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# Transition metal complexes with sulfur ligands. Part CXXVII [1]. Azido, halido and nitrido ruthenium complexes with sulfur-rich coordination spheres [2]

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**Abstract**

Ru(II) and Ru(III) azido complexes were synthesized as potential precursors for dinitrogen complexes with sulfur-dominated coordination spheres. $NEt_4[Ru(N_3)(PCy_3)('S_4')]$ (**1**) was obtained from the reaction of $[Ru(DMSO)(PCy_3)('S_4')]$ with $NEt_4N_3$ ('$S_4$'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2−)). The oxidation of $[Ru(DMSO)(PR_3)('S_4')]$ with $I_2$ yielded $[Ru(I)(PR_3)('S_4')]$ (R = Cy **2a**, $^i$Pr **2b**). The iodo ligand in **2a** and **2b** could be exchanged for azide and chloride yielding $[Ru(N_3)(PR_3)('S_4')]$ (R = Cy **3a**, $^i$Pr **3b**) and $[Ru(Cl)(PCy_3)('S_4')]$ (**4**). The azido ligand of **1** could not be transformed into a $N_2$ ligand, and the reaction of **3a** with $HBF_4$ yielded the nitrido complex $[\mu\text{-}N\{Ru(PCy_3)('S_4')\}_2](PF_6)$ ($[\mathbf{5}]PF_6$) via a labile intermediate exhibiting an IR band at 2070 $cm^{-1}$ at −40°C. The molecular structures of **2a**, **4** and $[\mathbf{5}]^+$ as the $BPh_4^-$ salt were determined by X-ray structure analysis. Crystal data of (a) **2a**·$C_7H_8$: triclinic space group $P\bar{1}$; $a$ = 1087.4(1), $b$ = 1089.5(1), $c$ = 1988.8(1) pm; $\alpha$ = 74.13(1), $\beta$ = 78.66(1), $\gamma$ = 61.22(1)°; $Z$ = 2; (b) **4**·$CH_2Cl_2$: triclinic space group $P\bar{1}$; $a$ = 1088.7(5), $b$ = 1065.6(3), $c$ = 1778.4(6) pm; $\alpha$ = 80.66(2), $\beta$ = 72.10(4), $\gamma$ = 67.52(3)°; $Z$ = 2; (c) $[\mathbf{5}]BPh_4$·3THF: orthorhombic space group $Pna2_1$; $a$ = 1972.9(6), $b$ = 2606.3(6), $c$ = 1831.1(12) pm; $Z$ = 4. The metal centers of all three complexes show pseudo-octahedral coordination and exhibit no anomalies in distances and angles. The two Ru centers in $[\mathbf{5}](BPh_4)$·3THF are linked via a bent nitrido bridge. © 1998 Elsevier Science S.A.

*Keywords:* Ruthenium complexes; Halido complexes; Sulfur complexes; Azido complexes; Nitrido complexes

## 1. Introduction

Transition metal azido complexes exhibit a versatile chemistry which is due to the inherent instability of the azido ion [2]. Azido complexes can serve as precursors in the synthesis of isocyanato, isothiocyanato [3], nitrene [4], nitrido [5], cyano [6], phosphorane-iminato [7], nitrosyl [8], or isotetrazene complexes [9]. A rich chemistry has also been developed, in particular by Beck's group, using azido complexes for the synthesis of five membered heterocyclic ligands via 1,3 dipolar addition reactions [10]. Our interest in azido complexes results from thermal, photolytic, or protolytic decomposition reactions of azido complexes that in a few cases have yielded dinitrogen complexes [11]. One of the very first examples was $[Ru(NH_3)_5(N_2)]^{2+}$ that forms according to Eq. (1) [11a].

$$[Ru(N_3)(NH_3)_5]^{2+} \xrightarrow{\Delta T} [Ru(N_2)(NH_3)_5]^{2+} + 0.5N_2 \quad (1)$$

It is noted that in this reaction a Ru(III) center is reduced to Ru(II) by the electron which is formally released according to $N_3^- \rightarrow 1.5N_2 + e^-$. We have tried to use azido complexes as precursors for dinitrogen complexes with sulfur-rich coordination spheres, which are of interest as functional model compounds for nitrogenases [12]. In the course of these investigations we have synthesized Ru(II) and Ru(III) complexes of the type $[Ru(L)(PR_3)('S_4')]$ (L = halide, azide, R = Cy, $^i$Pr, '$S_4$'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2−)):

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[1] For Part CXXVI see Ref. [1].

[2] Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday.


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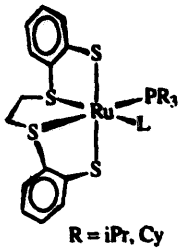



R = iPr, Cy

Attempts to obtain dinitrogen complexes remained unsuccessful, although protonation and subsequent decomposition of [Ru($N_3$)($PCy_3$)('$S_4$')] (**3a**) gave the $\mu$-nitrido complex [$\mu$-N{Ru($PCy_3$)('$S_4$')}$_2$]($PF_6$) ([**5**]$PF_6$). Starting compounds have been the [Ru(DMSO)($PR_3$)('$S_4$')] complexes (R = $^i$Pr, Cy) that contain labile DMSO ligands [13].

## 2. Experimental

### 2.1. General

Unless noted otherwise, all reactions and operations were carried out at room temperature under nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded on the following instruments. IR: Perkin-Elmer 983, 1620 FT IR, and 16PC FT-IR. Spectra of solids were recorded in KBr discs. Spectra of solutions were recorded in $CaF_2$ cuvettes. Low temperature measurements were carried out with $CaF_2$ cuvettes whose windows were heated. Solvent bands were compensated. NMR: Jeol FT-JNM-GX 270, EX 270, and Lambda LA 400 spectrometers with the protio-solvent signal used as a reference. Chemical shifts are quoted on the $\delta$ scale (downfield shifts are positive) related to tetramethylsilane ($^1$H, $^{13}$C{$^1$H} NMR) or 85% $H_3PO_4$ ($^{31}$P{$^1$H} NMR). Electron paramagnetic resonance (EPR): Bruker ESP 300 (diphenylpikrylhydrazyl as external standard ($\langle g \rangle = 2.0036$) [14]). Magnetic moments of solids were determined on a Johnson Matthey magnetic susceptibility balance at room temperature. Mass spectra: Varian MAT 212 and Jeol MSTATION 700 spectrometers. UV–Vis: Shimadzu UV-3101 PC. Elemental analysis: Carlo Erba EA 1106 or 1108 analyzer. Cyclic voltammetry was performed with a PAR 264A potentiostat using a three electrode cell with glassy carbon ROTEL A working, Ag/AgCl reference and Pt counter electrodes. Solutions were $10^{-3}$ M in substance. TBA[$PF_6$] ($10^{-1}$ M) was used as conducting electrolyte. Potentials were referenced to normal hydrogen electrode via $Fc/Fc^+$ as internal standard ($E_{Fc/Fc+} = +0.4$ V versus normal hydrogen electrode [15]).

[Ru(DMSO)($PCy_3$)('$S_4$')] [13], [Ru(DMSO)($P^iPr_3$)('$S_4$')] [13], and $NEt_4N_3$ [16] were prepared as described in the literature. $HBF_4$ (54% in $Et_2O$) was purchased from Merck-Schuchardt.

### 2.2. Syntheses

#### 2.2.1. $NEt_4$[Ru($N_3$)($PCy_3$)('$S_4$')] (1)

$NEt_4N_3$ (310 mg, 1.80 mmol) was added to a yellow–green suspension of [Ru(DMSO)($PCy_3$)('$S_4$')] (478 mg, 0.62 mmol) in acetone (25 ml). Under exclusion of light, the suspension was stirred for 2.5 days during which time a bright yellow solid precipitated. It was separated, washed with acetone (35 ml), THF (10 ml), and $Et_2O$ (15 ml), and dried in vacuo. The yellow solid was redissolved in $CH_2Cl_2$ (8 ml), filtered, and $Et_2O$ (30 ml) was added dropwise to the yellow filtrate. The resulting yellow precipitate was separated, washed with $Et_2O$ (20 ml) and dried in vacuo. Yield: 320 mg (56%). *Anal.* Calc. for **1**·0.75$CH_2Cl_2$, $C_{40.75}H_{66.5}Cl_{1.5}N_4PRuS_4$ (925.99): C, 52.86; H, 7.24; N, 6.05; S, 13.85. Found: C, 52.87; H, 7.39; N, 5.90; S, 13.64%. IR (KBr): $\tilde{\nu} = 2028$ cm$^{-1}$ ($N_3$). $^1$H NMR (269.6 MHz, $CD_3CN$): $\delta = 7.50$–$7.35$ (m, 3H, $C_6H_4$), 7.30 (d, 1H, $C_6H_4$), 6.95–6.70 (m, 4H, $C_6H_4$), 3.15 (q, 8H, $NCH_2$), 2.95 (d, 1H, $CH_2$), 2.65 (d, 1H, $CH_2$), 2.30–0.85 (m, 47H, $CH_2$, $CH_3$, $C_6H_{11}$). $^{31}$P{$^1$H} NMR (109.38 MHz, $CD_2Cl_2$): $\delta = +32.26$ (s).

#### 2.2.2. [Ru(I)($PCy_3$)('$S_4$')] (2a)

Elemental $I_2$ (127 mg, 0.5 mmol) was added to a stirred suspension of [Ru(DMSO)($PCy_3$)('$S_4$')] (752 mg, 0.98 mmol) in THF (15 ml). In the course of 5 min a clear red solution resulted from which dark red microcrystals crystallized. The solution was cooled to −78°C for 2 h to complete crystallization. The precipitated crystals were separated, washed with $Et_2O$ (30 ml) and dried in vacuo. Yield: 540 mg (62%). *Anal.* Calc for **2a**·0.5 THF, $C_{34}H_{49}IO_{0.5}PRuS_4$ (852.97): C, 47.88; H, 5.79; S, 15.04. Found: C, 47.61; H, 5.61; S, 14.72%. EPR ($CH_2Cl_2$, 120 K): $\langle g \rangle = 2.1275$. FD-MS ($^{102}$Ru, $CH_2Cl_2$); *m/z*: 817 [Ru(I)($PCy_3$)('$S_4$')]$^+$. $\mu_{eff} = 1.84$ $\mu_B$ (298°C).

#### 2.2.3. [Ru(I)($P^iPr_3$)('$S_4$')] (2b)

A green–yellow suspension of [Ru(DMSO)($P^iPr_3$)('$S_4$')] (229 mg, 0.35 mmol) in THF (10 ml) was combined with elemental $I_2$ (44 mg, 0.17 mmol) and stirred for 5 h. The resulting red solution was heated to reflux for 5 min, cooled to room temperature, filtered, and MeOH (25 ml) was added dropwise to the filtrate. Dark red microcrystals precipitated that were separated after 2 h, washed with MeOH (30 ml) and $Et_2O$ (10 ml) and dried in vacuo. Yield: 115 mg (47%). *Anal.* Calc. for $C_{23}H_{33}IPRuS_4$ (696.72): C, 39.65; H, 4.77; S, 18.41. Found: C, 39.85; H, 4.71; S, 18.42%. EPR ($CH_2Cl_2$, 6.8 K): $\langle g \rangle = 2.1249$. FD-MS ($^{102}$Ru, $CH_2Cl_2$); *m/z*: 697 [Ru(I)($P^iPr_3$)('$S_4$')]$^+$.

#### 2.2.4. [Ru($N_3$)($PCy_3$)('$S_4$')] (3a)

[Ru(I)($PCy_3$)('$S_4$')] (**2a**) was prepared in situ from elemental $I_2$ (105 mg, 0.41 mmol) and [Ru(DMSO)($PCy_3$)('$S_4$')] (626 mg, 0.81 mmol) in THF (20 ml) according to the procedure given above. A red suspension resulted to which $NEt_4N_3$ (418 mg, 2.43 mmol) was added. In the

course of 12 h the suspension changed its color to yellow–green. MeOH (35 ml) was added, the yellow–green precipitate separated, washed with MeOH (60 ml), acetone (40 ml), and $Et_2O$ (15 ml) and dried in vacuo. Yield: 350 mg (60%). *Anal.* Calc. for $C_{32}H_{45}N_3PRuS_4$ (732.04): C, 52.50; H, 6.20; N, 5.74; S, 17.52. Found: C, 52.64; H, 6.43; N, 5.56; S, 17.23%. IR (KBr): $\tilde{\nu} = 2019\ cm^{-1}$ ($N_3$).

### 2.2.5. *[Ru(N$_3$)(P$^i$Pr$_3$)('S$_4$')] (3b)*

[Ru(I)(P$^i$Pr$_3$)('S$_4$')] (**2b**) was prepared in situ from elemental $I_2$ (61 mg, 0.24 mmol) and [Ru(DMSO)-(P$^i$Pr$_3$)('S$_4$')] (313 mg, 0.48 mmol) in THF (10 ml) according to the procedure given above. A red solution of **2b** resulted, because **2b** is more soluble than **2a**. $NEt_4N_3$ (250 mg, 1.44 mmol) was added and the mixture was stirred for 24 h resulting in a yellow–brown suspension. It was filtered, the filtrate was reduced in volume to 2 ml and $Et_2O$ (50 ml) was added. The resultant brown precipitate was separated, washed with $Et_2O$ (30 ml) and dried in vacuo. Yield: 95 mg (33%). Despite repeated recrystallization, **2b** could not be obtained in analytically pure form. *Anal.* Calc. for $C_{23}H_{33}N_3PRuS_4$ (611.84): C, 45.15; H, 5.44; N, 6.87; S, 20.96. Found: C, 44.65; H, 5.54; N, 5.03; S, 21.38%. IR (KBr): $\tilde{\nu} = 2014\ cm^{-1}$ ($N_3$). FD-MS ($^{102}$Ru, $CH_2Cl_2$); *m/z*: 542 [Ru(P$^i$Pr$_3$)('S$_2$')$_2$]$^+$.

### 2.2.6. *[Ru(Cl)(PCy$_3$)('S$_4$')] (4)*

[Ru(I)(PCy$_3$)('S$_4$')] (**2a**) (119 mg, 0.14 mmol) and $NEt_4Cl$ (100 mg, 0.6 mmol) were combined in THF (15 ml) and stirred for 48 h. The resultant green suspension was filtered and MeOH (30 ml) was added to the filtrate. Yellow–green microcrystals precipitated which were separated after 2 h, washed with MeOH (20 ml) and $Et_2O$ (20 ml) and dried in vacuo. Yield: 80 mg (79%). *Anal.* Calc. for **4**·MeOH, $C_{33}H_{49}ClOPRuS_4$ (757.51): C, 52.32; H, 6.52; S, 16.93. Found: C, 52.38; H, 6.40; S, 17.30%. FD-MS ($^{102}$Ru, $CH_2Cl_2$); *m/z*: 725 [Ru(Cl)(PCy$_3$)('S$_4$')]$^+$.

### 2.2.7. *[μ-N{Ru(PCy$_3$)('S$_4$')}$_2$](PF$_6$) ([5]PF$_6$)*

Addition of $HBF_4 \cdot Et_2O$ (0.033 ml, 0.24 mmol) to a stirred yellow–green suspension of [Ru(N$_3$)(PCy$_3$)('S$_4$')] (**3a**) (179 mg, 0.24 mmol) in $CH_2Cl_2$ (10 ml) at −78°C instantaneously resulted in the formation of a clear red–violet solution. The solution was warmed to room temperature, stirred for 2 h and evaporated to dryness. The resultant brown residue was dissolved in MeOH (10 ml), insoluble material was removed by filtration and a solution of $NBu_4PF_6$ (95 mg, 0.25 mmol) in MeOH (3 ml) was added to the red filtrate. Violet microcrystals precipitated, which were separated after 2 h, washed with MeOH (5 ml) and $Et_2O$ (4 ml) and dried in vacuo. Yield: 50 mg (25%). *Anal.* Calc. for [5]$PF_6 \cdot Et_2O$, $C_{68}H_{100}F_6NOP_3Ru_2S_8$ (1613.13): C, 50.63; H, 6.25; N, 0.87; S, 15.90. Found: C, 50.38; H, 5.94; N, 0.64; S, 16.11%. IR (KBr): $\tilde{\nu} = 842\ cm^{-1}$ ($PF_6$). $^1$H NMR (269.6 MHz, $CD_2Cl_2$): δ = 7.6 (d, 2H, $C_6H_4$), 7.35 (d, 2H, $C_6H_4$), 7.25–6.6 (m, 12H, $C_6H_4$), 3.75–0.5 (m, 74H, $C_2H_4$, $C_6H_{11}$). $^{13}$C{$^1$H} NMR (67.9 MHz, $CD_2Cl_2$): δ = 156.94, 154.11 (d), 132.36, 130.77, 130.51, 130.39, 130.23, 129.74, 127.96, 124.47, 123.81 [C(aryl)], 42.24 (d), 41.09 ($C_2H_4$), 31.62–31.20, 29.02–28.35, 27.00–26.62 (br, $C_6H_{11}$). $^{31}$P{$^1$H} NMR (109.38 MHz, $CD_2Cl_2$): δ = +29 (s, $PCy_3$), −150 (m, $PF_6$). UV–Vis [$CH_2Cl_2$, (nm)]: 546 (=4094 l mol$^{-1}$).

### 2.3. *X-ray structure determination of [Ru(I)(PCy$_3$)('S$_4$')]·C$_7$H$_8$ (2a·C$_7$H$_8$), [Ru(Cl)(PCy$_3$)('S$_4$')]·CH$_2$Cl$_2$ (4·CH$_2$Cl$_2$) and [μ-N{Ru(PCy$_3$)('S$_4$')}$_2$](BPh$_4$)·3THF ([5]BPh$_4$·3THF)*

Black plates of [Ru(I)(PCy$_3$)('S$_4$')]·$C_7H_8$ (**2a**·$C_7H_8$) were obtained from a saturated solution of **2a** in toluene that was kept at room temperature for 10 days. Green columns of [Ru(Cl)(PCy$_3$)('S$_4$')]·$CH_2Cl_2$ (**4**·$CH_2Cl_2$) were obtained by layering a solution of **4** in $CH_2Cl_2$ with n-hexane. Black columns of [μ-N{Ru(PCy$_3$)('S$_4$')}$_2$](BPh$_4$)·3THF ([5]BPh$_4$·3THF) formed by diffusion of a saturated solution of $NaBPh_4$ in MeOH through a glass frit (porosity G4) into a solution of [5]$PF_6$ in THF. Suitable crystals were sealed in glass capillaries. The structures were solved by direct methods (SHELXTL 5.03 [17]). Non-hydrogen atoms were refined anisotropically (SHELXTL 5.03) with the exception of one THF molecule in [5]BPh$_4$·3THF whose atoms were refined with a common isotropic temperature factor. The positions of the hydrogen atoms in **2a**·$C_7H_8$, **4**·$CH_2Cl_2$ and [5]BPh$_4$·3THF were taken from difference Fourier syntheses except for the solvent molecule hydrogen atoms which were calculated in their ideal geometries. Hydrogen atoms of **2a**·$C_7H_8$ were refined isotropically while those of **4**·$CH_2Cl_2$ and [5]BPh$_4$·3THF were kept restricted with a common isotropic temperature factor during the refinement. Selected crystallographic data for **2a**·$C_7H_8$, **4**·$CH_2Cl_2$ and [5]BPh$_4$·3THF are summarized in Table 1, the fractional atomic coordinates and isotropic parameters are listed in Tables 2–5.

## 3. Results

### 3.1. *Syntheses and reactivity*

The reaction according to Eq. (2) yielded the Ru(II) azido complex $NEt_4$[Ru(N$_3$)(PCy$_3$)('S$_4$')] (**1**).

$$\mathrm{Ru(DMSO)(PCy_3)('S_4')] + NEt_4N_3 \xrightarrow[-\,DMSO]{\text{acetone, 20°C}} NEt_4[Ru(N_3)(PCy_3)('S_4')] \quad (2)$$

**1**

Complex **1** proved to be inert toward dioxygen and $H_2O_2$. Photolysis of **1** by UV irradiation or treating **1** with Brönsted acids such as $HBF_4$ yielded products which did not contain nitrogen nor could be identified. Treatment of **1** with $NOBF_4$ or $NO_2BF_4$ resulted in mixtures of products showing several

Table 1
Selected crystallographic data for $2a \cdot C_7H_8$, $4 \cdot CH_2Cl_2$, and $[5]BPh_4 \cdot 3THF$

| | $2a \cdot C_7H_8$ | $4 \cdot CH_2Cl_2$ | $[5]BPh_4 \cdot 3THF$ |
|---|---|---|---|
| Formula | $C_{39}H_{53}IPRuS_4$ | $C_{33}H_{47}Cl_3PRuS_4$ | $C_{100}H_{134}BNO_3P_2Ru_2S_8$ |
| FW | 908.99 | 810.34 | 1929.45 |
| Crystal dimensions (mm) | 0.60×0.30×0.15 | 0.40×0.40×0.20 | 0.50×0.40×0.40 |
| $F(000)$ | 926 | 838 | 4064 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $Pna2_1$ |
| Crystal system | triclinic | triclinic | orthorhombic |
| $a$ (pm) | 1087.4(1) | 1088.7(5) | 1972.9(6) |
| $b$ (pm) | 1089.5(1) | 1065.6(3) | 2606.3(6) |
| $c$ (pm) | 1988.8(1) | 1778.4(6) | 1831.1(12) |
| $\alpha$ (°) | 74.13(1) | 80.66(2) | 90 |
| $\beta$ (°) | 78.66(1) | 72.10(4) | 90 |
| $\gamma$ (°) | 61.22(1) | 67.52(3) | 90 |
| $V$ (nm$^3$) | 1.9805(3) | 1.812(1) | 9.415(7) |
| $Z$ | 2 | 2 | 4 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.524 | 1.485 | 1.361 |
| $\mu$ (mm$^{-1}$) | 1.453 | 0.952 | 0.583 |
| Diffractometer | Siemens P4 | Siemens P4 | Siemens P4 |
| Radiation (pm) | Mo K$\alpha$ ($\lambda$=71.073) | | |
| Temperature (K) | 200 | 200 | 153 |
| Scan technique | $\omega$-scan | $\omega$-scan | $\omega$-scan |
| $2\theta$ range (°) | 4–54 | 4–54 | 4–54 |
| Scan speed (° min$^{-1}$) | 3.0–30.0 | 3.0–30.0 | 3.0–30.0 |
| Measured reflections | 9978 | 10106 | 12941 |
| Independent reflections | 8590 | 7881 | 12922 |
| Observed reflections | 5468 | 4012 | 7947 |
| $\sigma$ criterion | $F_o > 4\sigma(F_o)$ | $F_o > 4\sigma(F_o)$ | $F_o > 4\sigma(F_o)$ |
| $R_1$; $wR_2$ (%) | 5.68; 15.22 | 8.41; 25.66 | 4.06; 9.22 |
| Refined parameters | 596 | 380 | 1023 |
| $S$ | 0.901 | 0.894 | 0.811 |

Table 2
Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters (pm$^2 \times 10^{-1}$) of the non-hydrogen atoms of $2a \cdot C_7H_8$

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| I1 | 2657(1) | 5192(1) | 3149(1) | 40(1) |
| Ru1 | 728(1) | 7693(1) | 3527(1) | 30(1) |
| S1 | 2152(2) | 8324(2) | 3905(1) | 37(1) |
| S2 | 823(2) | 6175(2) | 4646(1) | 36(1) |
| S3 | −1160(2) | 9547(2) | 4002(1) | 35(1) |
| S4 | −1011(2) | 7082(2) | 3345(1) | 36(1) |
| P1 | 782(2) | 9084(2) | 2359(1) | 32(1) |
| C10 | 2744(7) | 7104(6) | 4701(3) | 34(1) |
| C11 | 3824(8) | 7048(6) | 5000(3) | 38(2) |
| C12 | 4312(9) | 6098(7) | 5617(3) | 44(2) |
| C13 | 3698(8) | 5216(7) | 5961(3) | 47(2) |
| C14 | 2630(8) | 5250(7) | 5674(3) | 43(2) |
| C15 | 2139(7) | 6205(6) | 5038(3) | 36(1) |
| C16 | −793(8) | 7242(7) | 5137(3) | 40(2) |
| C20 | −2629(7) | 8527(6) | 3516(3) | 36(1) |
| C21 | −3882(8) | 8639(7) | 3358(4) | 44(2) |
| C22 | −5165(9) | 9774(8) | 3493(4) | 52(2) |
| C23 | −5226(9) | 10829(9) | 3777(5) | 56(2) |
| C24 | −3995(9) | 10735(8) | 3936(4) | 48(2) |
| C25 | −2719(7) | 9590(6) | 3815(3) | 36(1) |
| C26 | −1145(9) | 8812(7) | 4952(3) | 43(2) |
| C30 | −339(7) | 8990(7) | 1793(3) | 37(1) |
| C31 | 287(8) | 7521(7) | 1601(3) | 40(2) |

(*continued*)

Table 2 (*continued*)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| C32 | −780(9) | 7375(8) | 1279(3) | 48(2) |
| C33 | −1287(10) | 8525(9) | 618(4) | 53(2) |
| C34 | −1893(10) | 10008(9) | 788(4) | 55(2) |
| C35 | −822(9) | 10150(8) | 1119(4) | 49(2) |
| C40 | 2569(7) | 8436(6) | 1877(3) | 34(1) |
| C41 | 3825(7) | 7985(7) | 2291(3) | 38(2) |
| C42 | 5191(8) | 7261(8) | 1871(4) | 45(2) |
| C43 | 5331(9) | 8185(10) | 1172(4) | 57(2) |
| C44 | 4084(9) | 8721(11) | 757(4) | 57(2) |
| C45 | 2691(8) | 9445(8) | 1179(3) | 46(2) |
| C50 | 130(7) | 11048(6) | 2243(3) | 36(1) |
| C51 | −1429(9) | 11870(8) | 2461(5) | 48(2) |
| C52 | −1926(10) | 13485(7) | 2257(5) | 58(2) |
| C53 | −1057(11) | 13889(8) | 2584(5) | 65(3) |
| C54 | 497(11) | 13067(8) | 2403(5) | 61(2) |
| C55 | 998(9) | 11439(7) | 2593(4) | 45(2) |
| C60 | 6159(22) | 6180(29) | −947(15) | 197(14) |
| C61 | 6338(28) | 4990(33) | −646(22) | 274(22) |
| C62 | 7451(30) | 4440(23) | −21(16) | 219(17) |
| C63 | 7958(25) | 5303(29) | 27(11) | 174(10) |
| C64 | 7481(29) | 6601(27) | −488(13) | 168(10) |
| C65 | 6609(26) | 6943(28) | −944(12) | 170(9) |
| C66 | 5116(21) | 6900(31) | −1590(11) | 294(21) |

[a] Equivalent isotropic $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensors.

Table 3
Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($pm^2 \times 10^{-1}$) of the non-hydrogen atoms of $4 \cdot CH_2Cl_2$

| Atom | x | y | z | $U_{eq}$ [a] |
|---|---|---|---|---|
| Ru1 | 3321.9(9) | 2956.1(7) | 6581.4(4) | 13.4(3) |
| Cl1 | 1753(3) | 5179(2) | 7004(1) | 23.5(9) |
| S1 | 1894(3) | 2271(2) | 6159(1) | 18.1(9) |
| S2 | 3774(3) | 4085(2) | 5317(1) | 17.6(9) |
| S3 | 5104(3) | 1011(2) | 6031(1) | 16.2(9) |
| S4 | 5127(3) | 3548(2) | 6776(1) | 18.3(9) |
| C15 | 2630(10) | 3870(9) | 4856(5) | 18(4) |
| C14 | 2570(10) | 4500(10) | 4111(6) | 24(4) |
| C13 | 162(10) | 4440(10) | 3768(6) | 30(4) |
| C12 | 700(10) | 3769(10) | 4174(6) | 26(4) |
| C11 | 790(10) | 3128(9) | 4915(6) | 18(4) |
| C10 | 1790(10) | 3172(9) | 5250(5) | 18(4) |
| C25 | 6650(10) | 992(9) | 6210(5) | 18(4) |
| C24 | 7820(10) | −150(10) | 6029(7) | 31(4) |
| C23 | 9030(10) | −220(10) | 6158(8) | 37(5) |
| C22 | 9020(10) | 890(10) | 6502(8) | 34(5) |
| C21 | 7810(10) | 2020(10) | 6695(6) | 26(4) |
| C20 | 6570(10) | 2087(9) | 6560(6) | 20(4) |
| C16 | 5450(10) | 2899(10) | 4778(6) | 26(4) |
| C26 | 5480(10) | 1457(9) | 4967(6) | 20(4) |
| P1 | 2719(3) | 1991(2) | 7908(1) | 14.7(9) |
| C30 | 3579(10) | 2393(9) | 8561(5) | 17(3) |
| C31 | 3070(10) | 3897(10) | 8683(6) | 21(4) |
| C32 | 4010(10) | 4220(10) | 9079(6) | 28(4) |
| C33 | 4010(10) | 3420(10) | 9863(6) | 27(4) |
| C34 | 4450(10) | 1900(10) | 9774(6) | 30(5) |
| C35 | 3500(10) | 1610(10) | 9369(6) | 26(4) |
| C40 | 810(10) | 2660(10) | 8458(5) | 20(4) |
| C41 | −190(10) | 3070(10) | 7963(6) | 28(4) |
| C42 | −1680(10) | 3870(10) | 8434(7) | 37(5) |
| C43 | −2130(10) | 3020(20) | 9172(8) | 46(6) |
| C44 | −1130(10) | 2550(20) | 9662(7) | 47(6) |
| C45 | 370(10) | 1750(10) | 9179(7) | 35(5) |
| C50 | 3210(10) | 100(10) | 8029(5) | 25(4) |
| C51 | 4770(10) | −680(10) | 7884(6) | 27(4) |
| C52 | 5080(20) | −2220(10) | 8044(7) | 44(5) |
| C53 | 4450(10) | −2750(10) | 7543(7) | 40(5) |
| C54 | 2980(10) | −2000(10) | 7692(7) | 37(5) |
| C55 | 2630(10) | −450(10) | 7530(6) | 31(5) |
| C1 | 1190(40) | 2250(20) | 1880(10) | 240(20) |
| Cl2 | 296(6) | 3271(6) | 1084(3) | 100(3) |
| Cl3 | 1630(10) | 571(6) | 1502(4) | 208(6) |

[a] Equivalent isotropic $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensors.

$\nu$(NO) bands in the IR spectrum. One of these bands (1840 $cm^{-1}$) indicated the formation of the [Ru(NO)-($PCy_3$)('$S_4$')]$^+$ cation that was subsequently obtained by an independent route from [Ru(DMSO)($PCy_3$)('$S_4$')] and $NOBF_4$ [18]. Oxidation of **1** by equimolar amounts of elemental iodine gave a mixture of the Ru(III) complexes [Ru(I)($PCy_3$)('$S_4$')] (**2a**) and [Ru($N_3$)($PCy_3$)('$S_4$')] (**3a**). The formation of **2a** and **3a** could be ascertained by mass spectroscopy and IR spectrocopy, however, the mixture of both complexes was difficult to separate. For this reason, we tried to directly obtain the iodo complex from [Ru(DMSO)($PCy_3$)('$S_4$')] and $I_2$. The reaction according to Eq. (3) gave [Ru(I)($PCy_3$)('$S_4$')] (**2a**).

Table 4
Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($pm^2 \times 10^{-1}$) of the non-hydrogen atoms of [5]$BPh_4 \cdot 3THF$

| Atom | x | y | z | $U_{eq}$ [a] |
|---|---|---|---|---|
| Ru1 | 12876.0(3) | 6378.8(2) | 5694.1(3) | 14.5(2) |
| Ru2 | 12833.6(3) | 6329.7(2) | 7629.1(3) | 16.7(2) |
| S1 | 13977.8(8) | 6735.2(6) | 5661(1) | 18.6(5) |
| S2 | 13440.7(9) | 5565.1(6) | 5789(1) | 20.7(6) |
| S3 | 12993(1) | 6254.9(7) | 4339(1) | 21.1(6) |
| S4 | 11856.7(9) | 5868.4(7) | 5513(1) | 21.4(6) |
| S8 | 11968.3(9) | 6983.9(7) | 7823(1) | 24.1(6) |
| N1 | 12761(2) | 6365(2) | 6648(6) | 21(1) |
| S5 | 13787.8(9) | 5781.5(6) | 7647(1) | 20.5(5) |
| S6 | 13640.4(9) | 7019.4(6) | 7555(1) | 23.2(6) |
| S7 | 12984(1) | 6422.5(8) | 8990(1) | 25.2(7) |
| P1 | 12399.9(9) | 7246.7(7) | 5426(1) | 15.3(5) |
| P2 | 12106(1) | 5566.2(7) | 7873(1) | 20.1(6) |
| C10 | 14535(4) | 6221(2) | 5754(5) | 19(2) |
| C11 | 15244(3) | 6307(2) | 5765(4) | 22(2) |
| C12 | 15689(4) | 5909(3) | 5848(4) | 25(3) |
| C13 | 15463(3) | 5405(2) | 5934(4) | 18(2) |
| C14 | 14783(4) | 5310(2) | 5916(4) | 19(2) |
| C15 | 14327(3) | 5705(2) | 5833(4) | 15(2) |
| C16 | 13404(4) | 5315(3) | 4863(5) | 28(3) |
| C20 | 11763(4) | 5789(3) | 4575(5) | 25(2) |
| C21 | 11144(4) | 5551(3) | 4311(5) | 29(2) |
| C22 | 11046(4) | 5497(3) | 3581(5) | 37(2) |
| C23 | 11530(4) | 5660(3) | 3072(5) | 37(2) |
| C24 | 12116(4) | 5885(3) | 3303(5) | 33(1) |
| C25 | 12230(4) | 5951(3) | 4064(5) | 25(1) |
| C26 | 13560(4) | 5713(3) | 4282(5) | 27(3) |
| C30 | 11456(3) | 7280(2) | 5364(4) | 16(2) |
| C31 | 11165(4) | 7028(3) | 4671(4) | 21(2) |
| C32 | 10388(4) | 7037(3) | 4660(5) | 27(3) |
| C33 | 10117(4) | 6804(3) | 5367(6) | 40(3) |
| C34 | 10362(3) | 7078(3) | 6036(4) | 23(2) |
| C35 | 11136(4) | 7065(3) | 6058(4) | 21(2) |
| C40 | 12655(4) | 7510(3) | 4520(4) | 15(2) |
| C41 | 12333(4) | 8034(3) | 4329(5) | 26(3) |
| C42 | 12468(4) | 8195(3) | 3558(5) | 34(3) |
| C43 | 13222(4) | 8212(3) | 3367(5) | 35(3) |
| C44 | 13534(4) | 7695(3) | 3554(4) | 27(3) |
| C45 | 13419(4) | 7531(3) | 4337(5) | 28(3) |
| C50 | 12598(3) | 7727(3) | 6143(4) | 19(2) |
| C51 | 13339(4) | 7936(3) | 6080(4) | 20(2) |
| C52 | 13524(3) | 8272(3) | 6728(6) | 29(3) |
| C53 | 13046(3) | 8727(3) | 6781(4) | 21(2) |
| C54 | 12325(3) | 8544(3) | 6837(3) | 20(2) |
| C55 | 12116(4) | 8185(3) | 6203(4) | 26(2) |
| C60 | 14495(3) | 6189(3) | 7613(5) | 20(2) |
| C61 | 15149(4) | 5971(3) | 7671(5) | 25(2) |
| C62 | 15717(4) | 6271(3) | 7649(5) | 30(2) |
| C63 | 15665(4) | 6802(3) | 7563(5) | 32(3) |
| C64 | 15033(4) | 7020(3) | 7500(4) | 27(3) |
| C65 | 14453(3) | 6711(3) | 7531(4) | 22(2) |
| C66 | 13670(4) | 7264(3) | 8487(5) | 31(3) |
| C70 | 11914(4) | 7082(3) | 8767(4) | 27(2) |
| C71 | 11393(4) | 7416(3) | 9048(4) | 31(2) |
| C72 | 11360(5) | 7524(4) | 9766(5) | 40(2) |
| C73 | 11817(4) | 7315(3) | 10252(4) | 41(2) |
| C74 | 12314(4) | 6976(3) | 10033(4) | 35(2) |
| C75 | 12351(4) | 6862(3) | 9267(4) | 25(2) |
| C76 | 13714(4) | 6834(3) | 9063(5) | 30(3) |
| C80 | 12268(4) | 5251(3) | 8784(4) | 22(2) |

*(continued)*

Table 4 (*continued*)

| Atom | x | y | z | $U_{eq}$ [a] |
|---|---|---|---|---|
| C81 | 13009(4) | 5114(3) | 8957(5) | 23(2) |
| C82 | 13072(4) | 4932(3) | 9732(4) | 27(3) |
| C83 | 12606(5) | 4484(3) | 9910(5) | 42(3) |
| C84 | 11885(5) | 4623(3) | 9735(5) | 41(3) |
| C85 | 11792(4) | 4805(3) | 8964(5) | 32(3) |
| C90 | 12185(4) | 5065(3) | 7142(4) | 25(2) |
| C91 | 11547(4) | 4724(3) | 7033(5) | 38(3) |
| C92 | 11646(5) | 4371(3) | 6358(5) | 49(4) |
| C93 | 12271(4) | 4030(3) | 6440(4) | 37(3) |
| C94 | 12897(4) | 4356(2) | 6555(5) | 28(2) |
| C95 | 12802(4) | 4711(3) | 7247(4) | 25(2) |
| C100 | 11181(4) | 5685(3) | 7930(5) | 25(2) |
| C101 | 10937(4) | 5969(3) | 8607(4) | 33(3) |
| C102 | 10166(4) | 5995(4) | 8633(5) | 44(3) |
| C103 | 9860(4) | 6219(4) | 7916(6) | 54(4) |
| C104 | 10111(4) | 5931(3) | 7268(5) | 37(3) |
| C105 | 10896(4) | 5943(3) | 7244(5) | 33(3) |
| B1 | 14312(5) | 6213(3) | 1611(7) | 31(3) |
| C110 | 14041(4) | 6796(3) | 1439(4) | 26(2) |
| C111 | 14388(4) | 7114(3) | 944(5) | 29(3) |
| C112 | 14198(4) | 7620(3) | 768(6) | 45(3) |
| C113 | 13624(5) | 7812(3) | 1099(5) | 46(4) |
| C114 | 13259(4) | 7515(3) | 1575(6) | 45(3) |
| C115 | 13467(4) | 7022(3) | 1748(5) | 33(3) |
| C120 | 14739(4) | 6028(3) | 902(4) | 23(3) |
| C121 | 14459(4) | 5833(3) | 251(4) | 27(3) |
| C122 | 14831(5) | 5744(3) | −362(4) | 30(3) |
| C123 | 15519(5) | 5848(3) | −378(5) | 36(3) |
| C124 | 15834(4) | 6030(3) | 229(5) | 32(3) |
| C125 | 15453(4) | 6120(3) | 860(5) | 31(3) |
| C130 | 14737(4) | 6204(3) | 2370(5) | 33(3) |
| C131 | 14637(4) | 6540(3) | 2948(5) | 35(3) |
| C132 | 14955(5) | 6505(4) | 3624(5) | 42(3) |
| C133 | 15408(6) | 6105(5) | 3752(5) | 64(5) |
| C134 | 15522(6) | 5752(5) | 3206(6) | 79(5) |
| C135 | 15211(5) | 5800(3) | 2523(5) | 57(4) |
| C140 | 13652(5) | 5815(3) | 1714(7) | 41(3) |
| C141 | 13651(6) | 5386(3) | 2179(6) | 66(4) |
| C142 | 13110(8) | 5039(4) | 2213(8) | 89(6) |
| C143 | 12544(7) | 5126(6) | 1827(9) | 95(7) |
| C144 | 12504(6) | 5537(5) | 1379(6) | 70(5) |
| C145 | 13050(5) | 5868(4) | 1346(5) | 52(4) |
| O150 | 8418(5) | 2499(3) | 7144(5) | 107(4) |
| C150 | 8480(7) | 3039(4) | 7338(9) | 122(6) |
| C151 | 9259(7) | 3168(5) | 7270(10) | 220(1) |
| C152 | 9556(6) | 2706(6) | 7532(9) | 134(7) |
| C153 | 9091(6) | 2270(5) | 7189(8) | 119(6) |
| O160 | 12711(5) | 4050(4) | 3669(7) | 143(6) |
| C160 | 12182(8) | 4361(5) | 3920(10) | 180(1) |
| C161 | 11692(9) | 4135(6) | 4250(10) | 160(10) |
| C162 | 11885(9) | 3567(6) | 4240(10) | 146(8) |
| C163 | 12557(10) | 3554(6) | 3913(9) | 128(7) |

[a] Equivalent isotropic $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensors.

$$[Ru(DMSO)(PCy_3)('S_4')] + 0.5I_2 \xrightarrow[-DMSO]{THF,\ 20°C} [Ru(I)(PCy_3)('S_4')] \quad (3)$$

**2a**

Table 5
Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($pm^2 \times 10^{-1}$) of the isotropically refined non-hydrogen atoms of [5]$BPh_4 \cdot 3THF$

| Atom | x | y | z | $U_{iso}$ |
|---|---|---|---|---|
| O170 | 9720(10) | 4917(7) | 5900(20) | 360(7) |
| C170 | 9910(20) | 4560(10) | 5320(10) | 360(7) |
| C171 | 9310(10) | 4123(10) | 5600(20) | 360(7) |
| C172 | 9690(20) | 4043(9) | 6290(20) | 360(7) |
| C173 | 9500(10) | 4650(10) | 6550(10) | 360(7) |

In quite an analogous way $[Ru(I)(P^iPr_3)('S_4')]$ (**2b**) was obtained. The iodo ligands in **2a** and **2b** proved labile and could be exchanged for chloride or azide when **2a** or **2b** were treated with an excess of $NEt_4Cl$ or $NEt_4N_3$ according to Eq. (4).

$$[Ru(I)(PR_3)('S_4')] + NEt_4X \xrightarrow[-NEt_4I]{THF,\ 20°C} [Ru(X)(PR_3)('S_4')] \quad (4)$$

The resultant complexes $[Ru(N_3)(PCy_3)('S_4')]$ (**3a**), $[Ru(N_3)(P^iPr_3)('S_4')]$ (**3b**), and $[Ru(Cl)(PCy_3)('S_4')]$ (**4**) have been isolated and characterized. The molecular structures of **2a** and **4** were determined by X-ray structure analysis.

Anticipating that the sterically demanding $PCy_3$ rather than the less bulky $P^iPr_3$ ligand might better stabilize unstable species resulting from reactions of the azide ligand, we focused our efforts on **3a**. Heating in order to induce an intramolecular redox reaction between the Ru(III) center and the azide ligand as shown in Eq. (1) revealed that **3a** is stable up to 100°C in solid state. In contrast, **3a** instantaneously reacted when treated with $HBF_4$. Addition of equimolar amounts of $HBF_4$ in $Et_2O$ to a yellow–green suspension of **3a** in $CH_2Cl_2$ at −78°C immediately resulted in the formation of a clear red–violet solution. Monitoring the reaction by IR spectroscopy at −40°C showed that the $\nu(N_3)$ band of **3a** at 2020 $cm^{-1}$ had disappeared and a new band at 2070 $cm^{-1}$ had emerged (Fig. 1).

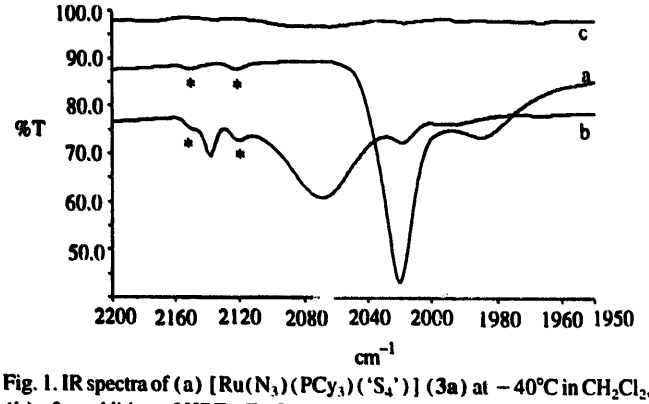



Fig. 1. IR spectra of (a) $[Ru(N_3)(PCy_3)('S_4')]$ (**3a**) at −40°C in $CH_2Cl_2$, (b) after addition of $HBF_4 \cdot Et_2O$, and (c) at room temperature (*, solvent bands due to insufficient compensation).

An additional small absorption at 2130 $cm^{-1}$ could be assigned to the $\nu(N_3)$ band of dissolved $HN_3$. When the solution was gradually warmed to room temperature, the bands at 2070 and 2130 $cm^{-1}$ slowly disappeared and the resulting red–violet solution no longer exhibited any band in the region of 2200–1950 $cm^{-1}$. Addition of $NBu_4PF_6$ and work-up of the red–violet solution yielded purple microcrystals that were identified as the diamagnetic dinuclear complex $[\mu\text{-}N\{Ru(PCy_3)('S_4')\}_2](PF_6)$ ([5]$PF_6$)] which contains formally Ru(IV) centers. Thus protonation of **3a** has led to decomposition of the azide ligand and a simultaneous Ru(III) → Ru(IV) oxidation according to Eq. (5).

$$\underset{\mathbf{3a}}{2[Ru(N_3)(PCy_3)('S_4')]} \xrightarrow[CH_2Cl_2,\ -78\,^\circ C]{+HBF_4/\ -N_2} \underset{[5]^+}{[\mu\text{-}N\{Ru(PCy_3)('S_4')\}_2]^+} \quad (5)$$

The labile species giving rise to the IR band at 2070 $cm^{-1}$ could not yet be identified. This band possibly indicates the intermediate formation of an $N_2$ complex such as $[Ru(N_2)(PCy_3)('S_4')]$, but neither this complex nor the potentially formed dinuclear derivative $[\mu\text{-}N_2\{Ru(PCy_3)('S_4')\}_2]$ could be isolated from the reaction solution.

### 3.2. Characterization of the complexes

The yellow Ru(II) complex $NEt_4[Ru(N_3)(PCy_3)('S_4')]$ (**1**) is diamagnetic and soluble in polar organic solvents such as $CH_2Cl_2$, $CH_3CN$, or DMF. All Ru(III) complexes are paramagnetic as indicated by their $^1H$ NMR spectra. The colors of the complexes range from yellow–green (**4**) over brown (**3a**, **3b**), to red (**2a**, **2b**). The magnetic moment of $[Ru(I)(PCy_3)('S_4')]$ (**2a**) has been determined ($\mu_{eff}$ = 1.84 $\mu_B$, 298°C). It is compatible with one unpaired electron and a low-spin $d^5$ Ru(III) center. The EPR spectrum of the iodo complex $[Ru(I)(PCy_3)('S_4')]$ (**2a**) shows one signal.

The IR spectra of all complexes in KBr exhibit the typical absorptions of $[M('S_4')]$ fragments. The azido complexes show characteristic $\nu(N_3)$ bands at 2019 $cm^{-1}$ (**3a**), 2014 $cm^{-1}$ (**3b**), and 2028 $cm^{-1}$ (**1**). The nitrido complex [5]$PF_6$ exhibits the characteristic $\nu(PF_6)$ band of the $PF_6^-$ ion at 842 $cm^{-1}$, but no $\nu$(RuN) band could be detected.

The splitting pattern of the $^1H$ NMR spectrum of [5]$PF_6$ and the number of the $^{13}C$ signals in the $^{13}C\{^1H\}$ NMR spectrum indicate that $[5]^+$ possesses an overall $C_2$ or $C_S$ symmetry in solution.

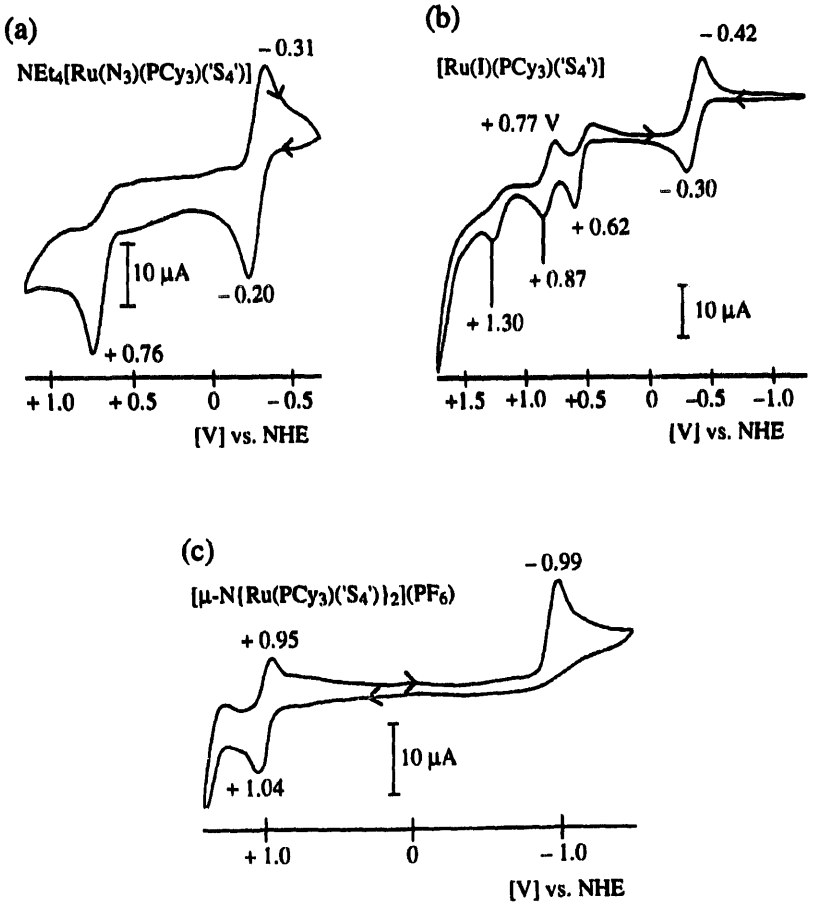



Fig. 2. Cyclic voltammograms of (a) $NEt_4[Ru(N_3)(PCy_3)('S_4')]$ (**1**) ($CH_2Cl_2$, 50 mV $s^{-1}$), (b) $[Ru(I)(PCy_3)('S_4')]$ (**2a**) ($CH_2Cl_2$, 20 mV $s^{-1}$), and (c) $[\mu\text{-}N\{Ru(PCy_3)('S_4')\}_2](PF_6)$ ([5]$PF_6$) ($CH_2Cl_2$, 50 mV $s^{-1}$).

### 3.3. Cyclic voltammetry

Cyclic voltammograms (CVs) were recorded of **1**, **2a** and [5]$PF_6$ (Fig. 2).

$NEt_4$[Ru($N_3$)($PCy_3$)('$S_4$')] (**1**) exhibits one quasi-reversible cathodic and one irreversible anodic redox wave. The chemical results demonstrating the ready oxidation **1**→**3a** (cf. above) suggest that the cathodic wave is to be assigned to a **1**↔**3a** redox process. Accordingly, the irreversible anodic wave can be assigned to a Ru(III)→Ru(IV) oxidation. The iodo complex **2a** shows a surprisingly extensive electrochemistry. In agreement with the assignment of the redox waves of **1**, the cathodic redox wave of **2a** can be assigned to a Ru(II)/Ru(III) redox process in which **2a** is reversibly reduced to give [**2a**]$^-$. The three anodic redox waves indicate that **2a** can be further oxidized, but the nature of the resulting species so far remains speculative. The CV of [$\mu$-N{Ru($PCy_3$)('$S_4$')}$_2$]($PF_6$) ([5]$PF_6$) indicates that the [**5**]$^+$ cation can be reversibly oxidized to give a [Ru(IV)/Ru(V)] species, but that reduction leads to decomposition.

### 3.4. Molecular structures of [Ru(I)($PCy_3$)('$S_4$')] (2a), [Ru(Cl)($PCy_3$)('$S_4$')] (4) and [$\mu$-N{Ru($PCy_3$)('$S_4$')}$_2$]($BPh_4$) ([5]$BPh_4$)

The X-ray structure determinations of [Ru(I)($PCy_3$)('$S_4$')]·$C_7H_8$ (**2a**·$C_7H_8$), [Ru(Cl)($PCy_3$)('$S_4$')]·$CH_2Cl_2$ (**4**·$CH_2Cl_2$), and [$\mu$-N{Ru($PCy_3$)('$S_4$')}$_2$]($BPh_4$)·3THF ([5]$BPh_4$·3THF) revealed that the Ru centers in all three complexes exhibit pseudo-octahedral coordination. The '$S_4$'$^{2-}$ ligands bind to the Ru centers in their characteristic helical way such that the thiolate S donors occupy trans positions and chiral [Ru('$S_4$')] fragments result. Fig. 3 depicts the molecular structures of **2a**, **4** and [**5**]$^+$, Table 6 lists selected distances and angles.

Numerous $C_2$ symmetrical [Ru(L)$_2$('$S_4$')] complexes exhibit equidistant M–S(thiolate) and M–S(thioether) bonds [13]. In contrast, these bonds differ in the $C_1$ symmetrical complexes **2a**, **4** and [**5**]$^+$. This can be plausibly traced back to the lower symmetry, and, in addition, to the steric influence of the very bulky $PCy_3$ ligand and the dissimilar *trans* influence of $PCy_3$, halide, and nitride ligands, respectively. In this respect, the distances and angles of **2a**

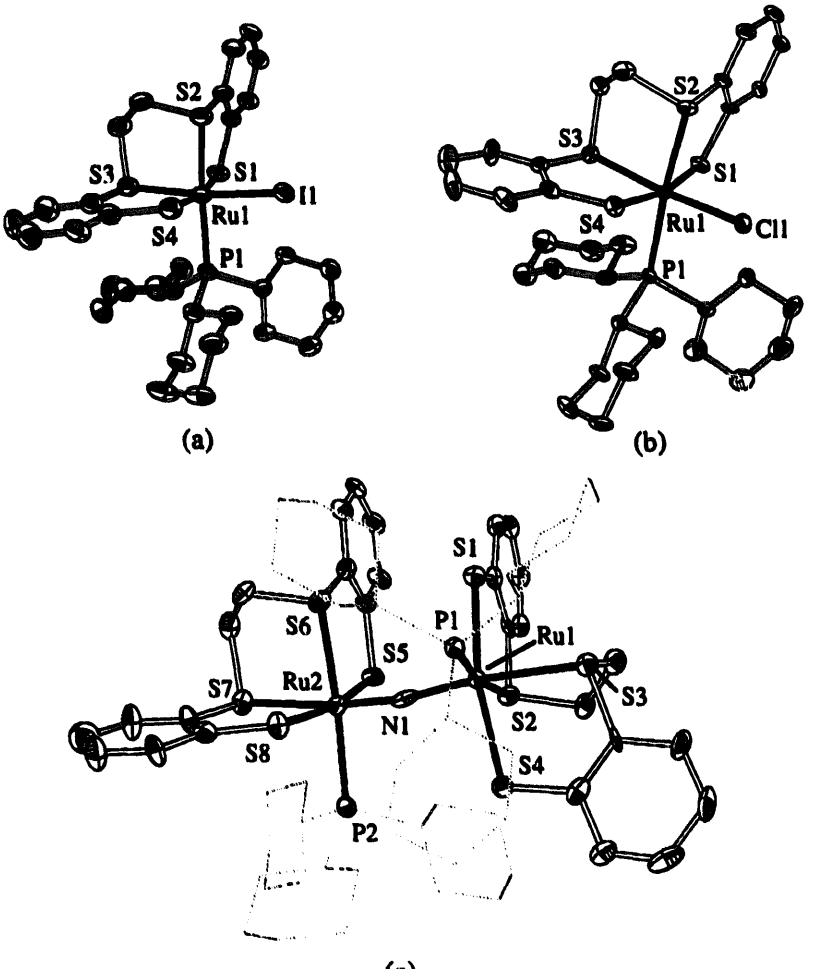



Fig. 3. Molecular structures of (a) [Ru(I)($PCy_3$)('$S_4$')] (**2a**), (b) [Ru(Cl)($PCy_3$)('$S_4$')] (**4**), and (c) the cation of [$\mu$-N{Ru($PCy_3$)('$S_4$')}$_2$]($BPh_4$) ([5]$BPh_4$) drawn with 50% probability ellipsoids (solvent molecules, counter ions, and H atoms omitted, cyclohexyl ring dotted).

Table 6
Selected distances (pm) and angles (°) of [Ru(I)(PCy$_3$)('S$_4$')] (**2a**), [Ru(Cl)(PCy$_3$)('S$_4$')] (**4**) and [$\mu$-N{Ru(PCy$_3$)('S$_4$')}$_2$](BPh$_4$) ([**5**]BPh$_4$)

| | **2a** | **4** | | | |
|---|---|---|---|---|---|
| Ru1–S1 | 228.0(2) | 229.7(3) | 236.5(2) | Ru2–S5 | 236.4(2) |
| Ru1–S2 | 236.8(2) | 237.6(3) | 240.2(2) | Ru2–S6 | 240.5(2) |
| Ru1–S3 | 234.0(2) | 233.1(3) | 251.4(3) | Ru2–S7 | 252.1(3) |
| Ru1–S4 | 240.1(2) | 241.1(3) | 243.4(2) | Ru2–S8 | 243.9(2) |
| Ru1–P1 | 241.0(2) | 241.4(3) | 249.8(2) | Ru2–P2 | 249.4(2) |
| Ru1–I1 | 271.78(7) | | | | |
| Ru1–Cl1 | | 240.6(3) | | | |
| Ru1–N1 | | | 176.2(10) | Ru2–N1 | 180.4(10) |
| S1–Ru1–S4 | 169.06(6) | 168.86(9) | 166.11(7) | S5–Ru2–S8 | 167.99(8) |
| S2–Ru1–S3 | 87.88(6) | 87.49(9) | 85.14(7) | S6–Ru2–S7 | 84.61(8) |
| S1–Ru1–I1 | 100.67(5) | | | | |
| S1–Ru1–Cl1 | | 99.49(10) | | | |
| S2–Ru1–P1 | 175.62(6) | 175.14(9) | 171.17(7) | S6–Ru2–P2 | 170.94(7) |
| S3–Ru1–N1 | | | 171.2(2) | S7–Ru2–N1 | 171.3(2) |
| Ru1–N1–Ru2 | | | 168.0(3) | | |

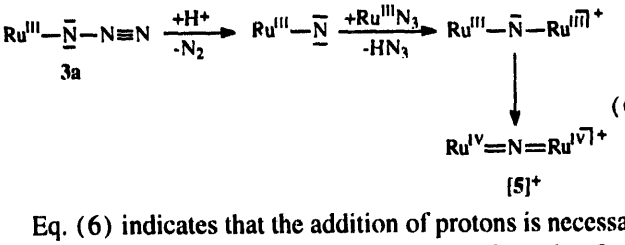
and **4** show no anomalies and are comparable with those of the analogous complex [Ru(Cl)(PPh$_3$)('$^{bu}$S$_4$')] ('$^{bu}$S$_4$'$^{2-}$ = 1,2-bis(3,5-di(t-butyl)-2-mercaptophenylthioethane(2−)) [19]. Furthermore, corresponding distances and angles in the two halide complexes **2a** and **4** are virtually identical.

When **2a** or **4** are compared with the nitrido complex [**5**]$^+$, it is to be noted that all corresponding Ru–S distances in [**5**]$^+$ are significantly elongated despite the formally higher oxidation state of the Ru(IV) centers. The particularly long Ru–S distances (251.4(3) and 252.1(3) pm) of [**5**]$^+$ certainly reflect the very strong *trans* influence of the nitrido ligand. It is further noted that the Ru–N–Ru bridge of [**5**]$^+$ is more strongly bent (168°) than in other [Ru–N–Ru] complexes (175°) [20]. This bending is probably due to the sterical crowding in [**5**]$^+$, which on the other hand is caused by the bonding in the [Ru–N–Ru] entity. In the cation [**5**]$^+$, the nitrido bridge connects two homochiral and sterically very demanding [Ru(PCy$_3$)('S$_4$')] fragments. Because the [Ru(PCy$_3$)('S$_4$')] fragments are homochiral, the acceptor orbitals of the fragments must be identical. Interaction of the (identical) $\pi$-acceptor orbitals of the [Ru(PCy$_3$)('S$_4$')] fragments with the orthogonal p-electron pairs at the N bridge then results in an allene-like [Ru=N=Ru] bonding system. It allows the Ru(IV) centers to reach an 18 valence electron configuration, but also results in the sterical crowding of [**5**]$^+$. This bonding system is analogous to that of [$\mu$-O{Mo(NO)('S$_4$')}$_2$] which has previously been discussed in detail [21].

## 4. Discussion and summary

The lability of the DMSO ligand in the recently reported [Ru(DMSO)(PR$_3$)('S$_4$')] complexes (R = Cy, $^i$Pr) has opened the access to [Ru(L)(PCy$_3$)('S$_4$')] complexes that had previously been inaccessible. This work describes complexes that were intended to serve as potential precursors for dinitrogen complexes.

Exchange of DMSO in [Ru(DMSO)(PCy$_3$)('S$_4$')] by azide ions yielded the Ru(II) species NEt$_4$[Ru(N$_3$)(PCy$_3$)('S$_4$')] (**1**). Complex **1** proved surprisingly inert toward $O_2$ or $H_2O_2$, but it could be readily oxidized by $I_2$ to give a mixture of the Ru(III) complexes [Ru(I)(PCy$_3$)('S$_4$')] (**2a**) and [Ru(N$_3$)(PCy$_3$)('S$_4$')] (**3a**). Complex **2a** could be obtained directly from [Ru(DMSO)(PCy$_3$)('S$_4$')] and elemental iodine and proved to be a well-suited precursor for the synthesis of the Ru(III) azido complex **3a** in pure state, because it readily exchanges its iodo ligand for azide from NEt$_4$N$_3$. Complex **2a** exchanges its iodo ligand also for chloride and allows the synthesis of [Ru(Cl)(PCy$_3$)('S$_4$')] (**4**) which is not accessible from [Ru(DMSO)(PCy$_3$)('S$_4$')] and elemental chlorine. The Ru(III) complex [Ru(N$_3$)(PCy$_3$)('S$_4$')] (**3a**) is thermally stable up to 100°C, but it instantaneously reacts with HBF$_4$ at −78°C. IR monitoring of the reaction showed that small amounts of free HN$_3$ and an unstable intermediate formed exhibiting an IR band at 2070 cm$^{-1}$. This unstable intermediate is possibly the $N_2$ complex [Ru(N$_2$)(PCy$_3$)('S$_4$')], but it could not yet be isolated or identified. The dinuclear Ru(IV) complex [$\mu$-N{Ru(PCy$_3$)('S$_4$')}$_2$](PF$_6$) ([**5**]PF$_6$), however, could be isolated and completely characterized. The formation of [**5**]PF$_6$ proves that protonation of **3a**, at least partially, leads to removal of $N_2$ from the azido ligand in **3a** and the formation of a [Ru(N)(PCy$_3$)('S$_4$')] species that is stabilized as binuclear [**5**]$^+$. The formation of [**5**]$^+$ can be rationalized according to Eq. (6).



(6)

Eq. (6) indicates that the addition of protons is necessary to induce the cleavage of the azido ligand in **3a** and to facilitate the release of $N_3^-$ from another molecule of **3a**. Intra-

molecular electron transfer from the Ru(III) centers to the N bridge finally yields the two Ru(IV) centers of [5]$PF_6$.

The molecular structures of [Ru(I)($PCy_3$)('$S_4$')] (**2a**), [Ru(Cl)($PCy_3$)('$S_4$')] (**4**), and [$\mu$-N{Ru($PCy_3$)('$S_4$')}$_2$]($BPh_4$) ([5]$BPh_4$) exhibit no anomalies. It is noted, however, that $[5]^+$ assumes a sterically highly crowded structure with a bent Ru–N–Ru bridge. This can be traced back to electronic reasons and an allene-like Ru=N=Ru bonding system that allows both Ru(IV) centers to gain an 18 valence electron configuration.

## 5. Supplementary material

Further details of the X-ray structure analyses have been deposited and can be obtained from the Fachinformationszentrum, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen by citing the depository No. CSD 406622 [Ru(I)($PCy_3$)('$S_4$')], CSD 406623 [Ru(Cl)($PCy_3$)('$S_4$')], CSD 406624 [$\mu$-N{Ru($PCy_3$)('$S_4$')}$_2$]($BPh_4$), the authors, and the reference.

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