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# A SELENOCYANATE DERIVATIVE OF AN ALLYL RUTHENIUM(IV) COMPOUND

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**Abstract**—Treatment of the ruthenium(IV) complex $[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ (**1**) with two equivalents of silver(I) selenocyanate gives the new dimeric compound $[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{SeCN})\}_2]$ (**2**). Although two diastereoisomers are observed in solution an X-ray structure determination reveals the $C_2$ isomer, which is isomorphous with the previously characterized thiocyanate analogue $[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{SCN})\}_2]$ (**3**). Attempts to isolate the $C_i$ isomer of **3** have resulted in the identification of a new polymorph of the $C_2$ isomer which differs from the previously reported structure in the nature of the intermolecular contacts.

The chemistry of the organometallic ruthenium(IV) chloride-bridged dimer $[\{\mathrm{dRu}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ (**1**)[1,2] has been extensively investigated by ourselves and others in recent years.[3–16] While the vast majority of derivatives are mononuclear, a number of interesting dinuclear compounds have also been identified[4,6,7,12,15,17] with oxygen, nitrogen and sulphur donor ligands. These compounds are interesting in that dinuclear compounds can exist as two diastereomers,[3] the *meso* and *rac* forms, of $C_i$ and $C_2$ symmetry, respectively. Although both generally exist in equilibrium in solution, it is usually the *meso* form which has been isolated and crystallographically characterized. Only in the case of $[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{SCN})\}_2]$ (**3**) has the *rac* form been studied crystallographically.[7] We now report the extension of our investigations to reactions of **1** with silver(I) selenocyanate, which gives crystallographically characterizable *rac*$[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{SeCN}\}_2]$ (**2**), the first allyl ruthenium(IV) compound to contain a Ru—Se bond, and describe a second polymorph of **3**.

## EXPERIMENTAL

IR spectra were recorded on a Nicolet 205 FT-IR spectrometer between 4000 and 400 cm$^{-1}$ as KBr discs 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 $[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ (**1**) was prepared by published methods. Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and was purified before use by dissolution in water and boiling to dryness. Silver(I) selenocyanate was prepared by reacting silver nitrate with an equimolar amount of potassium selenocyanate in aqueous solution. All other reagents and materials were obtained from the usual commercial sources.

### *Preparation*

$[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{SeCN})\}_2]$ (**2**). The compound $[\{\mathrm{Ru}(\eta^3:\eta^3\text{-}\mathrm{C}_{10}\mathrm{H}_{16})\mathrm{Cl}(\mu\text{-}\mathrm{Cl})\}_2]$ (0.1060 g, 0.180 mmol) was suspended in degassed acetone (10 cm$^3$). Silver (I) selenocyanate (0.0792 g, 0.372 mmol) was added and the mixture was stirred in the dark for 18 h. The resulting orange suspension was filtered through Celite. An orange filtrate was

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obtained. The material trapped on Celite was washed with chloroform and the orange washings collected. The volume of both solutions were reduced and orange solids were precipitated at low temperatures. Spectroscopic analysis indicated that both solids were identical. Combined yield: 0.0321 g, 0.043 mmol, 24%. Found: C, 34.5; H, 4.1; N, 3.3. Calc. for $C_{22}H_{32}C_{12}N_2Ru_2Se_2$: C, 35.0; H, 4.3; N, 3.7%. $^1$H NMR ($CDCl_3$): $C_2$ isomer: terminal allyl, $\delta$ 4.86 (s, 2 H), 4.74 (s, 2 H), 3.93 (s, 2 H), 3.44 (s, 2 H); internal allyl, $\delta$ 4.83 (m, 2 H), 4.65 (m, 2 H); $CH_{27}$ $\delta$ 3.20 (m, 4 H), 2.61 (m, 4 H); $CH_3$, $\delta$ 2.33 (s, 6 H), 2.24 (s, 6 H); $C_i$ isomer: terminal allyl, $\delta$ 4.86 (s, 2 H), 4.75 (s, 2H), 3.84 (s, 2 H), 3.54 (s, 2 H); internal allyl, $\delta$ 4.83 (m, 2 H), 4.65 (m, 2 H); $CH_2$, $\delta$ 3.20 (m, 4 H), 2.61 (m, 4 H); $\delta$ 2.28 (s, 6 H), 2.23 (s, 6 H). IR spectrum: $\nu$(CN) 2141, $\nu$(SeC) 619, $\delta$(SeCN) 499 cm$^{-1}$. Mass spectrum (based on $^{35}$Cl, $^{102}$Ru and $^{79}$Se): *m/z* 756 $[Ru_2(\eta^3:\eta^3\text{-}C_{10}H_{16})_2Cl_2(SeCN)_2]^+$; 721 $[Ru_2(\eta^3:\eta^3\text{-}C_{10}H_{16})_2Cl(SeCN)_2]^+$; 686 $[Ru_2(\eta^3:\eta^3\text{-}C_{10}H_{16})_2(SeCN)_2]^+$.

Crystals of isometrically pure compound **2b** were obtained by fractional crystallization from a dichloromethane solution.

### *X-ray procedures*

*Crystal data. Compound* **2**. $C_{22}H_{32}Cl_2N_2Ru_2Se_2$, $M = 755.48$, triclinic, space group $P\bar{1}$, $a = 7.794(1)$, $b = 13.090(2)$, $c = 14.099\ (3)$ Å, $\alpha = 112.36(1)$, $\beta = 99.18(1)$, $\gamma = 91.62(1)^\circ$, $V = 1307$ Å$^3$ (from least-squares refinement of diffractometer angles for 36 automatically centred reflections in the range $14 \leqslant 2\theta \leqslant 26^\circ$, $\lambda = 0.71073$ Å), $Z = 2$, $F(000) = 736$, $D_{calc} = 1.92$ g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 41.1 cm$^{-1}$. Orange plate crystal, $0.52 \times 0.25 \times 0.06$ mm.

*Data collection and processing.* The $\omega$–$2\theta$ technique was used to collect 4927 reflections (4574) in the range $5 \leqslant 2\theta \leqslant 50^\circ$ on a Nicolet R3mV diffractometer equipped with graphite monochromated Mo-$K_\alpha$ radiation. Three standard reflections measured every 97 scans showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarization effects, and empirically for absorption. The 3311 unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structure in the triclinic space group $P\bar{1}$.

*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, while hydrogens were placed in idealized positions (C—H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å$^2$). The final cycle of least-squares refinement included 272 parameters of 3311 variables and did not shift any parameter by more than 0.001 times its standard deviation. The residuals were $R = 0.0364$ and $R_w = 0.0380$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.000364F^2$] and the final difference-Fourier was featureless with no peaks greater than 0.68 e Å$^{-3}$.

*Crystal data. Compound* **3**. $C_{22}H_{32}Cl_2N_2Ru_2S_2$, $M = 661.67$, monoclinic space group $P2_1/c$, $a = 13.494(6)$, $b = 13.069(6)$, $c = 14.582(4)$ Å, $\beta = 95.99(3)^\circ$, $V = 2557.7$ Å$^3$ (from least-squares refinement of diffractometer angles for 23 automatically centred reflections in the range $10 \leqslant 2\theta \leqslant 24^\circ$, $\lambda = 0.71073$ Å), $Z = 4$, $F(000) = 1382$, $D_{calc} = 1.72$ g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 15.4 cm$^{-1}$. Yellow–orange plate, $0.60 \times 0.30 \times 0.04$ mm.

*Data collection and processing.* As described above. A total of 4741 data collected (4349 unique), with the 2250 observed reflections [$I \geqslant 3.0\sigma(I)$] used to solve and refine the structure in the monoclinic space group $P2_1/c$.

*Structure analysis and refinement.* As described above. Full matrix least-squares refinement gave $R = 0.0497$, $R_w = 0.0515$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.000617F^2$] for 272 independent

Table 1. Bond lengths (Å) and angles (°) for $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}SeCN)\}_2]$ (**2**) and $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}SCN)\}_2]$ (**3**)

| | **2** | **3** |
|---|---|---|
| Ru(1)—Cl(1) | 2.413(2) | 2.425(4) |
| Ru(2)—Cl(2) | 2.415(2) | 2.424(4) |
| Ru(1)—E(1) | 2.568(1) | 2.470(3) |
| Ru(1)—N(2) | 2.017(4) | 2.054(10) |
| Ru(2)—E(2) | 2.577(1) | 2.484(3) |
| Ru(2)—N(1) | 2.027(5) | 2.038(9) |
| E(1)—C(21) | 1.807(6) | 1.679(13) |
| C(21)—N(1) | 1.157(7) | 1.139(16) |
| E(2)—C(22) | 1.810(5) | 1.661(12) |
| C(22)—N(2) | 1.160(7) | 1.152(16) |
| Cl(1)—Ru(1)—E(1) | 79.4(1) | 78.5(1) |
| Cl(1)—Ru(1)—N(2) | 168.3(2) | 167.9(3) |
| E(1)—Ru(1)—N(2) | 88.9(2) | 89.4(3) |
| Cl(2)—Ru(2)—E(2) | 79.5(1) | 79.4(1) |
| Cl(2)—Ru(2)—N(1) | 169.2(2) | 168.5(3) |
| E(2)—Ru(2)—N(1) | 89.7(2) | 89.2(3) |
| Ru(1)—E(1)—C(21) | 100.7(3) | 105.2(4) |
| E(1)—C(21)—N(1) | 176.8(7) | 175.6(11) |
| C(21)—N(1)—Ru(2) | 169.8(6) | 168.7(9) |
| Ru(2)—E(2)—C(22) | 100.9(2) | 104.4(4) |
| E(2)—C(22)—N(2) | 176.4(7) | 177.6(10) |
| C(22)—N(2)—Ru(1) | 171.0(6) | 167.1(9) |

parameters. The largest shift/e.s.d. in the final cycle was 0.001, and the largest peak in the final electron density difference map was 0.84 e Å$^{-3}$.

Bond lengths and angles for both structures can be found in Table 1. All calculations were carried out using the SHELXTL PLUS programme package[18] on a MicroVax II computer.

## RESULTS AND DISCUSSION

The action of Ag[BF$_4$] on non-alcoholic solutions of **1** gives stable solutions containing the "Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)Cl$^+$" and "Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)$^{2+}$" moieties, which react rapidly with a wide range of Lewis bases, e.g. polypyridines.[13] If a silver salt with a coordinating counterion is employed then the new ligand can be directly introduced into the metal coordination sphere. For example, **1** reacts rapidly with two mole equivalents of Ag[O$_2$CCH$_3$] to give [Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)Cl(O$_2$CCH$_3$)][11] in high yield. We reported a short time ago that Ag[SCN] reacts readily with **1** to give [{Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)Cl($\mu$-SCN)}$_2$] (**3**).[7] If a similar procedure is used to react **1** with Ag[SeCN], then a moderate yield of the new dimeric compound [{Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)Cl($\mu$-SeCN)}$_2$] (**2**) is obtained. Evidence for the dimeric nature of the complex comes from the observation of the mass spectrum, which exhibits a parent ion peak at *m/z* 756 and fragmentation peaks corresponding to the sequential loss of two chlorine atoms. Characteristically, the $^1$H NMR spectrum showed an eight-line pattern for the terminal allyl protons and a four-line pattern for the methyl groups. This pattern is indicative of a binuclear diastereomeric material with inequivalent axial sites on each distorted trigonal bipyramidal ruthenium ion. The IR spectrum contained bands (see Experimental) which were typical of a bridging selenocyanate functionality within the molecule. Crystallization of the compound from dichloromethane gave a sample which exhibited only half the number of NMR resonances (terminal allyl, $\delta$ 4.86, 4.74, 3.93, 3.44; internal allyl, $\delta$ 4.83, 4.65; CH$_2$, $\delta$ 3.20, 2.61; CH$_3$, $\delta$ 2.33, 2.24) seen previously. The IR and mass spectra, and the microanalytical data, were essentially indistinguishable from those obtained earlier and hence it seemed very likely that the recrystallized product was a single diastereoisomer of **2**. This was subsequently confirmed by X-ray diffraction

The structure of **2** (see Fig. 1) is isomorphous with that of the already reported *rac*-[{Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)Cl($\mu$-SCN)}$_2$].[7] Each of the 2,7-dimethyl-2,6-octadiene-1,8-diyl ligands exhibits local $C_2$ symmetry with the two terminal chloride ligands having a long *trans* arrangement.[17] The unusual puckering of the eight-membered ring formed by the two metals plus two bridging thiocyanates observed for **3** is repeated in this structure and results in the observation of a Cl—Ru—Ru—Cl torsion angle of 170.9° (*cf* 170.6° in **2**). The geometry around the metal is similarly distorted [Cl—Ru—Se 79.4(1)°, 79.5(1)°; Cl—Ru—N 168.3(2)°, 169.2(2)°: *cf* Cl—Ru—S 80.3(1)°, 80.7°; Cl—Ru—N 169.1 (3)°; 169.9(3)° in **3**[7]] in both structures and in particular the Cl—Ru—E angles are compressed as a result of the steric interactions between the methyl substituents on the organic ligand and the axial chloride ions. The only difference between the two structures is in the angles formed at the chacogenide atom [Ru—E—C 100.7(3)°, 100.9(3)° for **2**; 102.8(5)°, 102.4(4)° for **3**]. This observation almost certainly results from the *ca* 0.09 Å difference in Ru—E bond lengths.

None of the binuclear compounds containing the "Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)$^{2+}$" moiety have, to date, been crystallographically characterized in both the *rac* and *meso* forms. Given that we had been initially

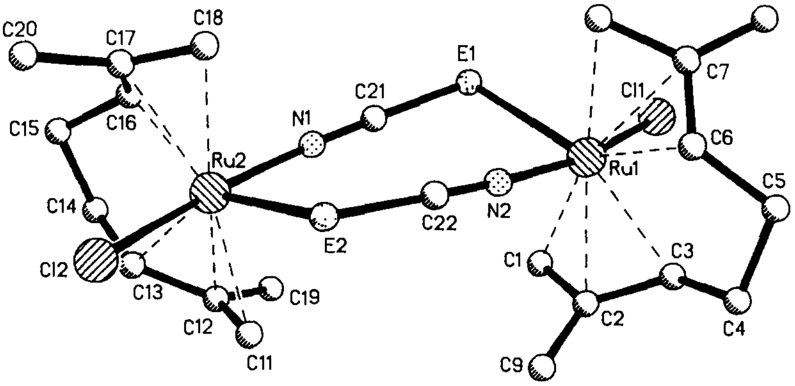

Fig. 1. The molecular structure of the compounds [{Ru($\eta^3$:$\eta^3$-C$_{10}$H$_{16}$)Cl($\mu$-ECN)}$_2$] [E = Se (**2**), E = S (**3**)] showing the common atom numbering scheme.

surprised to obtain *rac*-[{Ru($\eta^3:\eta^3$-$C_{10}H_{16}$)Cl($\mu$-SCN)}$_2$], we believed it feasible to try and isolate and characterize the *meso* form of this compound. Recrystallization from a range of solvents resulted in crystal formation. Only in the case of recrystallization from a 1 : 1 mixture of nitromethane and acetone, however, were crystals obtained in which the unit cell parameters were different (see Experimental) from those reported previously.[7] Despite these early encouraging indications, a full X-ray structural analysis clearly revealed the sample to be a polymorph of the previously characterized *rac*-[{Ru($\eta^3:\eta^3$-$C_{10}H_{16}$)Cl($\mu$-SCN)}$_2$]. There are no significant deviations between the molecular structures found in the triclinic and monoclinic forms (see ref. 7 and Table 1) and in particular the new (monoclinic) form exhibits a similar puckering of the "$Ru_2(SCN)_2$" ring. The solid state structures differ in their packing motif, with the monoclinic form exhibiting a typical "herring bone" arrangement. The packing arrangement in the monoclinic form results in the observation of short intermolecular S···S contacts of *ca* 3.55 Å. In the triclinic form, the shortest S···S contacts are of the order of 7 Å.

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