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# Cyclopentadienyl ruthenium(II) dithiocarbamate complexes: Crystal structures of [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNPr<sub>2</sub>)] and [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNMeBu)]

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Ruthenium and Osmium Chemistry Topical Issue

#### Abstract

Thermolysis of  $[CpRuCl(PPh_3)_2]$  and  $NaS_2CNPr_2$  or  $NaS_2CNMeBu$  in methanol affords the ruthenium(II) dithiocarbamate complexes,  $[CpRu(PPh_3)(S_2CNPr_2)]$  and  $[CpRu(PPh_3)(S_2CNMeBu)]$ , which have been crystallographically characterized. A similar treatment of two equivalents of  $[CpRuCl(PPh_3)_2]$  with the bis(dithiocarbamate) ligand derived from 1,3-homopiperazine affords  $[\{CpRu(PPh_3)\}_2(\mu-S_2CNC_5H_{10}NCS_2)]$ .

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## 1. Introduction

Dithiocarbamates are versatile ligands, capable of forming complexes with all the transition elements and able to stabilize most in a range of oxidation states [1]. The first ruthenium dithiocarbamate complexes,  $[Ru(S_2CNR_2)_3]$ , were prepared in the 1930s [2] and in the intervening years dithiocarbamates have been shown to stabilize this element with a wide variety of co-ligands in oxidation states +1 to +4. One of the attractive features of ruthenium dithiocarbamate chemistry is the extensive redox chemistry that they often show, the +2/+3 couple being reversible in a wide range of systems. This seemed attractive to us as we hoped to generate multimetallic arrays based on polyfunctional dithiocarbamate ligands and investigate their redox properties with the aim of preparing new materials with novel physical properties.

An attractive starting point for this program would appear to be ruthenium(II) complexes,  $[CpRu(PR_3)(S_2CNR_2)]$ . Here, the pseudo-octahedral ruthenium(II) centre is bound

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to three of the most ubiquitous and best understood ligands in coordination chemistry, potentially allowing for a wide range of variants and thus specific tuning of both chemical and physical properties. Such complexes are reportedly easy to prepare from dithio carbamate salts and  $[CpRuCl(PPh_3)_2]$ [3–6]. Shaver and co-workers [7] have also recently prepared complexes,  $[CpRu(PPh_3)(S_2CNR^1R^2)]$  (R<sup>1</sup> = Si-*i*-Pr<sub>3</sub>, R<sup>2</sup> = Ph, p-tol, 1-naphth;  $R^1 = H$ ,  $R^2 = Ph$ , 1-naphth), with arylsubstituents on the dithiocarbamate from the insertion of arylisothiocyanates into the ruthenium-sulfur bonds of [CpRu(PPh<sub>3</sub>)<sub>2</sub>(SSi-*i*-Pr<sub>3</sub>)] and [CpRu(PPh<sub>3</sub>)<sub>2</sub>(SH)]. This was of interest to us as it suggested the potential preparation and likely enhanced stability of materials containing ruthenium(II) centres linked via aryl bis(dithiocarbamate) ligands which might allow for a level of electronic communication between the metal centres.

# 2. Results and discussion

Thermolysis of a methanol solution of  $[CpRuCl(PPh_3)_2]$ and commercially available  $NaS_2CNMe_2 \cdot 3H_2O$  for

30 min afforded the known bright orange complex  $[CpRu(PPh_3)(S_2CNMe_2)]$  in 81% yield [6]. The work-up in this instance was very simple, removal of NaCl and PPh<sub>3</sub> being accomplished after washing successively with water and methanol. In order to extend this series of complexes we applied the same methodology with in situ generated NaS<sub>2</sub>CNPr<sub>2</sub> and NaS<sub>2</sub>CNMeBu. In both instances, however, reactions were slower, taking place over 24 h, and work-up more complicated. The latter seems to result from the initial formation of oily orange solids which show appreciable solubility in methanol, thus making removal of the phosphine more difficult. An attempt to convert the phosphine into a salt, upon addition of dilute HCl, lead only to the formation of purple solids with loss of the expected ruthenium products. The complexes [CpRu(PPh<sub>3</sub>)- $(S_2CNPr_2)$  and  $[CpRu(PPh_3)(S_2CNMeBu)]$  were eventually isolated in 62% and 51% yields, respectively, after extraction of the crude products into dichloromethane followed by precipitation with light petroleum. Spectroscopic and analytical data supported the proposed formulations and in order to confirm this, crystallographic studies were carried out on both, the results of which are summarized in Figs. 1 and 2, Table 1.



Somewhat surprisingly, only one simple complex of this type has previously been crystallographically characterized; structures of two polymorphs of [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNMe<sub>2</sub>)] being reported [6,8]. Key features of [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNPr<sub>2</sub>)]

and  $[CpRu(PPh_3)(S_2CNMeBu)]$  are as expected. The ruthenium(II) centre adopts a pseudo-octahedral coordination geometry with the small bite-angle dithiocarbamate  $[S-Ru-S 71.83(2)-72.00(3)^{\circ}]$  lying at an approximate right angles  $[P-Ru-S 90.92(2)-95.79(2)^{\circ}]$  to the phosphine. The dithiocarbamate binds approximately symmetrically [Ru-S 2.3779(8)-2.4014(6) Å] and in both structures the substituents are orientated towards the phosphine.

As noted in Section 1, Shaver and co-workers [7] have prepared complexes of this type upon insertion of arylisothiocyanates into [CpRu(PPh<sub>3</sub>)<sub>2</sub>(SH)]. Most interestingly, when 1,4-phenylenediisothiocyanate was used with two equivalents of [CpRu(PPh<sub>3</sub>)<sub>2</sub>(SH)] the dithiocarbamatebridged product,  $1,4-[{CpRu(PPh_3)}_2(\mu-S_2CNHC_6H_4-$ NHCS<sub>2</sub>)] was cleanly formed, which showed good stability, being characterized by X-ray crystallography. Further, in recent work we have prepared a number of binuclear complexes in which the metal centres are linked via piperazine bis(dithiocarbamate) ligand [9]. Hence, it seemed that such dithiocarbamate-bridged complexes should be realistic targets and in order to test out this, the bis(dithiocarbamate) derived from 1,3-homopiperazine was generated in situ and reacted with two equivalents of [CpRuCl(PPh<sub>3</sub>)<sub>2</sub>]. A very slow reaction took place over 48 h in refluxing methanol to give after work-up dithiocarbamate-bridged [{CpRu- $(PPh_3)$ <sub>2</sub>( $\mu$ -S<sub>2</sub>CNC<sub>5</sub>H<sub>10</sub>NCS<sub>2</sub>)] as a bright orange solid in 44% yield. Characterization was made on the basis of analytical and spectroscopic features, with all attempts to produce crystals suitable for crystallography proving futile. The <sup>1</sup>H NMR spectrum was quite complex as might be expected but importantly, a single cyclopentadienyl resonance was clearly observed. The protons of the homopiperazine unit appear in two groups; a complex multiple between  $\delta$  3.39 and 3.26 assigned to the nitrogen-bound methylene groups and a second multiplet between  $\delta$  1.57



Fig. 1. Molecular structure of [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNPr<sub>2</sub>)].



Fig. 2. Molecular structure of [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNMeBu<sub>2</sub>)].

and 1.52 assigned to the central methylene unit. The latter is very complex but clearly associated with two overlapping multiplets being assigned to axial and equatorial protons.



While the complexes described above are quite stable in the solid state, in solution in the presence of oxygen they slowly decompose. When a sample of  $[CpRu(PPh_3)-(S_2CNPr_2)]$  in CDCl<sub>3</sub> was monitored by NMR over a period two weeks a gradual darkening of the sample took place with concomitant formation of Ph<sub>3</sub>P=O, as shown by <sup>31</sup>P NMR spectroscopy. To date we have been unable to determine the fate of the organometallic fragment. While the phosphine oxide is clearly visible in the <sup>1</sup>H NMR spectrum, no other clear peaks are observed suggesting that ruthenium has been oxidized to +3 state. A UV– Vis spectrum revealed a strong transition at 550 nm, as compared to that at 355 nm found in [CpRu(PPh<sub>3</sub>) (S<sub>2</sub>CNPr<sub>2</sub>)]. A similar intense absorption at 550 nm was also observed for the purple product of HCl addition to [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNPr<sub>2</sub>)] (see above) and the precise nature of this is still under investigation.

In conclusion, we have shown that while complexes of the type  $[CpRu(PR_3)(S_2CNR_2)]$  are readily prepared, long reaction times, difficulties in product purification and long term stability does not make them the attractive targets that we had anticipated. In contrast we have recently found that cationic ruthenium(II) complexes,  $[Ru(diphosphine)_2(S_2CNR_2)]^+$ , are more readily prepared and purified [9].

# 3. Experimental

# 3.1. Synthesis of $[CpRu(PPh_3)(S_2CNPr_2)]$ [6]

A methanol solution  $(20 \text{ cm}^3)$  of NaS<sub>2</sub>CNMe<sub>2</sub> · 3H<sub>2</sub>O (84 mg, 0.59 mmol) and [CpRuCl(PPh<sub>3</sub>)<sub>2</sub>] (0.52 g, 0.70

Table 1		
Selected bond length	s (Å) and bond angles (°) for [CpR	$u(PPh_3)(S_2CNR_2)$

R <sub>2</sub>	Ru–S	Ru–P	C=N	S–Ru–S	P–Ru–S
Pr <sub>2</sub>	2.3957(8)	2.2735(7)	1.336(5)	72.00(3)	95.09(3)
	2.3779(8)				92.01(3)
Me/Bu	2.4014(6)	2.2782(6)	1.328(3)	71.83(2)	95.79(2)
	2.3971(6)				90.92(2)
Me <sub>2</sub> <sup>8</sup>	2.397(3)	2.285(2)	1.354(10)	71.88(9)	95.18(9)
	2.394(3)				98.82(9)
Si <sup>i</sup> Pr <sub>3</sub> /Naphth <sup>7</sup>	2.394(2)	2.269(2)	1.377(7)	71.69(8)	95.02(9)
	2.387(2)			~ /	92.56(9)

mmol) was refluxed for 30 min. Removal of volatiles under reduced pressure gave an orange solid which was washed successively with water (ca.  $2 \times 10 \text{ cm}^3$ ) and methanol (ca.  $2 \times 10 \text{ cm}^3$ ) to give [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNMe<sub>2</sub>)] [6] as a bright orange solid (0.26 g, 81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.34–7.08 (m, 15H, Ar), 4.36 (s, 5H, Cp), 2.75 (s, 6H, Me); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  38.1 (s); IR(KBr)  $\nu/\text{cm}^{-1}$  1558s, 1386m, 1259w, 1153w, 1085m, 1068w, 983w, 831w, 796w, 744m, 694s, 586w, 520s, 499m, 462w, 422w; mass spectrum (FAB) m/z 549 (M<sup>+</sup> + 1).

## 3.2. Synthesis of $[CpRu(PPh_3)(S_2CNPr_2)]$

To a hot methanol solution  $(5 \text{ cm}^3)$  of NaS<sub>2</sub>CNPr<sub>2</sub> (ca. 0.75 mmol) [generated from NaOH (37 mg, 0.93 mmol),  $Pr_2NH$  (74 mg, 0.73 mmol) and  $CS_2$  (57 mg, 0.75 mmol)] was added dropwise a methanol solution  $(15 \text{ cm}^3)$  of  $[CpRuCl(PPh_3)_2]$  (0.50 g, 0.70 mmol). The resulting solution was refluxed for 24 h after which the solvent was removed under reduced pressure to leave an oily orange solid. This was extracted in dichloromethane (ca.  $20 \text{ cm}^3$ ), filtered and dried over MgSO<sub>4</sub>. Removal of volatiles under reduced pressure again gave an orange oil which was washed with light petroleum (ca. 20 cm<sup>3</sup>) to afford after drying an oily orange solid. This was taken up in a minimum volume of dichloromethane and light petroleum added which lead to the precipitation of  $[CpRu(PPh_3)(S_2CNPr_2)]$  as an orange solid (0.26 g, 62%). Orange crystals suitable for crystallography resulted upon slow diffusion of light petroleum into a concentrated dichloromethane solution. <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 7.51-7.24 (m, 15H, Ar), 4.32 (s, 5H, Cp), 3.18 (t, J 7.0, 4H, NCH<sub>2</sub>), 1.38 (m, 4H, CH<sub>2</sub>), 0.77 (t, J 7.0, 6H, Me); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  37.2 (s); IR(KBr) v/cm<sup>-1</sup> 1481s, 1427m, 1365m, 1303m, 1242m, 1149m, 1095m, 995m, 794w, 694s, 532s, 432w; mass spectrum (FAB) m/z 605 (M<sup>+</sup> + 1); Anal. Calc. for C<sub>30</sub>H<sub>34</sub> NS<sub>2</sub>PRu: C, 59.57; H, 5.67; N, 2.32. Found: C, 60.85; H, 5.59; N, 1.88%.

## 3.3. Synthesis of $[CpRu(PPh_3)(S_2CNMeBu)]$

Following the procedure outlined above, NaS<sub>2</sub>CNMeBu (ca. 0.75 mmol) and [CpRuCl(PPh<sub>3</sub>)<sub>2</sub>] (0.50 g, 0.70 mmol) were heated in methanol (20 cm<sup>3</sup>), to provide after workup, [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNMeBu)] as a yellow-orange solid (0.20 g, 51%). Small yellow crystals were grown upon slow evaporation of a dichloromethane-light petroleum solution. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.56–7.27 (m, 15H, Ar), 4.37 (s, 5 H, Cp), 3.30 (m, 2H, NCH<sub>2</sub>), 3.15 (m, 2H, CH<sub>2</sub>), 2.80 (s, 3H, NMe), 1.26 (m, 2H, CH<sub>2</sub>), 0.88 (t, *J* 7.0, 3H, Me); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  37.0 (s); IR(KBr) *v*/cm<sup>-1</sup> 1651m, 1481m, 1434m, 1396m, 1257m, 1226m, 1095m, 1026m, 802m, 694w, 748w, 524w; mass spectrum (FAB) *m*/*z* 591 (M<sup>+</sup> + 1); *Anal.* Calc. for C<sub>29</sub>H<sub>32</sub>NS<sub>2</sub>PRu · 1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 57.56; H, 5.40; N, 2.28. Found: C, 56.01; H, 6.11; N, 2.24%.

## 3.4. Synthesis of $[ \{CpRu(PPh_3)\}_2(\mu - S_2CNC_5H_{10}NCS_2) ]$

To 1,3-homopiperazine (100 mg, 1.00 mmol) in methanol (10 cm<sup>3</sup>) was added NaOH (100 mg, 2.50 mmol) and  $CS_2$  (152 mg, 2.00 mmol). After strirring for 1 h,  $[CpRuCl(PPh_3)_2]$  (400 mg, 0.56 mmol) in methanol  $(20 \text{ cm}^3)$  was added and the mixture was refluxed for 2 d. Volatiles were removed under reduced pressure to leave an orange solid which was extracted in dichloromethane (ca. 20 cm<sup>3</sup>), filtered and dried over MgSO<sub>4</sub>. Removal of volatiles under reduced pressure gave an orange solid which was washed with light petroleum (ca.  $20 \text{ cm}^3$ ), taken up in a minimum volume of dichloromethane and light petroleum added which lead to the precipitation of  $[{CpRu(PPh_3)}_2(\mu-S_2CNC_5H_{10}NCS_2)]$  as an orange solid (0.15 g, 44%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.54–7.26 (m, 30H, Ar), 4.39 (s, 10H, Cp), 3.39-3.26 (m, 8H, NCH<sub>2</sub>), 1.57-1.52 (m, 2H, CH<sub>2</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 38.4 (s); IR(KBr) v/cm<sup>-1</sup> 1589m, 1481m, 1419m, 1218m, 1180m, 918m, 694w, 532w; mass spectrum (FAB) m/z 1107 (M<sup>+</sup> + 1); Anal. Calc. for  $C_{53}H_{50}N_2S_4P_2Ru_2 \cdot 11/2CH_2Cl_2$ : C, 53.45; H, 3.54; N, 2.29. Found: C, 53.58; H, 4.34; N, 2.18%.

#### 3.5. X-ray data collection and solution

Single crystals were mounted on glass fibres and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Κα radiation  $(\lambda =$ 0.71073 Å). Data reduction was carried out with SAINT PLUS and absorption correction applied using the program sadabs. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All nonhydrogen atoms were refined anisotropically. Hydrogens were generally placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package.

Crystallographic data for [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNPr<sub>2</sub>)]:  $T = 293 \pm 2$  K, orange block, dimensions  $0.24 \times 0.16 \times$ 0.15 mm, monoclinic, space group  $P2_1/n$ , a = 14.9462(8),  $b = 10.2897(6), \quad c = 19.7018(11) \text{ Å}, \quad \beta = 106.9020(10)^{\circ},$  $V = 2899.1(3) \text{ Å}^3$ , Z = 4,F(000) $d_{\text{calc}} =$ 1248, 1.386 g cm<sup>-3</sup>,  $\mu = 0.759$  mm<sup>-1</sup>. 25025 reflections were collected, 6916 unique  $[R_{(int)} = 0.0169]$  of which 6255 were observed  $[I > 2.0\sigma(I)]$ . At convergence,  $R_1 = 0.0431$ ,  $wR_2 = 0.1131 \ [I > 2.0\sigma(I)] \text{ and } R_1 = 0.0474, \ wR_2 = 0.1165$ (all data), for 316 parameters. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 277299.

Crystallographic data for [CpRu(PPh<sub>3</sub>)(S<sub>2</sub>CNMeBu)]:  $T = 150 \pm 2$  K, yellow block, dimensions  $0.08 \times 0.06 \times 0.05$  mm, triclinic, space group  $P\bar{1}$ , a = 10.4423(7), b = 11.1247(8), c = 11.5011(8) Å,  $\alpha = 97.1030(10)$ ,  $\beta = 106.9020(10)$ ,  $\gamma = 95.8550(10)$ , V = 1315.61(16) Å<sup>3</sup>, Z = 2, F(000) 608,  $d_{calc} = 1.491$  g cm<sup>-3</sup>,  $\mu = 0.834$  mm<sup>-1</sup>. 11698 reflections were collected, 6037 unique [ $R_{(int)} = 0.0202$ ] of which 5447 were observed  $[I > 2.0\sigma(I)]$ . At convergence,  $R_1 = 0.0316$ ,  $wR_2 = 0.0734$   $[I > 2.0\sigma(I)]$  and  $R_1 = 0.0364$ ,  $wR_2 = 0.0758$  (all data), for 307 parameters. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 277300.

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