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FULL PAPER

Synthesis, characterisation and reactions of ruthenium(II) complexes based upon $[RuL^3]^{2+}$ (L^3 = tripodal triseleno- or tritelluro-ether) fragments. Structures of $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$ and $[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$

William Levason, Simon D. Orchard and Gillian Reid

Department of Chemistry, University of Southampton, Southampton, UK SO17 1BJ

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The reaction of $[RuCl_2(PPh_3)_3]$ with tripodal Group 16 donor ligands L^3 $\{MeC(CH_2EMe)_3$ (E = Se or Te) and $MeC(CH_2TePh)_3\}$ gave $[RuCl_2(PPh_3)L^3]$ complexes which have been characterised by elemental analysis, IR and NMR spectroscopy and ES^+ mass spectrometry. The structure of $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$ reveals a distorted octahedral geometry with a facially co-ordinated triselenoether. The reaction of $[RuCl_2(dmso)_4]$ with L^3 gave $[RuCl_2(dmso)L^3]$ which have similarly been characterised, including a crystal structure of $[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$, which is *fac*-octahedral with S-bonded dmso. The $[RuCl_2(dmso)L^3]$ species react with $Ag[CF_3SO_3]$ in MeCN to produce $[Ru(MeCN)_3L^3]^{2+}$ $\{L^3 = MeC(CH_2SeMe)_3$ or $MeC(CH_2TePh)_3\}$. The MeCN is labile and readily replaced by a second tridentate ligand to give mixed tripod ligand complexes including $[Ru\{MeC(CH_2SMe)_3\}\{MeC(CH_2SeMe)_3\}][CF_3SO_3]_2$ and $[Ru\{MeC(CH_2SeMe)_3\}\{MeC(CH_2TePh)_3\}][CF_3SO_3]_2$. Attempts to generate hydride species by reaction of $[Ru(MeCN)_3L^3]^{2+}$ with $NaBH_4$ in ethanol bring about decomposition.

Introduction

The development of ruthenium based catalysts is a very active area. Good examples are provided by ruthenium(II) complexes of the tripodal triphosphine, $MeC(CH_2PPh_2)_3$ (triphos),[1] notably the work of Bianchini *et al.* who have developed ruthenium (and Rh and Ir) systems which mimic metal catalysed hydrodesulfurisation processes.[2–4] The chemistry of Ru^{II} with thioether ligands, in particular the macrocyclic $[9]aneS_3$, has received considerable attention,[5–8] with complexes such as $[Ru([9]aneS_3)_2]^{2+}$ and $[RuCl([9]aneS_3)(Me_2SO)_2]^+$ being reported. The species $[RuCl_2(PPh_3)([9]aneS_3)]$ and $[RuX(CS)(PPh_3)([9]aneS_3)][PF_6]$ (X = H, Cl, SCN or SC_6H_4Me-4) have been prepared as part of an investigation into organometallic macrocycle chemistry.[6] These studies have also reported the σ-vinyl and σ-aryl complexes $[Ru(CH{=}CH_2)(CO)(PPh_3)([9]aneS_3)]^+$ and $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)([9]aneS_3)]^+$.

The chemistry of ruthenium(II) with the heavier seleno- and telluro-ether ligands has generally been limited to the preparation and characterisation of bidentate analogues including $[RuCl_2(L–L)_2]$ (L–L = diseleno- or ditelluro-ether) and $[RuCl(PPh_3)(L–L)_2][PF_6]$ (L–L = ditelluroether).[9,10] The crystal structures of the macrocyclic *cis*-$[RuCl_2([16]aneSe_4)]$ and *trans*-$[RuCl(PPh_3)([16]aneSe_4)][PF_6]$ have also been reported.[11] The recent successful preparation of low and medium oxidation state rhodium and iridium organometallic complexes with the Group 16 tripodal ligands L^3 $\{L^3 = MeC(CH_2EMe)_3$ (E = Se or Te) or $MeC(CH_2TePh)_3\}$[12] led us to investigate their reaction chemistry on ruthenium(II) centres. Our investigation into homoleptic platinum metal complexes with L^3 reported the synthesis of the complexes $[Ru(L^3)_2]^{2+}$ $\{L^3 = MeC(CH_2EMe)_3$ (E = S, Se or Te) or $MeC(CH_2TePh)_3\}$.[13] Here we report on the preparation and reactions of species containing the $[RuL^3]^{2+}$ fragment.

Experimental

The complexes $[RuCl_2(PPh_3)_3]$[14] and $[RuCl_2(dmso)_4]$[15] were prepared by literature procedures, as were the ligands $MeC(CH_2SMe)_3$,[16] $MeC(CH_2SeMe)_3$,[17] $MeC(CH_2TeMe)_3$,[18] and $MeC(CH_2TePh)_3$.[19] Physical measurements were made as described previously.[10,12]

Preparations

$[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$. $[RuCl_2(PPh_3)_3]$ (208 mg, 2.2×10^{-4} mol) was added to $MeC(CH_2SeMe)_3$ (77 mg, 2.2×10^{-4} mol) in dry CH_2Cl_2 (40 cm^3) and stirred at room temperature for 18 h to give an orange solution. This was reduced to *ca.* 2 cm^3 *in vacuo* and diethyl ether (10 cm^3) added to precipitate an orange solid. Yield 113 mg, 66% (Found: C, 39.9; H, 4.4. Calc. for $C_{26}H_{33}Cl_2PRuSe_3$: C, 39.8; H, 4.2%). ^1H NMR ($CDCl_3$, 300 K): δ 1.37 (s, 1H, CCH_3), 1.6–2.0 (m, 3H, $SeCH_3$), 2.3–2.6 (m, 2H, $SeCH_2$) and 7.2–8.2 (m, 5H, Ph). ^{77}Se-$\{^1H\}$ NMR (CH_2Cl_2–CH_3OH–$CDCl_3$, 300 K): δ 165, 168, 171, 245, 247, 272 and 275. ^{31}P-$\{^1H\}$ NMR (CH_2Cl_2–CH_3OH–$CDCl_3$, 300 K): δ 35.2 and 34.4. ES^+ (MeCN): m/z = 792 and 751; calc. for $[^{102}Ru^{35}Cl(PPh_3)\{MeC(CH_2{}^{80}SeMe)_3\}(NCMe)]^+$ 794 and $[^{102}Ru^{35}Cl(PPh_3)\{MeC(CH_2{}^{80}SeMe)_3\}]^+$ 753. IR: 3050w, 2962w, 2940w, 1481m, 1433m, 1358s, 1090s, 989m, 907w, 834m, 746m, 697s, 614w, 523s, 499m, 459m, 422m, 290m and 216m cm^{-1}.

$[RuCl_2(PPh_3)\{MeC(CH_2TeMe)_3\}]$. This was prepared similarly as a light brown solid (61%) (Found: C, 31.9; H, 3.5. Calc. for $C_{26}H_{33}Cl_2PRuTe_3 \cdot CH_2Cl_2$: C, 31.9; H, 3.3%). ES^+ (MeCN): m/z = 938 and 897; calc. for $[^{102}Ru^{35}Cl(PPh_3)\{MeC(CH_2{}^{130}TeMe)_3\}(NCMe)]^+$ 944 and $[^{102}Ru^{35}Cl(PPh_3)\{MeC(CH_2{}^{130}TeMe)_3\}]^+$ 903. IR: 3051w, 2922w, 1481m, 1432s, 1360s, 1267w, 1217w, 1190w, 1090s, 998m, 835s, 744s, 697s, 614w, 526s, 459w, 309m and 223m cm^{-1}.

$[RuCl_2(PPh_3)\{MeC(CH_2TePh)_3\}]$. This was prepared similarly as an orange solid (72%) (Found: C, 43.7; H, 3.1. Calc. for $C_{41}H_{39}Cl_2PRuTe_3$: C, 44.1; H, 3.5%). ^{125}Te-$\{^1H\}$ NMR (CH_2Cl_2–CH_3OH–$CDCl_3$, 300 K): δ 566, 570, 741, 742 and

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770. $^{31}P-\{^1H\}$ NMR (CH_2Cl_2–CH_3OH–$CDCl_3$, 300 K): δ 25.6. ES$^+$ (MeCN): m/z = 1122 and 1081; calc. for $[^{102}Ru^{35}Cl(PPh_3)\{MeC(CH_2{}^{130}TePh)_3\}(NCMe)]^+$ 1130 and $[^{102}Ru^{35}Cl(PPh_3)\{MeC(CH_2{}^{130}TePh)_3\}]^+$ 1089. IR: 3052w, 1571m, 1476m, 1432s, 1358s, 1263w, 1187w, 1090s, 1017m, 998m, 834w, 797w, 735s, 694s, 524s, 456m and 250m cm^{-1}.

[RuCl$_2$(dmso){MeC(CH$_2$SeMe)$_3$}]. [RuCl$_2$(dmso)$_4$] (40 mg, 8.3×10^{-5} mol) was added to dry toluene (40 cm^3) and heated to 100 °C for 10 min. The resulting suspension was allowed to cool, $MeC(CH_2SeMe)_3$ (29 mg, 8.3×10^{-5} mol) in toluene (5 cm^3) added and the mixture heated to 100 °C for 24 h. The resulting precipitate was filtered off and washed with diethyl ether (10 cm^3) to give an orange solid (30 mg, 60%) (Found: C, 20.3; H, 3.8. Calc. for $C_{10}H_{24}Cl_2ORuSSe_3$: C, 20.0; H, 4.0%). ^1H NMR ($CDCl_3$, 300 K): δ 1.34 (s, 1H, CCH_3), 2.1–2.6 (m, 3H, $SeCH_3$), 2.61 (s, 2H, CH_3S) and 3.35–3.51 (m, 2H, $SeCH_2$). $^{77}Se-\{^1H\}$ NMR (CH_2Cl_2–$CDCl_3$, 300 K): δ 168, 170, 218, 219, 229 and 244. FAB MS (3-nitrobenzyl alcohol): m/z = 601, 567 and 523; calc. for $[^{102}Ru^{35}Cl_2\{dmso\}\{MeC(CH_2{}^{80}SeMe)_3\}]^+$ 604, $[^{102}Ru^{35}Cl(dmso)\{MeC(CH_2{}^{80}SeMe)_3\}]^+$ 569 and $[^{102}Ru^{35}Cl_2\{MeC(CH_2{}^{80}SeMe)_3\}]^+$ 526. IR: 2950w, 1413m, 1358s, 1262m, 1076s, 1017m, 924w, 834w, 802w, 713w, 678w, 614w, 540w, 427m and 238m cm^{-1}.

[RuCl$_2$(dmso){MeC(CH$_2$TeMe)$_3$}]. This was prepared similarly as a brown solid (61%) (Found: C, 16.5; H, 3.5. Calc. for $C_{10}H_{24}Cl_2ORuSTe_3$: C, 16.1; H, 3.2%). ^1H NMR ($CDCl_3$, 300 K): δ 1.26 (s, 1H, CCH_3), 2.1–2.4 (m, 3H, $TeCH_3$), 2.63 (s, 2H, CH_3S) and 3.40–3.55 (m, 2H, $TeCH_2$). $^{130}Te-\{^1H\}$ NMR (CH_2Cl_2–$CDCl_3$, 300 K): δ 222 see text. FAB MS (3-nitrobenzyl alcohol): m/z = 748; calc. for $[^{102}Ru^{35}Cl_2(dmso)\{MeC(CH_2{}^{130}TeMe)_3\}]^+$ 754. IR: 2925w, 1359s, 1095s, 1018m, 996m, 835m, 682w, 613w, 536w, 425w and 236m cm^{-1}.

[RuCl$_2$(dmso){MeC(CH$_2$TePh)$_3$}]. This was prepared similarly except an orange solution was produced upon heating for 24 h. The solvent volume was reduced *in vacuo* to 5 cm^3 and diethyl ether added to give an orange solid (69%) (Found: C, 31.8; H, 3.3. Calc. for $C_{25}H_{30}Cl_2ORuSTe_3$: C, 32.2; H, 3.2%). ^1H NMR ($CDCl_3$, 300 K): δ 1.26 (s, 1H, CCH_3), 2.57 (s, 2H, CH_3S), 3.10–3.50 (m, 2H, $TeCH_2$) and 6.8–8.2 (m, 5H, TePh). $^{130}Te-\{^1H\}$ NMR (CH_2Cl_2–$CDCl_3$, 300 K): δ 570, 677 and 737. FAB MS (3-nitrobenzyl alcohol): m/z = 821; calc. for $[^{102}Ru^{35}Cl\{MeC(CH_2{}^{130}TePh)_3\}]^+$ 827. IR: 3050w, 2951w, 1570w, 1475m, 1432m, 1359s, 1262m, 1089s, 1017s, 998s, 802m, 740m, 693m, 612w, 541w, 455w, 421w and 253m cm^{-1}.

[Ru(NCMe)$_3${MeC(CH$_2$SeMe)$_3$}][CF$_3$SO$_3$]$_2$. [RuCl$_2${dmso}{MeC(CH$_2$SeMe)$_3$}] (34 mg, 5.7×10^{-5} mol) was added to $AgCF_3SO_3$ (29 mg, 1.1×10^{-4} mol) in MeCN (40 cm^3). The mixture was refluxed for 2 h, cooled and filtered to remove the precipitated AgCl. The solvent volume was reduced *in vacuo* to 2 cm^3 and diethyl ether added to give a light yellow solid (40 mg, 80%) (Found: C, 21.9; H, 3.2; N, 4.8. Calc. for $C_{16}H_{27}F_6N_3O_6RuS_2Se_3$: C, 22.0; H, 3.1; N, 4.8%). ^1H NMR ($(CD_3)_2CO$, 300 K): δ 1.47 (s, 1H, CCH_3), 2.42 (s, 3H, $NCCH_3$), 2.51 (s, 3H, $SeCH_3$) and 2.85 (m, 2H, $SeCH_2$). $^{77}Se-\{^1H\}$ NMR (MeCN–$CDCl_3$, 300 K): δ 159. ES$^+$ (MeCN): m/z = 288 and 267; calc. for $[^{102}Ru(NCMe)_3\{MeC(CH_2{}^{80}SeMe)_3\}]^{2+}$ 290 and $[^{102}Ru(NCMe)_2\{MeC(CH_2{}^{80}SeMe)_3\}]^{2+}$ 269. IR: 2312w, 1360s, 1263s, 1225m, 1150m, 1098m, 1032m, 991w, 836w, 638s and 518w cm^{-1}.

[Ru(NCMe)$_3${MeC(CH$_2$TePh)$_3$}][CF$_3$SO$_3$]$_2$. This was prepared similarly as an orange solid (53%) (Found: C, 30.5; H, 2.4; N, 3.3. Calc. for $C_{31}H_{33}F_6N_3O_6RuS_2Te_3$: C, 30.9; H, 2.7; N, 3.5%). ^1H NMR ($(CD_3)_2CO$, 300 K): δ 1.91 (s, 1H, CCH_3), 2.29 (s, 3H, $NCCH_3$), 2.90 (s, 2H, $TeCH_2$) and 7.5–7.8 (m, 5H, TePh). $^{125}Te-\{^1H\}$ NMR (MeCN–$CDCl_3$, 300 K): δ 531. ES$^+$ (MeCN): m/z = 453, 432 and 414; calc. for $[^{102}Ru(NCMe)_3\{MeC(CH_2{}^{130}TePh)_3\}]^{2+}$ 458, $[^{102}Ru(NCMe)_2\{MeC(CH_2{}^{130}TePh)_3\}]^{2+}$ 437 and $[^{102}Ru(NCMe)\{MeC(CH_2{}^{130}TePh)_3\}]^{2+}$ 417. IR: 2315w, 1478w, 1435w, 1358m, 1276s, 1154s, 1093m, 1032s, 998m, 834w, 745m, 693m, 638s, 574w, 518m and 458w cm^{-1}.

[Ru{MeC(CH$_2$SMe)$_3$}{MeC(CH$_2$SeMe)$_3$}][CF$_3$SO$_3$]$_2$. $MeC(CH_2SMe)_3$ (17 mg, 7.9×10^{-5} mol) was added to [Ru(NCMe)$_3${MeC(CH$_2$SeMe)$_3$}][CF$_3$SO$_3$]$_2$ (69 mg, 7.9×10^{-5} mol) in CH_3OH (30 cm^3) and the reaction mixture refluxed for 18 h. After cooling the solvent volume was reduced *in vacuo* to 5 cm^3 and diethyl ether added to precipitate a light yellow solid (60 mg, 79%) (Found: C, 22.5; H, 3.5. Calc. for $C_{18}H_{36}F_6O_6RuS_5Se_3$: C, 22.5; H, 3.8%). ^1H NMR ($(CD_3)_2CO$, 300 K): δ 1.26 (s, 1H, $CH_3C(CH_2SCH_3)_3$), 1.38 (s, 1H, $CH_3C(CH_2SeCH_3)_3$), 2.34 (s, 3H, $SeCH_3$), 2.52 (s, 3H, SCH_3) and 2.7–2.9 (m, 4H, $SeCH_2$, SCH_2). $^{77}Se-\{^1H\}$ NMR ($MeNO_2$–$CDCl_3$, 300 K): δ 123. ES$^+$ (MeCN): m/z = 811 and 331; calc. for $([^{102}Ru\{MeC(CH_2SMe)_3\}\{MeC(CH_2{}^{80}SeMe)_3\}][CF_3SO_3])^+$ 815 and $[^{102}Ru\{MeC(CH_2SMe)_3\}\{MeC(CH_2{}^{80}SeMe)_3\}]^{2+}$ 333. IR: 2940w, 1461w, 1420m, 1358m, 1262s, 1227m, 1166m, 1096m, 1032s, 976w, 639s and 518m cm^{-1}.

[Ru{MeC(CH$_2$TePh)$_3$}{MeC(CH$_2$SeMe)$_3$}][CF$_3$SO$_3$]$_2$. This was similarly prepared *via* the reaction of [Ru(NCMe)$_3${MeC(CH$_2$TePh)$_3$}][CF$_3$SO$_3$]$_2$ with $MeC(CH_2SeMe)_3$ (73%) (Found: C, 27.4; H, 2.8. Calc. for $C_{33}H_{42}F_6O_6RuS_2Se_3Te_3$: C, 27.6; H, 2.9%). ^1H NMR ($(CD_3)_2CO$, 300 K): δ 1.16 (s, 2H, CH_3), 2.06 (s, 3H, $SeCH_3$), 2.4–2.9 (m, 4H, $SeCH_2$, $TeCH_2$) and 7.5–8.0 (m, 5H, TePh). $^{77}Se-\{^1H\}$ NMR ($MeNO_2$–$CDCl_3$, 300 K): δ 128. $^{125}Te-\{^1H\}$ NMR ($MeNO_2$–$CDCl_3$, 300 K): δ 485. ES$^+$ (MeCN): m/z = 569; calc. for $[^{102}Ru\{MeC(CH_2TePh)_3\}\{MeC(CH_2{}^{80}SeMe)_3\}]^{2+}$ 573. IR: 2929w, 1572w, 1476w, 1433w, 1358s, 1262s, 1224m, 1156m, 1096m, 1030s, 997m, 910w, 834w, 738m, 693m, 638s, 573w, 518m and 456m cm^{-1}.

X-Ray crystallographic studies

Details of the crystallographic data collection and refinement parameters for [RuCl$_2$(PPh$_3$){MeC(CH$_2$SeMe)$_3$}] and [RuCl$_2$(dmso){MeC(CH$_2$SeMe)$_3$}] are given in Table 1. The crystals were grown *via* vapour diffusion of diethyl ether into a solution of [RuCl$_2$(PPh$_3$){MeC(CH$_2$SeMe)$_3$}] in CH_2Cl_2–MeOH and by slow evaporation of CH_2Cl_2 from a solution of [RuCl$_2$(dmso){MeC(CH$_2$SeMe)$_3$}] in CH_2Cl_2–MeOH. Data collection used a Rigaku AFC7S four circle diffractometer operating at 150 K, with graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å). Structure solution and refinement were routine.[20,21] Crystal data are given in Table 1, and selected bond lengths and angles in Tables 2 and 3.

CCDC reference number 186/2252.

See http://www.rsc.org/suppdata/dt/b0/b007487j/ for crystallographic files in .cif format.

Results and discussion

[RuCl$_2$(PPh$_3$)L^3]

The reaction of [RuCl$_2$(PPh$_3$)$_3$] with ditelluroether ligands forms [RuCl(PPh$_3$)(L–L)$_2$][PF$_6$] (L–L = RTe(CH$_2$)$_3$TeR, R = Me or Ph, and $C_6H_4(TeMe)_2$-*o*).[10] We were interested in the reaction of Group 16 tripodal ligands with [RuCl$_2$(PPh$_3$)$_3$] and their chemistry, since such species would allow the study of complexes containing both phosphine and Group 16 donors, and provide complexes containing the $[RuL^3]^{2+}$ {L^3 = MeC(CH$_2$EMe)$_3$ (E = Se or Te) or MeC(CH$_2$TePh)$_3$} fragment, upon which further chemistry may be undertaken. Reaction of [RuCl$_2$(PPh$_3$)$_3$] with 1 mol equivalent of L^3 in CH_2Cl_2 at room temperature gave an orange (selenoether) or brown (telluroether) solution. After reduction of the solvent volume and addition of diethyl ether, the complexes [RuCl$_2$(PPh$_3$)L^3]

Table 1 Crystallographic data

	$[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$	$[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$
Formula	$C_{26}H_{33}Cl_2PRuSe_3$	$C_{10}H_{24}Cl_2ORuSSe_3$
Formula weight	785.38	601.22
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*Cc*
a/Å	16.001(7)	10.13(1)
b/Å	22.237(7)	13.486(6)
c/Å	15.686(5)	13.396(7)
β/°		101.49(5)
V/Å^3	5581(3)	1794(2)
Z	8	4
Observed reflections	5533	1733
Observed reflections $[I_o > 2\sigma(I_o)]$	2695	1417
R	0.036	0.040
R_w	0.037	0.054

were obtained in good yield. The ES^+ mass spectra (MeCN solution) showed clusters of peaks with the correct *m*/*z* and isotope patterns for $[RuCl(NCMe)(PPh_3)L^3]^+$. A further cluster of peaks corresponding to $[RuCl(PPh_3)L^3]^+$ was also observed. Elemental analysis confirmed the identity of the complexes. Although stable in the solid state, these complexes were found to be unstable in solution, even when thoroughly degassed with N_2, rapidly giving green solutions, assigned to ruthenium(III) species. Since such species are paramagnetic this led to complications when recording NMR spectra. To inhibit this process methanol (*ca.* 10%) was added to solutions of the complexes in CH_2Cl_2 for the multinuclear NMR studies where long accumulations were necessary. Even with these precautions the telluroether complexes showed NMR spectra consistent only with decomposition products.

The ^1H NMR spectra were recorded from freshly prepared solutions under N_2 and are, as expected, complicated due to the different environments for the tripod donor arms, and the potential presence of both *syn* and *anti* invertomers, since inversion at an Ru^{II}–Se/TeR_2 centre is expected to be slow.[9,10] Sharp resonances that may be assigned to PPh_3 and the tripod ligand were apparent for the selenoether complex, however only broad resonances, possibly associated with a paramagnetic species, were observed for the telluroether complexes. The ^{31}P-$\{^1H\}$ NMR spectra of the telluroether complexes only showed resonances corresponding to oxidised phosphine (Ph_3PO δ 26). This behaviour is common and has been observed for other ruthenium complexes,[22] although the reaction appears to be extremely rapid for these species. The selenoether complex exhibited two resonances in the ^{31}P-$\{^1H\}$ NMR spectrum of approximately equal intensity at δ 34.4 and 35.2, shifts consistent with co-ordinated PPh_3 and probably indicating the presence of two invertomers. The ^{77}Se-$\{^1H\}$ NMR spectrum of $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$ was also recorded and showed seven resonances over the range of 100 ppm, although $^2J_{Se-P}$ were poorly resolved. This is consistent with the inequivalence of the tripod arms with both Se-*trans*-Cl and Se-*trans*-P environments, together with the presence of both the *syn* and *anti* invertomers.

Interestingly the complexes $[RuCl_2(PPh_3)([9]aneS_3)]$, $[RuCl(PPh_3)([14]aneS_4)]^+$ [7] and $[RuCl(PPh_3)([16]aneSe_4)]^+$ [6] have been observed to be stable in solution and therefore similar in behaviour to $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$.

Despite their obvious vulnerability to oxidation and dissociation of PPh_3, it was hoped that by replacement of the phosphine and chloride co-ligands with labile solvent molecules such a $[RuL^3]^{2+}$ based system might be acquired. Unfortunately the reaction of $[RuCl_2(PPh_3)L^3]$ with 2 mol equivalents of $Ag[CF_3SO_3]$ in refluxing MeCN led to formation of dark grey materials (which decomposed rapidly to black oils). These showed no selenium or tellurium isotope pattern in the electrospray mass spectra, hence indicating that the target complexes $[Ru(NCMe)_3L^3]^{2+}$ or $[Ru(NCMe)_2(PPh_3)L^3]^{2+}$ had not been obtained.

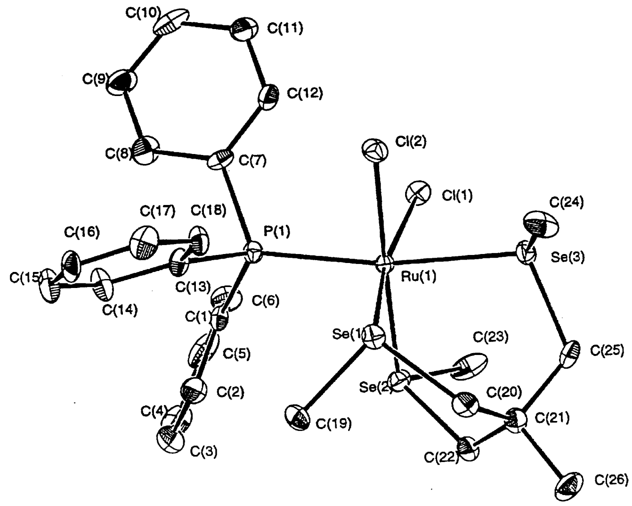

Fig. 1 Structure of $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$ with the numbering scheme adopted. Ellipsoids are drawn at 40% probability and H atoms omitted for clarity.

Crystal structure of $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$

Crystals of the complex were grown *via* slow diffusion of diethyl ether into a solution of the complex in MeOH–CH_2Cl_2 under N_2. The structure (Fig. 1, Table 2) shows Ru^{II} co-ordinated to all three arms of the facially bound selenoether ligand, with the Cl and PPh_3 auxiliary ligands completing the distorted octahedral geometry, d(Ru–Se) = 2.429(1), 2.423(1) and 2.492(1) Å with the longer bond *trans* to PPh_3, consistent with the higher *trans* influence of PPh_3 compared to Cl, d(Ru–Cl) = 2.453(2) and 2.454(2) Å, d(Ru–P) = 2.336(2) Å. The majority of the angles around Ru^{II} are close to the 90 or 180° expected for a regular octahedron, although Se(1)–Ru(1)–P(1) 99.91(6)° is noticeably larger. The Ru–Se bond lengths may be compared with those in *trans*-$[RuCl_2\{PhSe(CH_2)_2SePh\}_2]$ (2.433(1)–2.460(1) Å)[9] and *trans*-$[RuCl(PPh_3)([16]aneSe_4)]^+$ (2.465(3)–2.497(3) Å),[11] with the Ru–P and two Ru–Cl bond lengths also consistent with those found in *trans*-$[RuCl(PPh_3)([16]aneSe_4)]^+$ (d(Ru–P) = 2.307(6); d(Ru–Cl) = 2.499(5) Å). The methyl substituents on the selenoether adopt the *syn* arrangement.

$[RuCl_2(dmso)L^3]$

The sensitivity of the chloro-phosphine complexes was thought to be due to the presence of the phosphine ligand, and by using

Table 2 Selected bond lengths (Å) and angles (°) for $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$

Ru(1)–Se(1)	2.429(1)	Ru(1)–Se(2)	2.423(1)
Ru(1)–Se(3)	2.492(1)	Ru(1)–Cl(1)	2.453(2)
Ru(1)–Cl(2)	2.454(2)	Ru(1)–P(1)	2.336(2)
Se(1)–Ru(1)–Se(2)	89.34(4)	Se(1)–Ru(1)–Se(3)	87.47(3)
Se(1)–Ru(1)–Cl(2)	86.83(6)	Se(1)–Ru(1)–P(1)	99.91(6)
Se(2)–Ru(1)–Se(3)	93.53(4)	Se(2)–Ru(1)–Cl(1)	89.13(6)
Se(2)–Ru(1)–P(1)	92.86(6)	Se(3)–Ru(1)–Cl(1)	83.85(5)
Se(3)–Ru(1)–Cl(2)	84.15(6)	Cl(1)–Ru(1)–Cl(2)	94.33(7)
Cl(1)–Ru(1)–P(1)	88.95(7)	Cl(2)–Ru(1)–P(1)	89.94(7)

Table 3 Selected bond lengths (Å) and angles (°) for $[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$

Ru(1)–Se(1)	2.455(2)	Ru(1)–Se(2)	2.417(2)
Ru(1)–Se(3)	2.466(2)	Ru(1)–Cl(1)	2.441(4)
Ru(1)–Cl(2)	2.448(4)	Ru(1)–S(1)	2.258(4)
Se(1)–Ru(1)–Se(2)	91.29(6)	Se(1)–Ru(1)–Se(3)	91.75(8)
Se(1)–Ru(1)–Cl(1)	85.7(1)	Se(1)–Ru(1)–Cl(2)	89.4(1)
Se(2)–Ru(1)–Se(3)	87.49(6)	Se(2)–Ru(1)–Cl(1)	92.77(10)
Se(2)–Ru(1)–S(1)	92.6(1)	Se(3)–Ru(1)–Cl(2)	89.7(1)
Se(3)–Ru(1)–S(1)	94.0(1)	Cl(1)–Ru(1)–Cl(2)	90.1(1)
Cl(1)–Ru(1)–S(1)	88.5(1)	Cl(2)–Ru(1)–S(1)	87.0(1)

an alternative ruthenium(II) precursor these difficulties should be avoided. Similar work on complexes with $MeC(CH_2PPh_2)_3$ has shown that $[RuCl_2(dmso)_4]$ provides a convenient route into such chemistry, avoiding the use of phosphine co-ligands.[23] Treatment of $[RuCl_2(dmso)_4]$ with 1 mol equivalent of L^3 in toluene at 100 °C for 24 h afforded the complexes $[RuCl_2(dmso)L^3]$. For the ligands $MeC(CH_2EMe)_3$ (E = Se or Te) the complexes were precipitated as orange or brown powders respectively. For $L^3 = MeC(CH_2TePh)_3$ an orange solution was obtained from which the complex was isolated on concentration.

FAB mass spectrometry showed clusters of peaks with the correct *m*/*z* and isotope patterns for $[RuCl_2(dmso)\{MeC(CH_2EMe)_3\}]^+$ (E = Se or Te). For $[RuCl_2(dmso)\{MeC(CH_2TePh)_3\}]$ the molecular ion was not observed, however clusters of peaks were observed corresponding to $[RuCl\{MeC(CH_2TePh)_3\}]^+$. The IR spectra showed dmso ligands (ν(SO) 1080–1090 cm^{-1}) indicative of S-bound dmso.[22] The ^1H NMR spectra were again complex but resonances associated with the tripod and dmso ligands were apparent and, in contrast to the previous dichloro-triphenylphosphine species, these complexes were found to be stable in solution. Interestingly, from the reactions of $[RuCl_2(dmso)_4]$ with $MeC(CH_2EPh_2)_3$ (E = P or As) the chloro-bridge dimer $[Ru_2(\mu\text{-}Cl)_3\{MeC(CH_2PPh_2)_3\}_2]^+$ is obtained with the phosphine, although with the arsine $[RuCl_2(dmso)\{MeC(CH_2AsPPh_2)_3\}]$ is isolated.[23]

The $^{77}Se\text{-}\{^1H\}$ or $^{125}Te\text{-}\{^1H\}$ NMR spectra were also recorded. For the selenoether complex six resonances were observed (δ 168, 170, 218, 219, 229 and 244), with similar shifts to those observed for the dichloro-phosphine complex, showing inequivalence of the tripod donors (*trans*-dmso and *trans*-Cl) and the presence of both *syn* and *anti* invertomers. However since seven resonances are predicted for the presence of the three possible isomers this indicates coincidence of two of the Se-*trans*-dmso signals. The $MeC(CH_2TeMe)_3$ complex was highly insoluble in non-co-ordinating solvents and hence the spectrum obtained was too weak to provide useful information. For the $MeC(CH_2TePh)_3$ complex three resonances were observed of similar intensity which may be assigned to the presence of one major invertomer.

Structure of $[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$

Crystals were grown by slow evaporation of a solution of the complex in $CH_3OH–CH_2Cl_2$. The structure (Fig. 2, Table 3) shows the ruthenium co-ordinated to all three arms of the selenoether, with the methyl groups adopting the *syn* arrangement. The octahedral co-ordination sphere is completed by two chlorines, and one dmso molecule co-ordinated *via* the sulfur atom. Spectroscopic data for $[RuCl_2(dmso)\{MeC(CH_2AsPh_2)_3\}]$ also indicated S-bonded dmso, although the crystal structure was not reported.[23] The *d*(Ru–Se) = 2.455(2), 2.417(2) and 2.466(2) Å and *d*(Ru–Cl) = 2.441(4) and 2.448(4) Å are comparable to those in $[RuCl_2(PPh_3)\{MeC(CH_2SeMe)_3\}]$ (above) and $[Ru\{MeC(CH_2SeMe)_3\}_2]^{2+}$.[13]

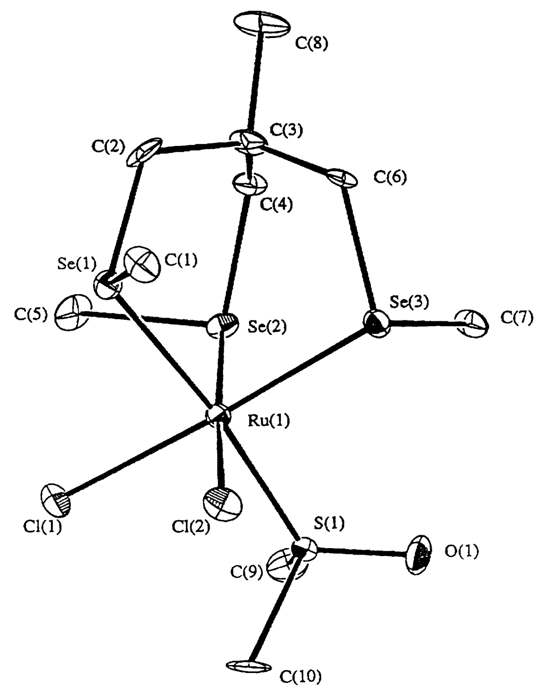

Fig. 2 Structure of $[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$. Details as in Fig. 1.

$[Ru(NCMe)_3L^3]^{2+}$ Complexes

Reaction of $[RuCl_2(dmso)\{MeC(CH_2ER)_3\}]$ (E = Se, R = Me; E = Te, R = Ph) with 2 mol equivalents of $Ag[CF_3SO_3]$ in refluxing MeCN for 2 h gave a light yellow solution and white precipitate. After removal of the AgCl through filtration, reduction of the solvent volume *in vacuo* and addition of diethyl ether, the complexes $[Ru(NCMe)_3\{MeC(CH_2ER)_3\}][CF_3SO_3]_2$ were obtained in good yield as yellow (selenoether) or orange (telluroether) solids. Unfortunately the $MeC(CH_2TeMe)_3$ complex could not be isolated despite numerous attempts, including the use of $TlPF_6$ instead of $Ag[CF_3SO_3]$. The reasons for this are unclear. The characterisation of these complexes was straightforward due to the higher symmetry compared to the previous species. The ES^+ mass spectra showed clusters of peaks with the correct isotopic distribution for doubly charged species $[Ru(NCMe)_3\{MeC(CH_2ER)_3\}]^{2+}$ and $[Ru(NCMe)_2\{MeC(CH_2ER)_3\}]^{2+}$. IR spectroscopy displayed peaks associated with the tripod ligand and $CF_3SO_3^-$ anion, along with weak bands assigned to the co-ordinated MeCN (ν(CN) 2310 cm^{-1}).

^1H NMR spectra showed signals assigned to the tripod ligand adopting the *syn* arrangement with a further resonance at δ 2.29 (telluroether) or 2.42 (selenoether) assigned to the co-ordinated MeCN molecules. These are comparable with that for the $MeC(CH_2PPh_2)_3$ complex where $\delta(CH_3CN)$ 2.34.[23] The $^{77}Se\text{-}\{^1H\}$ and $^{125}Te\text{-}\{^1H\}$ NMR spectra showed just one resonance probably indicating the presence of the *syn* invertomer, since fast inversion is unlikely with a weak *trans* donor MeCN. Both signals are to low frequency of the corresponding chloro-dmso species, consistent with substitution of the electronegative chloride ligands with acetonitrile; they are however to high frequency of those of the homoleptic ruthenium(II) seleno- and telluro-ether complexes.[12]

The reaction of $[RuCl_2(dmso)\{MeC(CH_2SeMe)_3\}]$ with two molar equivalents of $Ag[CF_3SO_3]$ in acetone was also studied, with the aim of preparing the tris(acetone) derivative $[Ru(Me_2CO)_3\{MeC(CH_2SeMe)_3\}]^{2+}$. The product obtained was found to be extremely unstable upon isolation, although the mass spectrum was recorded confirming its identity, with rapid oxidation to ruthenium(III) species occurring. However, this intermediate may be of use since it is stable in solution under N_2.

One aim of this research was to obtain a reactive $[RuL^3]^{2+}$ fragment upon which further chemistry could be conducted. Therefore we wished to confirm that the acetonitrile ligands could be substituted easily by other ligands, obviously a prerequisite if these complexes were to be able to carry out reaction chemistry. Addition of one mol equivalent of $MeC(CH_2SMe)_3$ to $[Ru(NCMe)_3\{MeC(CH_2SeMe)_3\}][CF_3SO_3]_2$ in methanol and reflux for 18 h led to isolation of the light yellow complex $[Ru\{MeC(CH_2SMe)_3\}\{MeC(CH_2SeMe)_3\}][CF_3SO_3]_2$. Crystals of this complex were obtained† and confirmed the expected cation, but due to disorder of the tripod ligands across the crystallographic inversion centre the structure is not described. The complex $[Ru\{MeC(CH_2TePh)_3\}\{MeC(CH_2SeMe)_3\}][CF_3SO_3]_2$ was obtained similarly *via* the reaction of $[Ru(NCMe)_3\{MeC(CH_2TePh)_3\}][CF_3SO_3]_2$ with 1 mol equivalent of $MeC(CH_2SeMe)_3$. IR spectra of these products displayed peaks associated with the co-ordinated tripodal ligands and $CF_3SO_3^-$ anion, with the ES^+ mass spectra showing clusters of peaks corresponding to the doubly charged cations. The ^1H NMR spectra were complex due to the number of overlapping signals, however resonances associated with both ligands in each complex could be identified. The $^{77}Se-\{^1H\}$ and $^{125}Te-\{^1H\}$ NMR spectra showed one resonance for each nucleus corresponding to the presence of the *syn* invertomers. For the $[Ru\{MeC(CH_2SMe)_3\}\{MeC(CH_2SeMe)_3\}]^{2+}$ complex $\delta(^{77}Se-\{^1H\})$ 123, a similar shift to that of the homoleptic complex $[Ru\{MeC(CH_2SeMe)_3\}_2]^{2+}$ (120).[13] The $[Ru\{MeC(CH_2TePh)_3\}\{MeC(CH_2SeMe)_3\}]^{2+}$ complex shows $\delta(^{77}Se-\{^1H\})$ 128 and $\delta(^{125}Te-\{^1H\})$ 485; both shifts are similar to those observed for the respective homoleptic Se_6 or Te_6 donor species reported previously.[13]

Having established the lability of the acetonitrile ligands and hence the availability of the $[RuL^3]^{2+}$ fragment, we were interested to study the reaction of these species with $NaBH_4$ in the expectation of generating hydride species, so important for hydrogenation and hydrodesulfurisation catalysis. Initially, an excess of solid $NaBH_4$ was added slowly to a solution of $[Ru(NCMe)_3\{MeC(CH_2ER)_3\}][CF_3SO_3]_2$ (E = Se, R = Me; E = Te, R = Ph) in dry ethanol at room temperature. A gas was evolved immediately along with precipitation of a black solid. Attempts to identify this product were unsuccessful, with the mass and ^1H NMR spectra showing no peaks that could be assigned to a tripod-containing product. It is likely that this product is largely ruthenium metal, obviously in contrast to the chemistry observed with $MeC(CH_2PPh_2)_3$, and is probably as a result of the poorer σ-donor/π-acceptor ligand properties of the Group 16 tripods. In an attempt to avoid the decomposition, the reaction was repeated by adding $NaBH_4$ to a slurry of $[Ru(NCMe)_3\{MeC(CH_2ER)_3\}][CF_3SO_3]_2$ in ethanol at −78 °C. No reaction was observed until the mixture was allowed to warm slowly, when a black precipitate was again formed indicating decomposition. This rather disappointing result does not necessarily exclude these complexes as potential catalysts, since co-ordination of the substrate may well stabilise the ruthenium centre. The complex $[Ru(NCMe)_3\{MeC(CH_2SeMe)_3\}]^{2+}$ did not react with carbon monoxide in CH_2Cl_2 solution at ambient temperatures, however reaction of the cation with PMe_3 in acetone resulted in replacement of MeCN by the phosphine. Details of these and related reactions will be reported in due course.

† Triclinic, space group $P\bar{1}$, $a = 8.791(2)$, $b = 11.406(8)$, $c = 8.555(2)$ Å, $\alpha = 107.53(3)$, $\beta = 91.38(2)$, $\gamma = 106.72(3)°$, $V = 777.6(6)$ Å^3.

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References

1 H. A. Meyer and W. C. Kaska, *Chem. Rev.*, 1994, **94**, 1239.
2 C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, *Coord. Chem. Rev.*, 1992, **120**, 193.
3 C. Bianchini, D. Masi, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, *Organometallics*, 1998, **17**, 2495; C. Bianchini, A. Meli, S. Moneti and F. Vizza, *Organometallics*, 1998, **17**, 2636.
4 C. Bianchini, A. Meli, S. Moneti, W. Oberhauser, F. Vizza, V. Herrera, A. Fuentes and R. Sanchez-Delgado, *J. Am. Chem. Soc.*, 1999, **121**, 7071.
5 M. N. Bell, A. J. Blake, H.-J. Kuppers, M. Schröder and K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 250.
6 N. W. Alcock, J. C. Cannadine, G. R. Clark and A. F. Hill, *J. Chem. Soc., Dalton Trans.*, 1993, 1131.
7 A. L. Hector and A. F. Hill, *Inorg. Chem.*, 1995, **34**, 3797.
8 J. C. Cannadine, A. F. Hill, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics*, 1996, **15**, 5409.
9 N. R. Champness, W. Levason, S. R. Preece and M. Webster, *Polyhedron*, 1994, **13**, 881.
10 W. Levason, S. D. Orchard, G. Reid and V.-A. Tolhurst, *J. Chem. Soc., Dalton Trans.*, 1999, 2071.
11 W. Levason, J. J. Quirk, G. Reid and S. M. Smith, *J. Chem. Soc., Dalton Trans.*, 1997, 3719.
12 W. Levason, S. D. Orchard, G. Reid and J. M. Street, *J. Chem. Soc., Dalton Trans.*, 2000, 2537.
13 W. Levason, S. D. Orchard and G. Reid, *Chem. Commun.*, 1999, 1071; W. Levason, S. D. Orchard and G. Reid, *Inorg. Chem.*, 2000, **39**, 3853.
14 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.
15 I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204.
16 R. Ali, S. J. Higgins and W. Levason, *Inorg. Chim. Acta*, 1984, **84**, 65.
17 D. J. Gulliver, E. G. Hope, W. Levason, G. L. Marshall, S. G. Murray and D. M. Potter, *J. Chem. Soc., Perkin Trans. 2*, 1984, 429.
18 E. G. Hope, T. Kemmitt and W. Levason, *Organometallics*, 1988, **7**, 78.
19 J. Connolly, A. R. J. Genge, W. Levason, S. D. Orchard, S. J. A. Pope and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1999, 2343.
20 PATTY, The DIRDIF Program System, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
21 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1995.
22 B. A. Moyer, B. K. Sipe and T. J. Meyer, *Inorg. Chem.*, 1981, **20**, 1475.
23 L. F. Rhodes, C. Sorato, L. M. Venanzi and F. Bachechi, *Inorg. Chem.*, 1988, **27**, 604.