Synthesis, Structure and Reactivity of Cationic Rhodium(I) and Iridium(I) Thioether Crowns: Structures of $[M([9]aneS_3)(cod)]^+$ (M = Rh, Ir; cod = cycloocta-1,5-diene) and $[Rh([9]aneS_3)(C_2H_4)_2]^+$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane)

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Reaction of M^I species with $[9]aneS_3$ affords half-sandwich complexes including $[M([9]aneS_3)(cod)]^+$, $[M([9]aneS_3)(coe)_2]^+$ (M = Rh, Ir; coe = cyclooctene), $[(Rh([9]aneS_3)(C_2H_4)_2]^+$, $[Rh([9]aneS_3)(C_2H_4)(PR_3)]^+$ (R = Ph, cyclohexyl), $[Rh([9]aneS_3)(CO)(PPh_3)]^+$ and $[Rh([9]aneS_3)(tcne)(NCMe)]^+$; crystal structure determinations of $[M([9]aneS_3)(cod)]^+$ (M = Rh, Ir) and $[Rh([9]aneS_3)(C_2H_4)_2]^+$ confirm these complexes to be five-coordinate, and the latter species reacts with C–X (X = halide) bonds.

The insertion of $[M(C_5Me_5)]$ and $[M(HBPz)]$ (Pz - pyrazolyl) fragments into C–H bonds of alkane and aromatic substrates has been reported for M = Rh^I and Ir^I.[1,2] We have been interested in developing alternative methodologies for the stabilisation of facially protected mononuclear Rh^I and Ir^I centres using 6-electron donor ligands. $[9]aneS_3$ is particularly attractive in this respect: its ability to act as an efficient facial blocking group for a range of transition metal centres is now well established,[3] and would afford thioether coordination at the metal centre rather than the more usual N- (pyrazolylborate), P- (triphos) or carbocyclic (arene, cyclopentadienyl) C-donation. In addition, few examples of genuinely low-valent metal complexes of thioether crowns have been reported.[4,5] Most of these are Mo^0 complexes incorporating S_4-donor ligands;[5] no structural or synthetic data on thioether crown complexes incorporating ethylene have been described previously.

Reaction of $[MCl(cod)]_2$ (cod = cycloocta-1,5-diene) with two molar equivalents of [9]aneS_3 in MeOH (for Rh) or in CH_2Cl_2 (for Ir) containing $NaBF_4$ affords [M([9]aneS_3)(cod)]$^+$ in 70% (Rh) and 30% (Ir) yields.† The single crystal X-ray structure‡§ of [Rh([9]aneS_3)(cod)]$^+$ shows (Fig. 1) five-coordination about Rh^I with [9]aneS_3 bound facially *via* all three S-donors. Two crystallographically independent complex cations are observed in the asymmetric unit each having the cod ligand bound in an η^4 manner. A similar five-coordinate structure is observed for [Ir([9]aneS_3)(cod)]$^+$.§¶ These complexes are therefore 18-electron species and this is reflected in their relative stability and inertness. Loss of the chelated cod ligand occurs slowly in solution under ambient conditions; thus, reaction of [Rh([9]aneS_3)(cod)]$^+$ with tcne (tcne = tetracyanoethylene) in MeCN affords [Rh[9]aneS_3(tcne)(NCMe)]$^+$ involving bound tcne.†

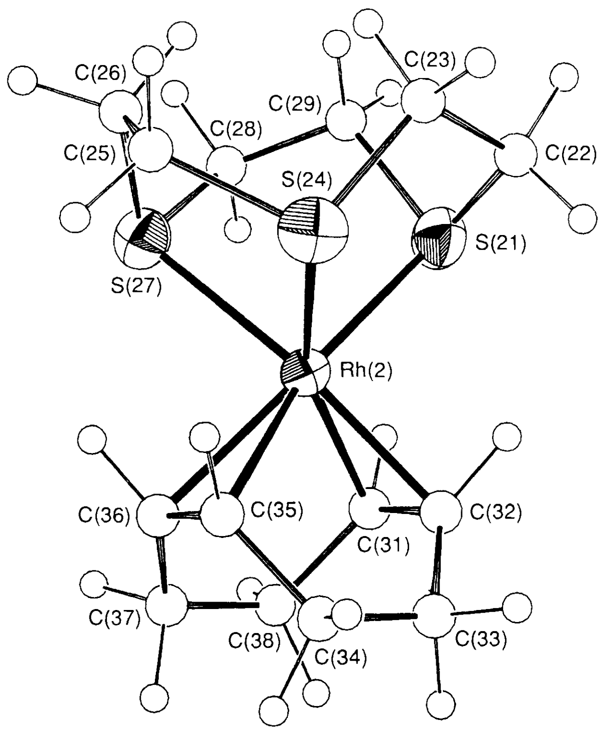

Fig. 1 Single crystal X-ray structure of [Rh([9]aneS_3)(cod)]$^+$. Bond lengths (Å) are given for independent cations (*a*) and (*b*). Cation (*b*) is shown. (*a*) Rh(1)–S(1) 2.322(3), Rh(1)–S(4) 2.400(3), Rh(1)–S(7) 2.451(3), Rh(1)–C(11) 2.069(12), Rh(1)–C(12) 2.133(12), Rh(1)–C(15) 2.223(12), Rh(1)–C(16) 2.199(12), C(11)–C(12) 1.424(17), C(15)–C(16) 1.377(17) Å. (*b*) Rh(2)–S(21) 2.305(3), Rh(2)–S(24) 2.441(3), Rh(2)–S(27) 2.436(3), Rh(2)–C(31) 2.108(13), Rh(2)–C(32) 2.080(11), Rh(2)–C(35) 2.193(15), Rh(2)–C(36) 2.214(18), C(31)–C(32) 1.408(17), C(35)–C(36) 1.279(23) Å. Bond lengths (Å) for [Ir([9]aneS_3)cod)]$^+$; Ir–S(1) 2.319(5), Ir–S(4) 2.343(4), Ir–S(7) 2.419(4), Ir–C(11) 2.188(15), Ir–C(12) 2.141(15), Ir–C(15) 2.166(14), Ir–C(16) 2.199(14), C(11)–C(12) 1.418(21), C(15)–C(16) 1.411(19) Å.

Reaction of $[MCl(C_2H_4)_2]_2$ with two molar equivalents of [9]aneS_3 in MeOH (for Rh) and in tetrahydrofuran (thf) (for Ir) containing $NaBF_4$ affords the reactive species [M([9]aneS_3)$(C_2H_4)_2$]$^+$ in 50% yield for both Rh and Ir. A crystal of the Rh^I complex was picked from the cold mother liquor and protected by an atmosphere of cold CO_2 gas during transfer to a Stoë STADI-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[6] The single crystal X-ray structure§ || of

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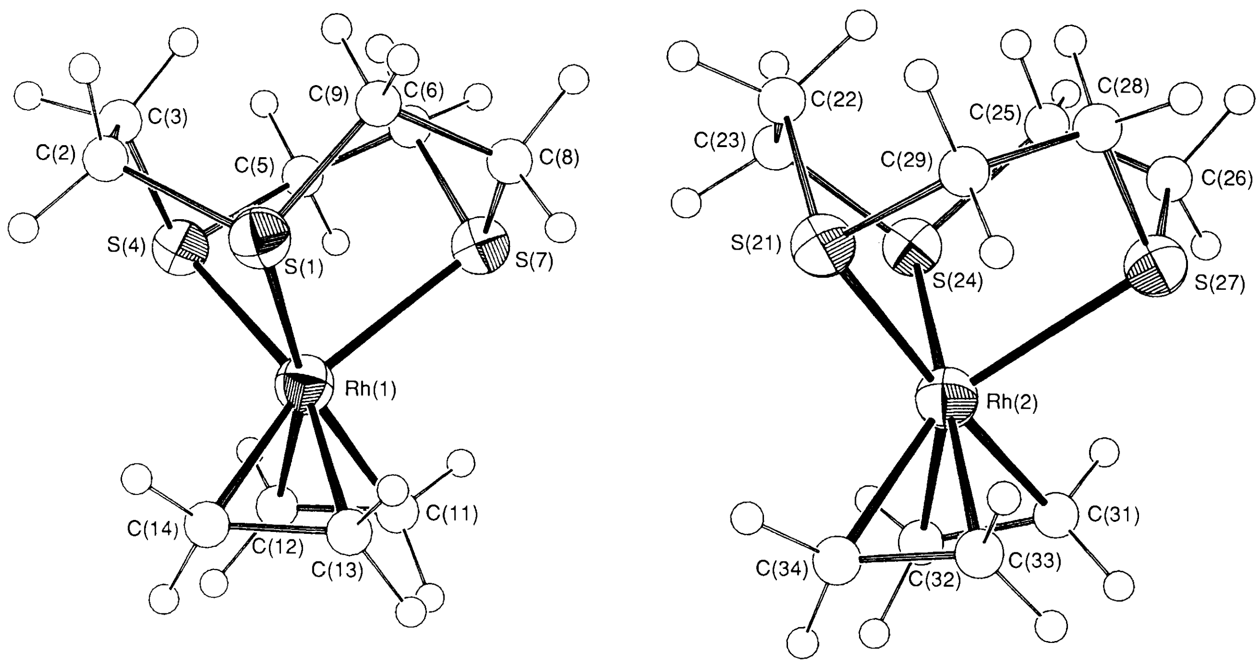
† These complexes have been characterised by IR and UV spectroscopy, ^1H, ^{13}C and, where appropriate, ^{31}P NMR and fast-atom bombardment mass spectroscopy, and by elemental analysis.

‡ *Crystal data* for $C_{14}H_{24}S_3Rh^+BF_4^-$, M = 478.20, triclinic, space group $P\bar{1}$, a = 11.491(13), b = 12.803(6), c = 13.377(15) Å, α = 88.12(7), β = 70.30(8), γ = 74.68(7)°, V = 1784 Å^3 (from setting angles for 14 reflections with 2θ = 42–44°, $\bar{\lambda}$ = 1.54184 Å, T = 298 K), Z = 4, D_c = 1.781 g cm^{-3}, μ = 11.482 mm^{-1}. $F(000)$ = 968. STADI-4 diffractometer, graphite-monochromated Cu-Kα X-radiation, T = 298 K, ω–2θ scans, 2838 unique data collected ($2\theta_{max}$ 90°, h $-9 \rightarrow 10$, k $-11 \rightarrow 11$, l $0 \rightarrow 12$), initial correction for absorption by means of Ψ scans (min. and max. transmission factors 0.0182, 0.0889 respectively), giving 2585 reflections with $F \geqslant 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement was observed. A Patterson synthesis located both Rh atoms and iterative cycles of least-squares refinement and difference Fourier synthesis located the remaining non-H atoms. At isotropic convergence, final corrections (min. 0.794, max. 1.631) were applied empirically using DIFABS.[11] The structure was then refined (by least-squares on F[12]) with anisotropic thermal parameters for Rh, S, F and C and with H atoms included at fixed, calculated positions.[12] At final convergence R, R_w = 0.0590, 0.0866 respectively, S = 1.069 for 407 refined parameters and the final ΔF synthesis showed no feature above 1.01 e Å^{-3}. An isotropic extinction correction refined to 1.0×10^{-6}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.007284F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.008.

§ Atomic scattering factors were inlaid[12] or taken from ref. 15, molecular geometry calculations utilised CALC[16] and the Figures were produced by ORTEPII.[17] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ *Crystal data* for $C_{14}H_{24}S_3Ir^+PF_6^-$: M = 625.7, monoclinic, space group $P2_1/c$, a = 9.6404(8), b = 11.9222(14), c = 17.2174(18) Å, β = 103.957(8)°, V = 1920.5 Å^3 [from 2θ values of 42 reflections measured at $\pm\omega$ (2θ = 24–26°, $\bar{\lambda}$ = 0.71073 Å), T = 298 K], Z = 4, D_c = 2.164 g cm^{-3}, μ = 7.372 mm^{-1}. A pale yellow plate, 0.031 × 0.084 × 0.290 mm, grown from MeCN–Et_2O, was mounted on a Stoë STADI-4 four-circle diffractometer. Data collection employing graphite-monochromated Mo-Kα X-radiation, ω–2θ scans and the learnt-profile method[13] yielded 3709 amplitudes to $2\theta_{max}$ = 45°. Initial corrections for absorption were applied by means of Ψ scans. Merging of equivalent reflections gave 2372 unique data (R_{int} = 0.035), of which 1919 with $F \geqslant 6\sigma(F)$ were used in all calculations. No significant crystal decay or movement was observed. A Patterson synthesis located the Ir and iterative cycles of least-squares refinement and difference Fourier synthesis located the remaining non-H atoms. At isotropic convergence, final corrections for absorption were applied empirically using DIFABS.[11] The structure was then refined (by least-squares on F[12]) with anisotropic thermal parameters for Ir, S, P, F and the C atoms of the cod ligand. The C atoms in the [9]aneS_3 ligand were found to be disordered but the application of constraints (S–C = 1.83, C–C = 1.52 Å; $\angle$SCC = 109.5°) allowed the refinement of two equally occupied conformations. H atoms were included at fixed, calculated positions.[12] At final convergence R, R_w = 0.0407, 0.0521 respectively, S = 1.162 for 220 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 1.40 e Å^{-3}.

|| *Crystal data* for $C_{10}H_{20}S_3Rh^+\cdot BF_4^-$, M = 426.12, monoclinic, space group $P2_1/c$, a = 10.720(12), b = 8.547(17), c = 32.89(5) Å, β = 92.62(11)°, V = 3011 Å^3 (from setting angles for 12 reflections with 2θ = 15–26°, $\bar{\lambda}$ = 0.71073 Å, T = 173 ± 0.1 K), Z = 8, D_c = 1.880 g cm^{-3}, μ = 1.541 mm^{-1}, $F(000)$ = 1712. STADI-4 diffractometer, graphite-monochromated Mo-Kα X-radiation, T = 173 K, ω–2θ scans, 5030 data collected ($2\theta_{max}$ 45°, h $-11 \rightarrow 11$, k $0 \rightarrow 9$, l $0 \rightarrow 35$), 3237 unique (R_{int} = 0.091), giving 1612 reflections with $F \geqslant 4\sigma(F)$. A drift curve based on the variation in the intensity of three standard reflections was applied to the data during processing. A Patterson synthesis located both Rh atoms and iterative cycles of least-squares refinement and difference Fourier synthesis located the remaining non-H atoms. At isotropic convergence, final corrections (min. 1.127, max. 1.689) were applied empirically using DIFABS.[11] The structure was then refined (by least-squares on F[12]) with anisotropic thermal parameters for Rh, S and F. Macrocyclic H atoms were included at fixed, calculated positions,[12] while those of the ethylene molecules were placed by analogy with a related complex.[14] At final convergence R, R_w = 0.0825, 0.0910 respectively, S = 1.179 for 233 refined parameters and the final ΔF synthesis showed no feature above 1.17 e Å^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.00185F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.017.



Cation (*a*) Cation (*b*)

Fig. 2 Single crystal X-ray structure of $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$. Bond lengths (Å) are given for independent cations (*a*) and (*b*). Both cations are shown. (*a*) Rh(1)–S(1) 2.322(9), Rh(1)–S(4) 2.437(9), Rh(1)–S(7) 2.432(9), Rh(1)–C(11) 2.21(4), Rh(1)–C(12) 2.21(5), Rh(1)–C(13) 2.12(5), Rh(1)–C(14) 2.05(4), C(11)–C(12) 1.33(6), C(13)–C(14) 1.43(6) Å. (*b*) Rh(2)–S(21) 2.337(9), Rh(2)–S(24) 2.327(10), Rh(2)–S(27) 2.469(10), Rh(2)–C(31) 2.11(3), Rh(2)–C(32) 2.18(4), Rh(2)–C(33) 2.15(4), Rh(2)–C(34) 2.22(3), C(31)–C(32) 1.43(5), C(33)–C(34) 1.41(5) Å.

$[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$ confirms (Fig. 2) five-coordination at the $\mathrm{Rh^I}$ centre. As with $[\mathrm{Rh([9]aneS_3)(cod)}]^+$, two crystallographically independent cations are observed in the asymmetric unit; cation (*a*) shows one short and two long Rh–S distances while the other, cation (*b*), shows two short and one long distances. Cations (*a*) and (*b*) also differ in the relative orientation of the [9]aneS$_3$ ring to the coordinated ethylene. The Rh–S bond lengths in these $\mathrm{Rh^I}$ structures are longer than in related $\mathrm{Rh^{III}}$ complexes.[7] The related species $[\mathrm{M([9]aneS_3)(coe)_2}]^+$ (coe = cyclooctene) can be prepared by reaction of $[\mathrm{MCl(coe)_2}]_2$ with two molar equivalents of [9]aneS$_3$, while reaction of [9]aneS$_3$ with $[\mathrm{RhCl(CO)(PPh_3)_2}]$ affords $[\mathrm{Rh([9]aneS_3)(CO)(PPh_3)}]^+$.†

The $\mathrm{C_2H_4}$ ligands in $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$ are not particularly labile and substitution of $\mathrm{C_2H_4}$ by $\mathrm{PR_3}$ or CO does not readily occur up to the decomposition temperature of the compound in solution. Thus, no carbonyl complex could be isolated on reaction of $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$ with CO in refluxing thf. This may reflect the inertness of the 18-electron metal centre. The related complex $[\mathrm{Rh(C_5Me_5)(C_2H_4)_2}]$ likewise adds nucleophiles only under vigorous conditions, with alkene exchange occurring very slowly at room temperature.[8] Reaction of $[\mathrm{Rh_2Cl_2(C_2H_4)_2}]$ with $\mathrm{PR_3}$ followed by addition of [9]aneS$_3$ and $\mathrm{NaBF_4}$ or $\mathrm{NH_4PF_6}$ affords $[\mathrm{Rh([9]aneS_3)(PR_3)(C_2H_4)}]^+$ [R = Ph, cyclohexyl (Cy)] and $[\mathrm{Rh([9]aneS_3)(PPh_3)_2}]^+$.

Weak metal → alkene π back-bonding would be expected in $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$ owing to the cationic charge on the complex. The ^{1}H NMR spectrum (233 K, $\mathrm{CD_3COCD_3}$, 360 MHz) of $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$ shows alkene resonances at δ 2.76 (d, $^2J_{\mathrm{H-Rh}}$ 1.56 Hz) and the ^{13}C NMR spectrum (233 K, $\mathrm{CD_3COCD_3}$, 50.32 MHz) shows δ 51.41 (d, $^1J_{\mathrm{C-Rh}}$ 9.63 Hz) for the alkene C-centres. Alkene rotation is not frozen out for this complex down to 183 K. $[\mathrm{Ir([9]aneS_3)(C_2H_4)_2}]^+$ shows alkene resonances at δ 2.19 and 34.35 by ^{1}H (298 K, $\mathrm{CD_3COCD_3}$, 360 MHz) and ^{13}C (50.32 MHz) NMR spectroscopy respectively. Lowering the temperature to 178 K leads to near collapse of the ^{1}H NMR signals for the coordinated ethylene suggesting a coalescence temperature of near 170 K, beyond the range of the solvent. The Raman spectrum of $[\mathrm{Rh([9]aneS_3)(PCy_3)(C_2H_4)}]^+$ shows the C=C stretching vibration, $\nu_{\mathrm{C=C}}$, at 1550 cm^{-1}.

The results described herein confirm that five-coordinate half-sandwich species incorporating the $[\mathrm{Rh([9]aneS_3)}]^+$ fragment, the thioether analogues of $[\mathrm{Rh(C_5Me_5)}]$ and [Rh(HBPz)], can be synthesised, and suggest that the $\mathrm{Rh^I}$ complex[7] $[\mathrm{Rh([9]aneS_3)_2}]^+$ is most likely five-coordinate in the solid state. Loss of ethylene from $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$ would, in principle, afford the 16-electron fragment $[\mathrm{Rh([9]aneS_3)(C_2H_4)}]$ which should insert into substrate molecules.[10] Indeed, dissolution of $[\mathrm{Rh([9]aneS_3)(C_2H_4)_2}]^+$ or $[\mathrm{Rh([9]aneS_3)(C_2H_4)PR_3}]^+$ in $\mathrm{CH_2Cl_2}$ affords $[\mathrm{Rh([9]aneS_3)(CH_2Cl)Cl(C_2H_4)}]^+$ and $[\mathrm{Rh([9]aneS_3)(CH_2Cl)Cl(PR_3)}]^+$ in low yield; the final product in both reactions is the highly insoluble $[\mathrm{Rh([9]aneS_3)Cl_3}]$. It is not clear whether slippage of the tridentate [9]aneS$_3$ to a bidentate coordination to afford a 16-electron intermediate is of relevance here, although examples of bidentate [9]aneS$_3$ have been reported for d^8 complexes.[3,9]

Current work is aimed at studying the reactions of these half-sandwich $[\mathrm{M([9]aneS_3)}]^+$ complexes with electrophiles, nucleophiles, aromatics and alkanes.

We are very grateful to ICI Colours and Fine Chemicals Plc and the SERC for a CASE Award to M. A. H., Dr R. Peacock

(University of Glasgow) for Raman spectra, Dr Robin Perutz (University of York) for helpful discussions, the SERC for support, and Johnson Matthey Plc for generous loans of platinum metals.

Received, 6th September 1990; Com. 0/04076B

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