

A Novel Organometallic Ruthenium(IV) Thiocyanato-bridged Dimer†

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Treatment of the ruthenium(IV) chloro-bridged dimer $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-Cl})\}_2]$ **1** with silver thiocyanate in acetone–water gives the thiocyanato S,N-bridged dimer $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-SCN})\}_2]$ **2** which exists as two diastereomeric forms respectively of C_i **2a** and C_2 **2b** symmetry. The X-ray crystal structure of **2b** shows the molecule to contain an unusually puckered eight-membered 'Ru₂(SCN)₂' ring.

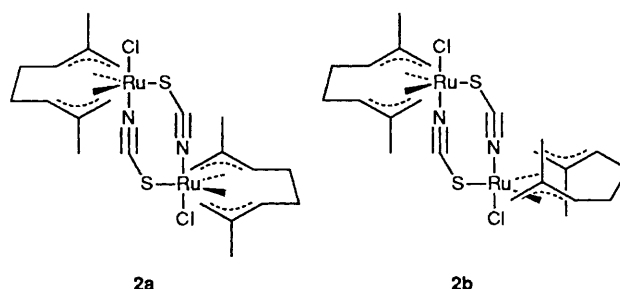
The relatively unexplored chemistry of the ruthenium(IV) chloro-bridged dimer $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-Cl})\}_2]$ **1**^{1,2} is an area of fast growing interest.^{3–5} Compound **1** has been shown, by ¹H NMR spectroscopy, to exist as two diastereoisomers,⁶ the *meso* and *rac* forms, of C_i and C_2 symmetry respectively. Although the latter is slightly more stable in solution⁶ $\{[C_2]/[C_i]\}$ (298 K) = 1.25 it is the *meso* form which has been crystallographically characterised.² We have prepared a related pyrazine-bridged binuclear compound⁷ $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\}_2(\mu\text{-N}_2\text{C}_4\text{H}_4)]$ **3** which also exists as two diastereoisomers as a consequence of the chirality of the '($\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16}$)Ru' fragment. Once again it is the C_i form which has been crystallographically characterised. We now report the synthesis of the *meso* and *rac* forms of a second dimeric species derived from **1**, namely $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-SCN})\}_2]$ **2a** and **2b** respectively, and describe for the first time the crystal structure of a C_2 isomer, **2b**.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 983 grating spectrometer between 4000 and 200 cm⁻¹ as KBr discs and Nujol mulls on CsI plates and NMR spectra on a Varian VXR400 spectrometer at University College London. Microanalyses were carried out by the departmental service. Mass spectra were run by the University of London Intercollegiate Research Service at the School of Pharmacy. All manipulations were carried out under nitrogen with degassed solvents using conventional Schlenk-line techniques.

The compound $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-Cl})\}_2]$ was prepared by published methods.^{1,3,6} Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and was purified before use by dissolution in water and boiling to dryness. All other reagents and materials were obtained from the usual commercial sources.

Preparation of $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-SCN})\}_2]$ **2.**—The compound $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-Cl})\}_2]$ (0.1107 g, 0.180 mmol) was suspended in degassed acetone (2.5 cm³) and degassed water (2.5 cm³). Silver(I) thiocyanate (0.0614 g, 0.370 mmol) was added and the mixture stirred for 1 h. The resulting yellow solution was filtered through Celite to remove the precipitate of AgCl and the volume was reduced to about one quarter, resulting in precipitation of the yellow product which was isolated by filtration, washed with acetone and diethyl ether and air dried. Yield: 0.0514 g, 0.078 mmol, 43% (Found: C, 40.0; H, 4.9; N, 3.9. Calc. for C₂₂H₃₂Cl₂N₂Ru₂S₂: C, 39.9; H, 4.9; N,



4.2%). ¹H NMR (CDCl₃): C_2 isomer: terminal allyl, δ 4.77 (s, 2 H), 4.70 (s, 2 H), 4.13 (s, 2 H), 3.56 (s, 2 H); internal allyl, δ 4.90 (m, 2 H), 4.68 (m, 2 H); CH₂, δ 3.14 (m, 4 H), 2.57 (m, 4 H); CH₃, δ 2.35 (s, 6 H), 2.26 (s, 6 H); C_i isomer: terminal allyl, δ 4.81 (s, 2 H), 4.65 (s, 2 H), 4.05 (s, 2 H), 3.68 (s, 2 H); internal allyl, δ 4.90 (m, 2 H), 4.68 (m, 2 H); CH₂, δ 3.14 (m, 4 H), 2.57 (m, 4 H); CH₃, δ 2.29 (s, 6 H), 2.26 (s, 6 H). Infrared spectrum: $\nu(\text{CN})$ 2141, $\nu(\text{CS})$ 723, $\nu(\text{RuCl})$ 280 and $\nu(\text{RuS})$ 251 cm⁻¹. Mass spectrum (based on ³⁵Cl and ¹⁰²Ru): m/z 662, $[\text{Ru}_2(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})_2\text{Cl}_2(\text{SCN})_2]^+$; 627, $[\text{Ru}_2(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})_2\text{Cl}(\text{SCN})_2]^+$; 273, $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}]^+$; and 238, $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})]^+$.

Crystals of isomerically pure compound **2b** were obtained by fractional crystallisation from a nitromethane solution.

Crystallography.—*Crystal data.* C₂₂H₃₂Cl₂N₂Ru₂S₂ **2b**, $M = 661.67$, triclinic, space group $P\bar{1}$, $a = 7.831(3)$, $b = 12.882(3)$, $c = 14.109(6)$ Å, $\alpha = 112.48(3)$, $\beta = 100.52(3)$, $\gamma = 91.45(3)^\circ$, $U = 1285(1)$ Å³ (by least-squares refinement of diffractometer angles for 29 automatically centred reflections in the range $13 \leq 2\theta \leq 22^\circ$, $\lambda = 0.71073$ Å), $Z = 2$, $F(000) = 664$, $D_c = 1.71$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 15.3$ cm⁻¹. Orange block $0.10 \times 0.20 \times 0.50$ mm.

Data collection and processing. The ω - 2θ technique was used to collect 4448 unique reflections in the range $5 \leq 2\theta \leq 50^\circ$ on a Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-K α radiation. Three standard reflections measured every 97 reflections showed no significant change in intensity throughout the data collection. The data were corrected for Lorentz and polarisation effects and for absorption, based on additional azimuthal scan data. Of the 4448 data measured ($+h, \pm k, \pm l$), 2772 reflections were judged to be observed [$I \geq 3\sigma(I)$] and were employed in the analysis.

Structure analysis and refinement. The structure was solved by conventional Patterson and Fourier-difference techniques, the asymmetric unit containing one complete molecule. All non-hydrogen atoms were refined anisotropically and hydrogen

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

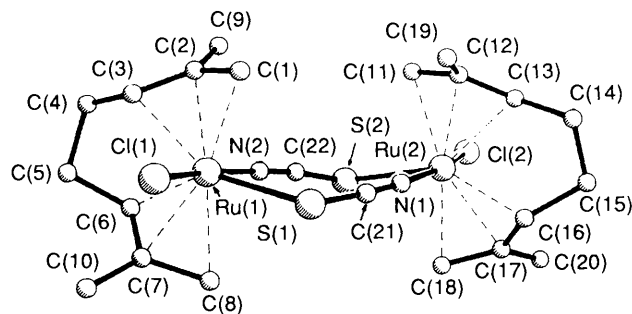
Table 1 Atomic coordinates ($\times 10^4$) for $rac\text{-}[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-SCN})\}_2]$

Atom	x	y	z
Ru(1)	1733(1)	1543(1)	2919(1)
Ru(2)	4561(1)	3529(1)	7276(1)
Cl(1)	783(5)	-335(3)	1610(3)
Cl(2)	5187(5)	5420(3)	8612(3)
S(1)	2941(5)	414(3)	3929(3)
S(2)	4456(4)	4606(3)	6138(3)
N(1)	3961(13)	2106(8)	5976(8)
N(2)	2713(13)	2990(8)	4193(9)
C(1)	-674(17)	1295(13)	3538(13)
C(2)	-836(16)	2233(12)	3240(13)
C(3)	-754(16)	2010(12)	2191(14)
C(4)	-583(25)	2903(15)	1716(15)
C(5)	884(24)	2652(14)	1208(14)
C(6)	2425(21)	2504(13)	1975(12)
C(7)	3414(22)	1628(14)	1783(13)
C(8)	4488(16)	1523(15)	2669(13)
C(9)	-983(21)	3398(13)	4008(14)
C(10)	3303(25)	755(15)	703(14)
C(11)	1766(16)	3868(11)	7176(11)
C(12)	1911(16)	2993(11)	7490(11)
C(13)	3165(17)	3171(11)	8401(10)
C(14)	3806(20)	2260(12)	8767(12)
C(15)	5792(20)	2380(12)	8924(11)
C(16)	6170(18)	2472(11)	7953(10)
C(17)	7323(18)	3314(12)	7965(11)
C(18)	7273(16)	3449(13)	7026(11)
C(19)	886(18)	1856(11)	6829(11)
C(20)	8452(19)	4128(13)	8938(11)
C(21)	3593(14)	1392(9)	5147(10)
C(22)	3431(16)	3661(10)	4970(10)

Table 2 Selected bond lengths (Å) and angles ($^\circ$) for $rac\text{-}[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-SCN})\}_2]$

Ru(1)-Cl(1)	2.409(3)	Ru(1)-S(1)	2.490(4)
Ru(1)-N(2)	2.039(8)	Ru(1)-C(1)	2.280(16)
Ru(1)-C(2)	2.271(13)	Ru(1)-C(3)	2.239(15)
Ru(1)-C(6)	2.255(20)	Ru(1)-C(7)	2.283(20)
Ru(1)-C(8)	2.248(14)	Ru(2)-Cl(2)	2.412(3)
Ru(2)-S(2)	2.483(4)	Ru(2)-N(1)	2.004(8)
Ru(2)-C(11)	2.232(13)	Ru(2)-C(12)	2.278(14)
Ru(2)-C(13)	2.257(16)	Ru(2)-C(16)	2.236(16)
Ru(2)-C(17)	2.273(14)	Ru(2)-C(18)	2.214(13)
S(1)-C(21)	1.671(11)	S(2)-C(22)	1.666(11)
N(1)-C(21)	1.158(14)	N(2)-C(22)	1.136(14)
C(1)-C(2)	1.425(26)	C(2)-C(3)	1.410(27)
C(2)-C(9)	1.500(20)	C(3)-C(4)	1.551(30)
C(4)-C(5)	1.442(29)	C(5)-C(6)	1.535(25)
C(6)-C(7)	1.354(24)	C(7)-C(8)	1.429(26)
C(7)-C(10)	1.493(22)	C(11)-C(12)	1.360(24)
C(12)-C(13)	1.404(19)	C(12)-C(19)	1.511(17)
C(13)-C(14)	1.514(24)	C(14)-C(15)	1.525(22)
C(15)-C(16)	1.500(24)	C(16)-C(17)	1.386(22)
C(17)-C(18)	1.394(25)	C(17)-C(20)	1.475(16)
Cl(1)-Ru(1)-S(1)	80.3(1)	Cl(1)-Ru(1)-N(2)	169.9(4)
S(1)-Ru(1)-N(2)	89.6(4)	Cl(2)-Ru(2)-S(2)	80.7(1)
Cl(2)-Ru(2)-N(1)	169.1(4)	S(2)-Ru(2)-N(1)	88.5(4)
Ru(1)-S(1)-C(21)	102.9(5)	Ru(2)-S(2)-C(22)	102.8(6)
Ru(2)-N(1)-C(21)	169.7(12)	Ru(1)-N(2)-C(22)	167.0(12)
S(1)-C(21)-N(1)	175.7(11)	S(2)-C(22)-N(2)	177.2(15)

atoms were placed in their predicted positions and allowed to ride on the atoms to which they were attached (C-H 0.96 Å, U_{iso} 0.08 Å²). The final full-matrix least-squares refinement included 271 parameters and gave $R = 0.0557$, $R' = 0.0596$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.0012167F^2$], and did not shift any parameter by more than 0.002 times its standard deviation. The largest residual peak was 1.21 e Å⁻³ associated with one of the metal atoms. No short intermolecular contacts were observed.

**Fig. 1** Molecular structure of $rac\text{-}[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-SCN})\}_2]$ showing the atom labelling scheme

All calculations were carried out using the SHELXTL PLUS program package⁸ on a MicroVax II computer. Final fractional atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

In alcoholic solvents the chloro-bridged dimer **1** is reduced to solvated Ru^{2+} ions by the action of $\text{Ag}[\text{BF}_4]$.⁹ However in less-reducing media the abstraction of chloride ions results in the formation of stable solutions containing the $(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}^{2+}$ and $(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Ru}^{2+}$ moieties, which readily react with Lewis bases such as nitriles⁴ and polypyridines.¹⁰ Other silver salts will also abstract halide ions from **1**, and if the counter ion is a co-ordinating one it can be directly introduced onto the metal centres. In mixed acetone-water solvent, over short reaction times, $\text{Ag}[\text{SCN}]$ reacts with **1** to give a yellow material, in ca. 50% yield, displaying a $\nu(\text{CN})$ band at 2141 cm^{-1} in the solid-state infrared spectrum, indicative of an S,N-bridged complex.¹¹ The binuclear nature of the complex was confirmed by an electron-impact mass spectrum which showed a molecular ion peak at m/z 662 ($[\text{C}_{22}\text{H}_{32}\text{Cl}_2\text{N}_2\text{-Ru}_2\text{S}_2]^+$) with an isotope distribution characteristic of two ruthenium atoms. The ¹H NMR spectrum of this material showed a typical eight-line pattern for the terminal allyl protons of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand (δ 4.81, 4.77, 4.70, 4.65, 4.13, 4.05, 3.68 and 3.56) and four-line pattern for the methyl groups (δ 2.35, 2.29, 2.26 and 2.26) similar to that observed⁶ for the parent compound **1** and characteristic of a binuclear, diastereomeric material with an inequivalence of the axial sites on the distorted trigonal-bipyramidal ruthenium ions. Over reaction times of several hours the product displays progressively less of one subset of these signals until, after 24 h, the spectrum contains predominantly only four terminal allyl signals (δ 4.77, 4.70, 4.13 and 3.56) and two methyl resonances (δ 2.35 and 2.26) consistent with the survival of only one of the diastereoisomers. In order to characterise fully this material a single-crystal structure determination was undertaken.

Fractional crystallisation of a reaction mixture containing compound **2** gave a single isomer (NMR evidence) which was examined by X-ray diffraction. The results of that study, in contrast to those on two related binuclear compounds,^{2,7} show the isomer to be of C_2 symmetry (Fig. 1). The molecule consists of two distorted trigonal-bipyramidal ruthenium ions with two of the equatorial co-ordination sites occupied by the bis(allyl) ligand which exhibit the usual local C_2 symmetry^{2,4,7} and one axial site occupied by a chloride ligand [Ru-Cl 2.409(3) and 2.412(3) Å]. The two ruthenium ions are linked by two S,N-bound thiocyanate bridges [Ru-S 2.490(4) and 2.483(4), Ru-N 2.039(8) and 2.004(8) Å] with the more bulky sulfur atoms occupying the remaining less-hindered, equatorial co-ordination sites. In contrast to most if not all other structures containing

two thiocyanate ligands bridging a pair of metal ions¹²⁻¹⁴ the two halves of the molecule are not related by a crystallographic inversion centre because the atoms of the thiocyanate bridge do not lie in the same plane. Instead, a puckered 'butterfly' type conformation is adopted by the eight-membered ring. This results in a torsion angle in the Cl-Ru-Ru-Cl linkage which deviates from the ideal value of 180° by 9.4°. It has been suggested^{12,15} that π overlap renders a planar conformation for thiocyanate-bridged structures significantly more stable and it therefore seems likely that it is the large steric requirement of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand which, in this instance, causes the distortions from planarity. Steric interactions between the methyl substituents on the bis(allyl) ligand and the axial chloride ligands cause a significant reduction in the Cl-Ru-(equatorial ligand) angle in all compounds of this type^{2,4,7} and the Cl-Ru-S angles in this case are significantly compressed [80.3(1)° and 80.7(1)°] in spite of the bulk of the sulfur atom. The corresponding angle (Cl-Ru-N) in [$\{\text{Ru}(\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\}_2(\mu\text{-N}_2\text{C}_4\text{H}_4)$] **3** is 85.4(2)°. The puckering of the ring system is thus due to the increased Cl...S interactions which, synergically, cause further chloride-methyl interactions.

From these observations it is easy to rationalise the thermodynamic preference for the C_2 isomer. The chloride ligands are constrained by the geometry of the 'Ru(SCN)₂Ru' unit to adopt a transoid configuration and, in the *rac* form, their out-of-plane distortion is angled away from the methyl groups of the bis(allyl) ligand. In the C_1 isomer the opposite effect would be in evidence and so give rise to greater unfavourable chloride-methyl steric interactions which destabilise the *meso*, **2a**, form.

Low-temperature dissolution of crystalline compound **2b** allowed the unequivocal assignment of the resonances observed in the room-temperature ¹H NMR spectrum.

Investigations are in progress into the reactions of **2** and the kinetics of the isomerisation process.

Acknowledgements

We thank the SERC for provision of the diffractometer and for a studentship (to J. W. S.), and Johnson Matthey plc for generous loans of ruthenium trichloride.

References

- 1 L. Porri, M. C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Lett.*, 1965, **47**, 4187.
- 2 A. Colombo and G. Allegra, *Acta Crystallogr., Sect. B*, 1971, **27**, 1653.
- 3 J. G. Toerien and P. H. van Rooyen, *J. Chem. Soc., Dalton Trans.*, 1991, 1563.
- 4 D. N. Cox, R. W. H. Small and R. Roulet, *J. Chem. Soc., Dalton Trans.*, 1991, 2013.
- 5 S. O. Sommerer and G. J. Palenik, *Organometallics*, 1991, **10**, 1223.
- 6 D. N. Cox and R. Roulet, *Inorg. Chem.*, 1990, **29**, 1360.
- 7 J. W. Steed and D. A. Tocher, *J. Organomet. Chem.*, 1991, **412**, C34.
- 8 G. M. Sheldrick, SHELXTL PLUS, University of Gottingen, 1986.
- 9 D. N. Cox and R. Roulet, *J. Chem. Soc., Chem. Commun.*, 1988, 951.
- 10 J. W. Steed and D. A. Tocher, *Inorg. Chim. Acta*, in the press.
- 11 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Complexes*, 4th edn., Wiley, New York, 1986, pp. 283-287.
- 12 U. A. Gregory, J. A. J. Jarvis, B. T. Kilbourn and P. G. Owston, *J. Chem. Soc. A*, 1970, 2771.
- 13 M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3277.
- 14 T. Rojo, R. Cortés, L. Lezama, M. I. Arriortua, K. Urtiaga and G. Villeneuve, *J. Chem. Soc., Dalton Trans.*, 1991, 1779.
- 15 J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1953, 2363; 1960, 2807.

Received 10th October 1991; Paper 1/05146F