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Organometallic macrocycle chemistry

I. The reactions of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with 1,4,7-trithiacyclononane and 1,4,8,11-tetrathiacyclotetradecane

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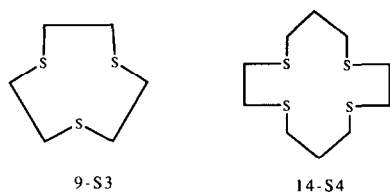
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Abstract

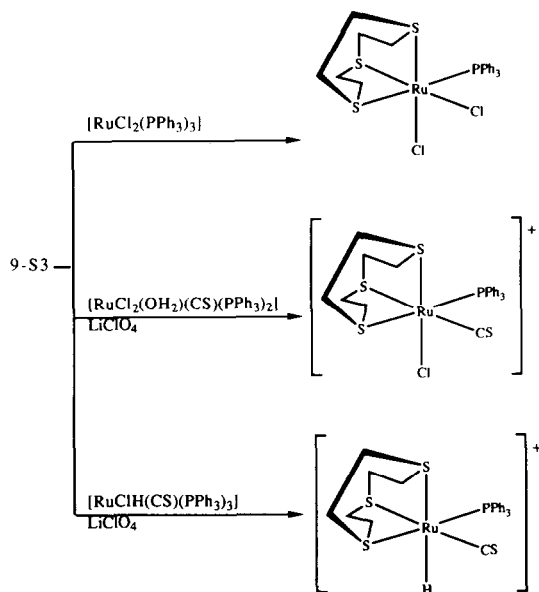
The reactions of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with the thiacycrown ethers 1,4,7-trithiacyclononane (9-S3) and 1,4,8,11-tetrathiacyclotetradecane (14-S4) provide the crystallographically characterised complexes $[\text{RuCl}_2(\text{PPh}_3)(9\text{-S3})]$ and *cis*- $[\text{RuCl}(\text{PPh}_3)(14\text{-S4})]^+$. The thiocarbonyl containing salts $[\text{RuCl}(\text{CS})(\text{PPh}_3)(9\text{-S3})]\text{ClO}_4$ and $[\text{RuH}(\text{CS})(\text{PPh}_3)(9\text{-S3})]\text{ClO}_4$ are obtained by treatment of the complexes $[\text{RuCl}_2(\text{OH}_2)(\text{CS})(\text{PPh}_3)_2]$ and $[\text{RuClH}(\text{CS})(\text{PPh}_3)_3]$ with 9-S3.

The coordination chemistry of thiamacrocycles $[\text{x-Sy}]$ (x = ring size, y = number of sulphur donors), the sulphur analogues of crown ethers, has been predominantly concerned with their reactions with simple metal halides or salts [1]. In particular the structural and electrochemical properties of cationic bis(macrocycle) complexes, *e.g.*, $[\text{M}(\text{macrocycle})_2]^{n+}$ and neutral halide adducts $[\text{MX}_n]_y(\text{macrocycle})_z$ have been well defined for many metals. The reactivity of such complexes is however a considerably less developed field of interest. Furthermore, the chemistry of thiamacrocycle complexes with mixed ligand sets is ripe for study given the comparative ignorance of the ligand reactions which such coordination spheres might support. We report herein a simple synthesis of phosphine(thiamacrocycle) complexes of ruthenium(II) and their crystallographic characterisation.

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Scheme 1. Thiacycrows 1,4,7-tetrathiacyclononane (9-S3) and 1,4,8,11-tetrathiacyclotetradecane.



Scheme 2. Synthesis of 9-S3 phosphine complexes (9-S3 = 1,4,7-trithiacyclononane).

Wilkinson's complex $[\text{RuCl}_2(\text{PPh}_3)_3]$ reacts rapidly with the potentially tridentate facial ligand 1,4,7-trithiacyclononane (9-S3, Scheme 1) to give the yellow air stable complex $[\text{RuCl}_2(\text{PPh}_3)(9\text{-S3})]$ [2*] (Scheme 2). The complex forms sparingly soluble crystals of a monosolvate from solutions in chloroform. The composition of the complex follows from elemental microanalysis, the observation of two absorbances in the far infrared spectrum attributable to a *cis*- RuCl_2 unit, a singlet resonance in the ^{31}P -NMR spectrum and a molecular ion in the FAB-mass spectrum.

The formulation of $[\text{RuCl}_2(\text{PPh}_3)(9\text{-S3})]$ was finally confirmed by X-ray crystallography [3*] (Fig. 1). In addition to verifying the octahedral coordination sphere, the crystal structure revealed an extensive hydrogen bonding network involving the chloroform solvent, the ruthenium chloride ligands and the macrocycle ethylene protons.

The reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with the tetradentate macrocycle [14-S4] does not lead to a neutral adduct, rather a cationic complex of composition

* Reference number with asterisk indicates a note in the list of references.

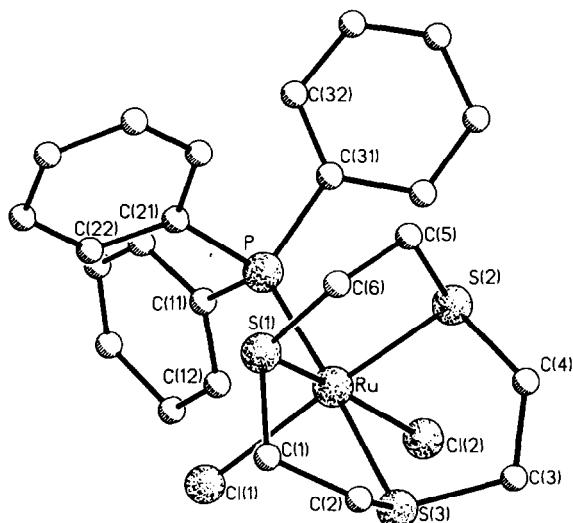
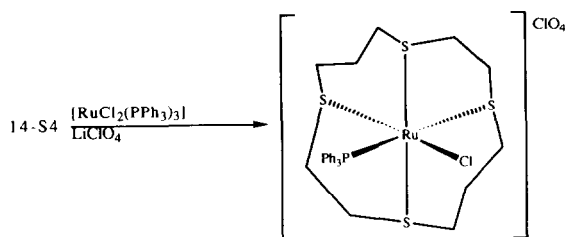


Fig. 1. Molecular geometry of the complex $[\text{RuCl}_2(\text{PPh}_3)(9\text{-S}3)]$. Bond lengths ($\text{\AA}$): Ru–P 2.345(2), Ru–Cl(1) 2.456(2), Ru–Cl(2) 2.449(2), Ru–S(1) 2.356(2), Ru–S(2) 2.270(2), Ru–S(3) 2.269(2). Hydrogen atoms are omitted for clarity.

$[\text{RuCl}(\text{PPh}_3)(14\text{-S}4)]^+$ is obtained as a chloride salt (Scheme 3) [4*]. Alternatively more crystalline materials may be obtained by anion metathesis with NaAsF_6 or LiClO_4 . Spectroscopic data for the complex do not allow an unambiguous distinction between the possible *cis* or *trans* arrangement of the phosphine and chloride ligands. However, the preliminary results of an X-ray diffraction study [5*] indicate that it is the former *cis* geometry that is adopted, as might be expected for a stepwise coordination of the sulphur donors of the macrocycle. It is believed that the small ring size of 14-S4 disfavors the *trans* coordination of ligands in octahedral $\text{ML}_2(14\text{-S}4)^{n+}$ complexes [1], as illustrated by the complexes *cis*- $[\text{RhCl}_2(14\text{-S}4)]^+$ and *trans*- $[\text{RhCl}_2(16\text{-S}4)]^+$ [6]. Nevertheless, *cis* coordination is possible as established for the complexes *trans*- $[\text{RuClH}(\text{Me}_4\text{-}14\text{-S}4)]$ (prepared from *cis*- $[\text{RuCl}_2(\text{Me}_4\text{-}14\text{-S}4)]$!) [7] and the square planar coordinated complex $[\text{Rh}(\text{Me}_4\text{-}14\text{-S}4)]_2^{2+}$ [8]. However, these complexes involve permethylated derivatives of 14-S4 and the question of the resulting introduction of a steric bias towards the *trans* coordination must be considered.



Scheme 3. Synthesis of *cis*- $[\text{RuCl}(\text{PPh}_3)(14\text{-S}4)]\text{ClO}_4$.

Thiocarbonyl ligated ruthenium complexes of 9-S3 are readily prepared by the reactions of suitable preformed precursor complexes with 9-S3: $[\text{RuCl}_2(\text{OH}_2)(\text{CS})(\text{PPh}_3)_2]$ [9] with 9-S3 followed by anion metathesis with LiClO_4 provides the salt $[\text{RuCl}(\text{CS}(\text{PPh}_3)(9\text{-S3}))\text{ClO}_4]$ [10*] whilst a hydrido derivative $[\text{RuH}(\text{CS})(\text{PPh}_3)(9\text{-S3})]\text{ClO}_4$ [10*] results from a similar treatment of $[\text{RuClH}(\text{CS})(\text{PPh}_3)_3]$.

We are currently investigating the reactions of these complexes and the general approach of using labile phosphine complexes as precursors for the coordination of thioether crown ligands.

Acknowledgement. We are grateful to Johnson Matthey Ltd for a generous loan of ruthenium salts.

Note added in proof. The complex $[\text{RuCl}_2(\text{PPh}_3)(9\text{-S3})]$ has recently been referred to in a review [11*].

References and notes

- 1 S. Cooper and S.C. Rawle, *Struct. Bond.*, 72 (1990) 1.
- 2 Data for $[\text{RuCl}_2(\text{PPh}_3)(9\text{-S3})]$. IR (Nujol) 270, 250 $\nu(\text{RuCl}_2)$. FAB-MS (nitrobenzyl alcohol matrix) m/z 613 $[M]^+$. ^1H NMR (CDCl_3 , 25°C) 1.80, 2.15, 2.42, 3.10 $[m \times 4, 12 \text{ H}, 9\text{-S3}]$, 7.30–7.65 ppm $[m \times 6, 15 \text{ H}, \text{PPh}_3]$. ^{31}P - $\{^1\text{H}\}$ 35.0 ppm. Anal. Found: C, 42.9; H, 4.2%. $\text{C}_{24}\text{H}_{27}\text{Cl}_2\text{S}_3\text{PRu} \cdot \text{CH}_2\text{Cl}_2$ calc.: C, 42.0; H, 4.4%.
- 3 X-ray structure analysis of $[\text{RuCl}_2(\text{PPh}_3)(9\text{-S3})] \cdot \text{CDCl}_3$: yellow crystals ($0.17 \times 0.31 \times 0.12 \text{ mm}$), $M_r = 758.04$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.652(4)$, $b = 14.598(7)$, $c = 18.956(7) \text{ \AA}$, $\beta = 92.47(3)^\circ$, $V = 2945(2) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.71 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.25 \text{ mm}^{-1}$, Nicolet P3m, $T = \text{ambient}$, 5755 symmetry independent reflections ($2\theta_{\text{max}} = 50^\circ$), 3577 with $|F| > 4\sigma(F)$ used for the structure determination (Patterson methods) and refinement, non-H atoms anisotropically refined, metallacycle hydrogens isotropically refined, aryl-H atoms in calculated positions, analytical absorption correction; $R = 0.036$ ($R_w = 0.036$, $w^{-1} = \sigma^2(F) + 0.00475F^2$), residual electron density +0.40 to $-0.51 \text{ e \AA}^{-3}$. Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
- 4 Data for $[\text{RuCl}(\text{PPh}_3)(14\text{-S4})]\text{AsF}_6$. IR (Nujol) 275 $\nu(\text{RuCl})$. FAB-MS (nitrobenzyl alcohol matrix) m/z 667 $[M]^+$, 407 $[M - (14\text{-S4})]^+$, 262 $[\text{PPh}_3]^+$. ^1H NMR (CDCl_3 , 25°C) δ 2.30, 2.40, 2.75, 2.80, 3.02, 3.10, 3.21, 3.75 $[m \times 8, 20 \text{ H}, 14\text{-S4}]$, 7.25–7.58 ppm $[m \times 5, 15 \text{ H}, \text{PPh}_3]$. ^{31}P - $\{^1\text{H}\}$ 33.0 ppm. Anal. Found: C, 39.3; H, 4.2%. $\text{C}_{24}\text{H}_{27}\text{Cl}_2\text{S}_3\text{PRu} \cdot \text{CH}_2\text{Cl}_2$ calc.: C, 39.3; H, 4.1%.
- 5 Whilst preliminary crystallographic results clearly establish the composition and coordination sphere geometry of $[\text{RuCl}(\text{PPh}_3)(14\text{-S4})]\text{ClO}_4$, difficulties have been encountered in the structure refinement which are currently being addressed and will be reported subsequently.
- 6 A.J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, (1989) 1675.
- 7 T. Yoshida, T. Acachi, T. Ueda, T. Tanaka and F. Goto, *J. Chem. Soc., Chem. Commun.*, (1990) 342.
- 8 T. Yoshida, T. Ueda, T. Adachi, K. Yamamoto and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, (1985) 1137.
- 9 P.J. Brothers, C.E.L. Headford and W.R. Roper, *J. Organomet. Chem.*, 195 (1980) C29.
- 10 Data for $[\text{RuCl}(\text{CS})(\text{PPh}_3)(9\text{-S3})]\text{ClO}_4$. IR (Nujol) 1408, 1298 $[\nu(\text{CS})]$, 937, 906, 835, 828 (9-S3). FAB-MS (nitrobenzyl alcohol matrix) m/z 622 $[M]^+$. ^1H NMR (CDCl_3 , 25°C) δ 2.34, 2.46, 3.02, 3.17, 3.32, 3.49 $[m \times 6, 12 \text{ H}, 9\text{-S3}]$, 7.46–7.74 ppm $[m \times 2, 15 \text{ H}, \text{PPh}_3]$. Data for $[\text{RuH}(\text{CS})(\text{PPh}_3)(9\text{-S3})]\text{ClO}_4$. IR (Nujol) 1913 $[\nu(\text{RuH})]$, 1281 $[\nu(\text{CS})]$, 933, 903, 821 (9-S3). FAB-MS (nitrobenzyl alcohol matrix) m/z 588 $[M]^+$. ^1H NMR (CDCl_3 , 25°C) δ -7.63 [d, 1 H, Ru-H, $J(\text{PH})$ 21.2 Hz], 1.75, 2.03, 2.61, 2.81, 3.04, 3.30 $[m \times 6, 12 \text{ H}, 9\text{-S3}]$, 7.44–7.64 ppm $[m \times 2, 15 \text{ H}, \text{PPh}_3]$.
- 11 R.M. Christie, Ph.D. Thesis, University of Edinburgh, 1989, referred to in: A.J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 35 (1990) 1.