2(1)
P(1)-Ru-N(4)	93.6(1)	S(6)-Ru-N(4)	88.5(2)
S(5)-Ru-C(1)	89.2(1)	P(2)-Ru-N(4)	87.0(1)
P(1)-Ru-C(1)	89.4(1)	S(6)-Ru-C(1)	91.6(1)
N(4)-Ru-C(1)	177.1(1)	P(2)-Ru-C(1)	92.2(1)
Re-N(4)-Ru	170.9(2)	Ru-C(1)-O(1)	178.1(3)

#### 4. Supplementary material

Supplementary materials containing listings of atomic coordinate and thermal parameters, final atomic coordinates, and bond distances and angles are available from the authors (Ian D. Williams (chwill@ust.hk) for 1 and 4-6, and Wing-Tak Wong (wtwong@hku.hk) for 3) on request.

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