# Transition metal complexes with wide-angle dithio-, diseleno- and ditelluroethers: properties and structural systematics

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The ligands o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>EMe)<sub>2</sub> (E = S or Se) have been prepared and characterised spectroscopically. A systematic study of the coordination chemistry of these, together with the telluroether analogue,  $o-C_6H_4(CH_2TeMe)_2$ , with late transition metal centers has been undertaken. The planar complexes  $[MCl_{2}{o-C_{6}H_{4}(CH_{2}SMe)_{2}}]$  and  $[M{o-C_{6}H_{4}(CH_{2}EMe)_{2}}_{2}](PF_{6})_{2}$  (M = Pd or Pt; E = S or Se), the distorted octahedral [RhCl<sub>2</sub>{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>EMe)<sub>2</sub>]<sub>2</sub>]Y (E = S or Se: Y = PF<sub>6</sub>; E = Te: Y = Cl) and  $[RuCl_2{o-C_6H_4(CH_2EMe)_2}_2] (E = S, Se or Te)$ , the dithioether-bridged binuclear  $[\{\operatorname{RuCl}_{2}(p-\operatorname{cymene})\}_{2}\{\mu-o-C_{6}H_{4}(\operatorname{CH}_{2}\operatorname{SMe})_{2}\}]$  and the tetrahedral  $[M'_{4}\{o-C_{6}H_{4}(\operatorname{CH}_{2}\operatorname{EMe})_{2}\}_{2}]BF_{4}(M'=$ Cu or Ag; E = S, Se or Te) have been obtained and characterised by IR and multinuclear NMR spectroscopy (1H, 63Cu, 77Se{1H}, 125Te{1H} and 195Pt), electrospray MS and microanalyses. Crystal structures of the parent  $o-C_6H_4(CH_2SMe)_2$  and seven complexes are described, which show three different stereoisomeric forms for the chelated ligands, as well as the first example of a bridging coordination mode in  $[{RuCl_2(p-cymene)}_2 \{\mu - o - C_6H_4(CH_2SMe)_2\}]$ . These studies reveal the consequences of the sterically demanding o-xylyl backbone, which typically leads to unusually obtuse E–M–E chelate angles of  $\sim 100^{\circ}$ .

### Introduction

The majority of comparative studies on the neutral Group 16 chalcogenoether ligands have focused upon those systems containing short linkages between the chalcogen atoms, giving rise to five- and six-membered chelate rings upon coordination to a metal ion.<sup>1-4</sup> However, within Group 15, wide-angle diphosphine ligands, especially those with four or more carbon atoms between the P atoms, are of major interest in organometallic and catalytic systems giving much improved product selectivities, presumably a consequence of both their significant steric requirements and the electronic effect of the substituents.5 In the neutral chalcogenoethers,  $o-C_6H_4(CH_2ER)_2$ , the situation is somewhat different since the presence of only one terminal substituent is expected to lead to a reduced steric requirement, although coordination to a metal atom is usually through one lone pair on each chalcogen atom. Hence a further lone pair remains, the structural consequences of which seem to be significant as we describe below. In terms of neutral Group 16 ligands, the 'oxylyl'  $(1,2-(CH_2)_2C_6H_4)$  linking group has been incorporated in a number of systems, mainly in (macro)cyclic species such as I-III (Scheme 1), and aspects of their coordination chemistry have been studied.<sup>6-8</sup> However, it is widely recognised that the ring structure in these species significantly influences their coordinating properties and hence these are of limited relevance to the present study. In our preliminary work we have described the preparation of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub> and undertook some initial studies on its



ligating behaviour.9 No systematic studies have been undertaken to probe the differences between these ligands and analogues with shorter (dimethylene and trimethylene, o-phenylene etc.) linkages.

Here we report the preparations of the xylyl ligands o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> and o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeMe)<sub>2</sub>, which provide the direct comparators to the o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>, and a series of transition metal complexes of these three ligands with Pd(II), Pt(II), Rh(III), Ru(II), Cu(I) and Ag(I) to probe the coordinating properties of the xylyl-ligands in different coordination geometries and ligand binding modes. The new complexes have been characterised spectroscopically by  ${}^{1}$ H,  ${}^{77}$ Se{ ${}^{1}$ H},  ${}^{63}$ Cu,  ${}^{125}$ Te{ ${}^{1}$ H} and  ${}^{195}$ Pt NMR, IR and electrospray MS, and by microanalysis. X-ray structure determinations on the parent dithioether,  $o-C_6H_4(CH_2SMe)_2$  and seven complexes serve to confirm the coordination environments present, and provide bond length and angle distributions which reflect the steric demands and the degree of coordinative flexibility of these xylyl dichalcogenoether ligands.

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#### **Results and discussion**

The o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> and o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeMe)<sub>2</sub> were obtained as colourless (S) or light yellow (Se) solids in good yield from treatment of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub> with MeSNa in refluxing EtOH or with MeSeLi (itself obtained by addition of freshly ground elemental Se to a frozen (77 K) solution of MeLi in thf and warming to room temperature) in cold thf solution respectively. These ligands have been characterised by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>77</sup>Se{<sup>1</sup>H} (selenoether:  $\delta$ <sup>77</sup>Se: +149 ppm) NMR spectroscopy and EI MS.

The crystal structure of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> shows (Fig. 1, Table 1) that the molecule adopts a crystallographic twofold symmetry, with unexceptional bond length and angle distributions, although these provide a useful comparison with the complexes – see below. The conformation of the molecule is such that the S atoms are directed outwards, presumably to minimise lone pair–lone pair interactions, giving  $d(S1 \cdots S1a) = 4.609(1)$  Å. There is a further intermolecular S1  $\cdots$  S1' contact of 3.568(1) Å.



Fig. 1 View of the structure of the o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Symmetry operation: a = 1 - x, y, 1/2 - z.

Treatment of  $[MCl_2(MeCN)_2]$  (M = Pd or Pt) with one mol. equiv. of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> in refluxing MeCN gives the neutral orange (Pd) or yellow (Pt) powdered solids  $[MCl_2{o-C_6H_4(CH_2SMe)_2}]$  in good yield. These have been characterised by IR spectroscopy (two  $\nu$ (M–Cl) bands confirming the *cis* geometric isomer) and microanalyses, and although they are poorly soluble in common solvents (chlorocarbons, MeCN, acetone, thf, dmf, MeNO<sub>2</sub>), <sup>1</sup>H NMR spectra were obtained from d<sup>6</sup>-dmso solution. Using two mol equiv. of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>EMe)<sub>2</sub> (E = S or Se),  $[MCl_2(MeCN)_2]$  and two mol equiv. of TIPF<sub>6</sub> gives (after

Table 1 Selected bond lengths (Å) and angles (°) for o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>

S1–C1 C2–C3 C3–C3a C5–C5a	1.7936(15) 1.5057(17) 1.410(2) 1.389(3)	S1–C2 C3–C4 C4–C5 S1 · · · S1a	1.8257(14) 1.3939(18) 1.389(2) 4.6091(12)	
C1–S1–C2 C4–C3–C3a C3a–C3–C2 C4–C5–C5a	100.26(7) 118.93(7) 122.05(7) 119.56(8)	C3-C2-S1 C4-C3-C2 C5-C4-C3	113.61(9) 119.02(11) 121.51(12)	

Symmetry operation: a = 1 - x, y, 1/2 - z.

Table 2 Selected bond lengths (Å) and angles (°) for  $[Pd\{o-C_6H_4(CH_2SMe)_2\}_2](PF_6)_2$ 

Pd1–S1	2.3353(13)	Pd1–S2	2.3401(13)	
Pd1–S3	2.3327(13)	Pd1–S4	2.3424(13)	
S1–Pd1–S2	101.87(5)	S1-Pd1-S3	178.80(5)	
S1–Pd1–S4	77.93(5)	S2-Pd1-S3	78.11(4)	
S2–Pd1–S4	178.39(5)	S3-Pd1-S4	102.12(5)	

removal of the TlCl precipitate) the homoleptic planar [M{o- $C_6H_4(CH_2EMe)_2$  [(PF<sub>6</sub>)<sub>2</sub> as light yellow solids. Their identities follow from IR (confirms PF<sub>6</sub><sup>-</sup> anion and the absence of M-Cl bonds), <sup>1</sup>H, <sup>77</sup>Se{<sup>1</sup>H} and <sup>195</sup>Pt NMR spectroscopy which are in accord with related species,10 electrospray MS and microanalyses. The NMR spectra are consistent with fast pyramidal inversion at the coordinated chalcogen atoms, in line with earlier detailed work.<sup>1,2</sup> The crystal structure of  $[Pd{o-C_6H_4(CH_2SMe)_2}_2](PF_6)_2$ shows that the Pd(II) cation sits on a general position and adopts a distorted square planar geometry with two chelating dithioethers (Fig. 2, Table 2). The coordinated ligands are each in the meso-1 form<sup>†</sup> with both Me groups in a single ligand lying on the same side of the PdS<sub>4</sub> plane, and further, the *o*-C<sub>6</sub>H<sub>4</sub> unit in the ligand backbone lies on the same side of the plane as the Me groups of the same ligand. The Pd–S distances of  $\sim 2.33$  Å are similar to those in other Pd(II) thioethers.<sup>10</sup>



Fig. 2 View of the structure of the  $[Pd\{o-C_6H_4(CH_2SMe)_2\}_2]^{2+}$  cation with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

Chlorine-saturated CCl<sub>4</sub> was added to a CCl<sub>4</sub> suspension of the cream (E = S) or light yellow (E = Se) [Pt{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>EMe)<sub>2</sub>}<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> complexes, resulting in deposition of deeper yellow solids and indicating some reaction takes place. However, dissolving the resulting solids for solution NMR spectroscopic studies revealed no evidence for Pt(IV) complexes. This contrasts with the tetrathia- and tetraselenamacrocyclic systems which give [PtCl<sub>2</sub>([*n*]aneS<sub>4</sub>)]<sup>2+</sup> (*n* = 12, 14 or 16)<sup>11</sup> and [PtCl<sub>2</sub>([16]aneSe<sub>4</sub>)]<sup>2+</sup> (confirmed by X-ray structure determination),<sup>12</sup> which are stable in solution and in the solid state.

The octahedral  $[RhCl_2{o-C_6H_4(CH_2EMe)_2}_2]Y (E = S, Se: Y = PF_6; E = Te: Y = Cl)$  were obtained as yellow–orange solids from reacting  $RhCl_3 \cdot 3H_2O$  with 2 mol equiv. of the appropriate ligand in aqueous EtOH in the presence of  $NH_4PF_6$  and were

<sup>†</sup> Bidentate coordination of the *o*-xylyl dichalcogenoethers leads to chirality at the coordinated donor atoms and gives rise to three possible NMR distinguishable diastereoisomers, for convenience we define these as *meso*-1, DL (enantiomeric pair) and *meso*-2 ((i)–(iii), respectively, in Fig. 9).

characterised similarly (the  $PF_6^-$  anion is not incorporated in the telluroether complex which reproducibly retains Cl<sup>-</sup> as anion, presumably reflecting the low solubility of the complex with the chloride anion which preferentially precipitates from the reaction solution). The <sup>1</sup>H, <sup>77</sup>Se{<sup>1</sup>H} and <sup>125</sup>Te{<sup>1</sup>H} NMR spectra indicate the presence of mixtures of invertomers and/or geometric isomers.

The crystal structures of  $[RhCl_2\{o-C_6H_4(CH_2EMe)_2\}_2]PF_6$  (E = S; Fig. 3(a), Table 3; E = Se: Fig. 4, Table 4) are isomorphous and therefore show very similar geometric arrangements, with the

C10

S2

CI1

S1

Rh1

C15

. C13

C12

C18

C19

(C) C11

C20

S3

Cl2

(a)

X

Fig. 3 (a) View of the structure of the  $[RhCl_2\{o-C_6H_4(CH_2SMe)_2\}_2]^+$  cation with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. (b) View of the packing of the  $[RhCl_2\{o-C_6H_4(CH_2SMe)_2\}_2]^+$  cations showing the intermolecular

Table 3 Selected bond lengths (Å) and angles (°) for  $[RhCl_2\{\mathit{o}-C_6H_4(CH_2SMe)_2\}_2]PF_6$ 

 $\pi$ -stacking interactions between the aromatic rings.

Rh1–Cl1	2.3601(12)	Rh1–Cl2	2.3474(12)
Rh1–S1	2.3756(12)	Rh1–S2	2.3587(12)
Rh1–S3	2.3933(12)	Rh1–S4	2.3529(12)
Cl1-Rh1-Cl2 S2-Rh1-Cl1 S4-Rh1-Cl1 Cl2-Rh1-S2 Cl2-Rh1-S4 S1-Rh1-S3 S2-Rh1-S3 S4-Rh1-S3	95.74(4) 82.40(4) 171.67(4) 169.24(4) 88.82(4) 171.39(4) 81.73(4) 103.75(4)	Cl1-Rh1-S1 Cl1-Rh1-S3 Cl2-Rh1-S1 Cl2-Rh1-S1 S2-Rh1-S1 S4-Rh1-S1 S4-Rh1-S2	88.71(4) 83.46(4) 89.72(4) 87.53(4) 100.81(4) 84.34(4) 94.39(4)

Table 4 Selected bond lengths (Å) and angles (°) for  $[RhCl_2{o-C_6H_4(CH_2SeMe)_2}]PF_6$ 

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
Cl1-Rh1-Cl2         95.72(7)         Cl1-Rh1-Se1         81.69(6           Cl1-Rh1-Se2         90.06(5)         Cl1-Rh1-Se3         81.88(5)           Cl1-Rh1-Se2         90.06(6)         Cl2-Rh1-Se3         81.88(5)           Cl1-Rh1-Se2         88.36(6)         Cl2-Rh1-Se3         88.60(6)           Cl2-Rh1-Se4         89.94(6)         Se1-Rh1-Se2         101.36(4)           Se1-Rh1-Se3         81.38(3)         Se1-Rh1-Se4         93.69(4)	Rh1-Cl1 Rh1-Se1 Rh1-Se3	2.376(2) 2.4601(11) 2.5005(11)	Rh1-Cl2 Rh1-Se2 Rh1-Se4	2.357(2) 2.4849(11) 2.4427(10)
Se2-Rh1-Se3 1/1.06(4) Se2-Rh1-Se4 84.31(3) Se3-Rh1-Se4 104.09(3)	Cl1-Rh1-Cl2 Cl1-Rh1-Se2 Cl1-Rh1-Se4 Cl2-Rh1-Se2 Cl2-Rh1-Se3 Se2-Rh1-Se3 Se3-Rh1-Se4	$\begin{array}{c} 95.72(7)\\ 90.06(5)\\ 171.90(6)\\ 88.36(6)\\ 89.94(6)\\ 81.38(3)\\ 171.06(4)\\ 104.09(3) \end{array}$	Cl1-Rh1-Se1 Cl1-Rh1-Se3 Cl2-Rh1-Se1 Cl2-Rh1-Se3 Se1-Rh1-Se2 Se1-Rh1-Se4 Se2-Rh1-Se4	81.69(6) 81.88(5) 169.91(6) 88.60(6) 101.36(4) 93.69(4) 84.31(3)



Fig. 4 View of the structure of the  $[RhCl_2{o-C_6H_4(CH_2SeMe)_2}_2]^+$  cation with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

Rh on a general position in a distorted octahedral arrangement comprised of two chelating thioether/selenoether ligands and two mutually *cis* Cl ligands. The *cis*-octahedral geometry at Rh(III) in these species is unusual and we also note that the two dithioethers coordinated to Rh adopt different configurations—one in the *meso*-2 form while the other is in a DL arrangement. These are the first cases where the *meso*-2 configuration has been observed for bidentate o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>EMe)<sub>2</sub>. The Rh–E bond distances are in line with other rhodium(III) thio- and seleno-ether complexes.<sup>1,13</sup> Examination of the packing within the crystals of *cis*-[RhCl<sub>2</sub>{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>EMe)<sub>2</sub>]<sub>2</sub>]PF<sub>6</sub> (E = S or Se) also reveals that the aromatic rings in adjacent cations are aligned parallel ~3.5 Å apart, indicative of intermolecular  $\pi$ -stacking interactions (*e.g.* Fig. 3(b)), and forming infinite chains of associated cations.

Treatment of RuCl<sub>3</sub>·3H<sub>2</sub>O with two mol equiv. of *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> or *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeMe)<sub>2</sub> in refluxing methoxyethanol gave, after work-up, yellow/orange solids. Spectroscopic analysis showed that these solids contained the Ru(II) complexes, [RuCl<sub>2</sub>(L-L)<sub>2</sub>], however, these were impure, with dimers and possibly also some Ru(III) impurities thought to be present (electrospray MS evidence), indicating incomplete reduction of the Ru. We note that similar reaction of RuCl<sub>3</sub>·3H<sub>2</sub>O with *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub> in methoxyethanol gives pure [RuCl<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>] in good yield. We have described the preparation of this complex previously from [Ru(dmf)<sub>6</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>, LiCl and the telluroether in EtOH.<sup>9</sup> The spectroscopic data from the product of the new method are in accord with the original data. The increased

C!

C

C2

reducing power of the telluroether over the thio- and seleno-ether homologues may assist the clean reduction of the RuCl<sub>3</sub>·3H<sub>2</sub>O to Ru(II) in methoxyethanol. [RuCl<sub>2</sub>{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>EMe)<sub>2</sub>}<sub>2</sub>] (E = S or Se) were obtained cleanly and in high yield by reacting RuCl<sub>3</sub>·3H<sub>2</sub>O and the ligand in aqueous EtOH in the presence of H<sub>3</sub>PO<sub>2</sub> to assist the reduction of the metal. The electrospray MS shows [RuCl<sub>2</sub>(L-L)<sub>2</sub>]<sup>+</sup> to be the highest mass species present for all three complexes, and IR spectroscopy shows one  $\nu$ (RuCl) band for each species. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy also show that only one geometric isomer (*trans*) is present in these species, and that the thioether complex is undergoing fast pyramidal inversion at ambient temperature, whereas at 298 K the <sup>77</sup>Se{<sup>1</sup>H} NMR spectrum for the selenoether complex shows four broadened resonances at  $\delta$  247, 235, 219, 213, consistent with a mixture of stereoisomers and slow pyramidal inversion at Se.

The crystal structure of  $[\text{RuCl}_2\{o\text{-}C_6\text{H}_4(\text{CH}_2\text{SMe})_2\}_2]$  (Fig. 5, Table 5) confirms a centrosymmetric *trans* dichloro arrangement with the two dithioethers in the square plane and both adopting a *meso*-1 configuration such that the two Me groups on one ligand lie on the same side of the RuS<sub>4</sub> plane. The Ru–S bond distances of 2.3565(6) and 2.3571(8) Å are very similar to those in other Ru(II) thioether species, *e.g.* [Ru{MeC(CH<sub>2</sub>SMe)<sub>3</sub>}<sub>2</sub>]<sup>2+</sup> d(Ru-S) =2.367(2)–2.375(2) Å.<sup>14</sup>



**Fig. 5** View of the structure of  $[\text{RuCl}_{2}\{o\text{-C}_{6}\text{H}_{4}(\text{CH}_{2}\text{SMe})_{2}\}_{2}]$  with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Symmetry operation: a = 1 - x, -y, -z.

In order to probe further the ligating modes of the xylyl dichalcogenoether ligands we also treated  $[Ru(\eta^6-p\text{-cymene})Cl_2]_2$  with two mol. equivs. of  $o\text{-}C_6H_4(CH_2SMe)_2$  in  $CH_2Cl_2$  solution to give the neutral, binuclear  $[\{RuCl_2(p\text{-cymene})\}_2\{\mu\text{-}o\text{-}C_6H_4(CH_2SMe)_2\}]$  as an orange solid. The formulation follows from the spectroscopic data, together with a crystal structure analysis. The structure shows (Fig. 6, Table 6) the complex has crystallographic two-fold symmetry with the dithioether ligand functioning as a bridging bidentate through coordination *via* one thioether S atom each to the two Ru atoms. The geometry at Ru is a distorted pseudo-octahedron through an  $\eta^6\text{-}p\text{-cymene}$ 

Table 5 Selected bond lengths (Å) and angles (°) for  $[RuCl_2\{\textit{o-}C_6H_4\text{-}(CH_2SMe)_2\}_2]$ 

Ru1–S1 Ru1–S2 Ru1–Cl1	2.3565(6) 2.3571(8) 2.4175(6)
S1–Ru1–S2 S1–Ru1–Cl1 S2–Ru1–Cl1	99.99(2) 85.49(3) 85.55(2)

Table 6 Selected bond lengths (Å) and angles (°) for  $[{RuCl_2(p-cymene)}_2(\mu-o-C_6H_4(CH_2SMe)_2)]$ 

S1–Ru1 Cl2–Ru1	2.4021(10) 2.4058(11) 2.105(4)	Cl1–Ru1 C1–Ru1 C2 Pu1	2.4112(9) 2.183(4) 2.170(2)
C2–Ru1 C4–Ru1 C6–Ru1	2.195(4) 2.167(3) 2.203(4)	C3–Ru1 C5–Ru1	2.179(3) 2.213(4)
S1–Ru1–Cl2 Cl2–Ru1–Cl1	87.99(4) 86.34(4)	S1–Ru1–Cl1	88.38(3)



**Fig. 6** View of the structure of  $[{RuCl_2(p-cymene)}_2{\mu-o-C_6H_4-(CH_2SMe)_2}]$  with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. There is disorder in the isopropyl group (C7a, C9a, C10a) with only the major conformation shown. Symmetry operation: i = -x, y, -1/2 - z.

ligand, one thioether S donor atom and two mutually *cis* Cl atoms, giving d(Ru-S) = 2.402(1) Å, slightly longer than in [RuCl<sub>2</sub>{ $o-\text{C}_6\text{H}_4(\text{CH}_2\text{SMe})_2$ }] above. This is the first example of  $o-\text{C}_6\text{H}_4(\text{CH}_2\text{EMe})_2$  bridging two metal centres. The conformation of the bridging dithioether is little different from that of the parent dithioether, with  $d(\text{S}\cdots\text{S}) = 4.768(2)$  Å.

The complexes  $[M'{o-C_6H_4(CH_2EMe)_2}_2]BF_4$  (M' = Cu or Ag; E = S, Se or Te) were obtained in good yield from  $[Cu(MeCN)_4]BF_4$  or AgBF<sub>4</sub> with two mol equiv. of the appropriate ligand in acetone or MeOH solution respectively. The formulae follow from IR, <sup>1</sup>H, <sup>77</sup>Se, <sup>125</sup>Te and <sup>63</sup>Cu NMR spectroscopic studies, electrospray MS, for which the  $[M(L-L)_2]^+$  cation is always prevalent, and microanalyses. Copper-63 NMR spectroscopic studies on  $[Cu{o-C_6H_4(CH_2EMe)_2}_2]BF_4$  reveal strong resonances at +132, -2 and +16 ppm, respectively, for E = S, Se, Te. These resonances are evident at room temperature and do not shift significantly on cooling, strongly suggesting that the Cu(I) complexes retain their approximately tetrahedral CuE<sub>4</sub> coordination environment in solution.<sup>15</sup>

The silver compounds are both light and thermally sensitive, rapidly turning black in solution at room temperature. The best yields of the pure compounds were obtained when the reactions were undertaken in foil-wrapped flasks and the temperature maintained at ~0 °C. The solids were also stored in foil-wrapped bottles in the fridge. We have commented previously on the extreme sensitivity of the  $[Ag\{o-C_6H_4(CH_2TeMe)_2\}_2](CF_3SO_3)$ , which darkens rapidly in solution, giving a weak  $\delta(^{125}Te)$  resonance at 260 ppm.<sup>9</sup> In our present work we have found that replacing the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anion with BF<sub>4</sub><sup>-</sup> leads to much improved stability, and in CH<sub>2</sub>Cl<sub>2</sub> solution the [Ag{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>}]BF<sub>4</sub> reproducibly gives a strong <sup>125</sup>Te{<sup>1</sup>H} NMR resonance at 107 ppm. Hence we conclude that the weak resonance previously reported for the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> salt is in fact not due to the complex, but is almost certainly due to some uncoordinated o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub> ('free' ligand:  $\delta$ (<sup>125</sup>Te) = 264), resulting from decomposition in solution. Thus, in line with our previous work using other chalcogenoether ligands, the Cu(1) and Ag(1) selenoether and telluroether complexes give rise to significant low frequency shifts by <sup>77</sup>Se{<sup>1</sup>H} and <sup>125</sup>Te{<sup>1</sup>H} NMR spectroscopy upon coordination to the metal.<sup>15</sup>

We have also been able to grow single crystals of both the  $[Ag\{o C_6H_4(CH_2TeMe)_2$ ]BF<sub>4</sub> and the [Cu{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>]]BF<sub>4</sub> suitable for a crystallographic structure determination. The structure of  $[Cu\{o-C_6H_4(CH_2SMe)_2\}_2]BF_4$  shows (Fig. 7, Table 7) the Cu atom in a distorted tetrahedral environment with the two dithioethers chelating, both of which adopt a meso-1 configuration, giving d(Cu-S) = 2.3288(8) and 2.2846(9) Å. These are in line with other Cu(I) thioethers based upon four-coordination.<sup>15</sup> The cation has crystallographic twofold symmetry. The angles subtended at Cu are in the range 95.29(4)-120.23(5)° and are discussed in more detail below. The  $[Ag\{o-C_6H_4(CH_2TeMe)_2\}_2]BF_4$  shows (Fig. 8, Table 8) two independent molecules in the asymmetric unit, and some disorder at one of the Te atoms-see Experimental section. The Ag atoms are in a similar distorted tetrahedral geometry as expected, giving d(Ag-Te) = 2.7593(5)-2.8078(5) Å and angles around Ag in the range 100.90(2)-124.28(2)°. There is a short intermolecular interaction between two Ag1 containing cations, shown in Fig. 8(a). The Te  $\cdots$  Te1a distance is 3.371(1) Å, resulting in weakly held dimeric species. Structurally characterised examples of Ag(I) species with homoleptic telluroether coordination are very rare, e.g. the polymeric  $[Ag\{MeTe(CH_2)_3TeMe\}_2]^+$  which has distorted tetrahedral Ag with bridging ditelluroethers, giving

C10

ัรว

C<sub>6</sub>

C5



S2a

Table 7 Selected bond lengths (Å) and angles (°) for  $[Cu\{\mathit{o}\text{-}C_6H_4\text{-}(CH_2SMe)_2\}_2]BF_4$ 

Cu1–S1	2.3288(8)	Cu1–S2	2.2846(9)
S1–Cu1–S1a S2–Cu1–S1	95.29(4) 110.24(3)	S2–Cu1–S2a S2–Cu1–S1a	120.23(5) 109.00(3)
Symmetry operation: $a = 3/2 - x$ , y, $3/2 - z$ .			



**Fig. 8** View of the structures of the two crystallographically independent  $[Ag\{o-C_6H_4(CH_2TeMe)_2\}_2]^+$  cations with numbering scheme adopted. (a) The Ag1 centred cation showing the weak Te1...Te1i interaction as a broken line. Symmetry operation: i = 2 - x, 1 - y, 1 - z. (b) The Ag2 centred cation showing the major component of the disordered model at Te6/Te6A. In both diagrams H atoms are omitted for clarity and ellipsoids are shown at the 50% probability level.

 $d(Ag-Te) = 2.785(2)-2.837(2) \text{ Å},^{16}$  and the tetrahedral monomer  $[Ag(1,3-dihydrobenzo[c]tellurophene)_4]^+$ ,  $d(Ag-Te) = 2.7676(7)-2.8104(8) \text{ Å}.^{17}$  Unusually, and in contrast to the Cu thioether complex described above, in  $[Ag\{o-C_6H_4(CH_2TeMe)_2\}_2]^+$  the two chelating ditelluroethers with Ag1 adopt different configurations, one *meso*-1 and one DL.

The multinuclear NMR spectroscopic studies show that the coordinated xylyl-linked dichalcogenoethers exhibit similar trends to other ligands in terms of the relative ease of pyramidal inversion, both in terms of the chalcogen atom (S > Se > Te),

Table 8 Selected bond lengths (Å) and angles (°) for  $[Ag\{\mathit{o}-C_6H_4(CH_2TeMe)_2\}_2]BF_4$ 

Ag1–Te1	2.8039(5)	Ag2–Te5	2.7664(5)
Ag1–Te2	2.7617(5)	Ag2–Te6	2.7805(6)
Ag1–Te3	2.7593(5)	Ag2–Te7	2.7908(5)
Ag1–Te4	2.7682(5)	Ag2–Te8	2.8078(5)
Te2-Ag1-Te1	100.903(16)	Te5-Ag2-Te6	111.281(17)
Te3-Ag1-Te1	101.844(16)	Te5-Ag2-Te7	110.351(17)
Te4-Ag1-Te1	109.458(16)	Te5-Ag2-Te8	108.893(17)
Te3-Ag1-Te2	124.282(17)	Te6-Ag2-Te7	107.757(17)
Te2-Ag1-Te4	113.638(17)	Te6-Ag2-Te8	115.748(17)
Te3-Ag1-Te4	105.328(17)	Te7-Ag2-Te8	102.409(16)

 $\label{eq:comparative structural data for non-cyclic chelating dichalcogenoethers involving the \textit{o-C}_6H_4(CH_2ER)_2 linkage^{at}$ 

Compound	$d(\mathbf{E}\cdots\mathbf{E})^{b}/\mathbf{\mathring{A}}$	E–M–E chelate angle/ $^{\circ}$	Reference
$o-C_6H_4(CH_2SMe)_2$	4.61	_	This work
$[Pd{o-C_6H_4(CH_2SMe)_2}_2](PF_6)_2$	3.63, 3.64	101.87(5), 102.12(5)	This work
$[PtMe_{3}I\{o-C_{6}H_{4}(CH_{2}SeMe)_{2}\}]$	3.87	98.32(1)	17
$[\operatorname{RuCl}_{2} \{ o - C_{6} H_{4} (CH_{2} SMe)_{2} \}_{2}]$	3.61	99.99(2)	This work
$[RhCl_2{o-C_6H_4(CH_2SMe)_2}_2]PF_6$	3.65, 3.74	100.81(4), 103.75(4)	This work
$[RhCl_2{o-C_6H_4(CH_2SeMe)_2}_2]PF_6$	3.83, 3.90	101.36(4), 104.09(3)	This work
$[Cu\{o-C_6H_4(CH_2SMe)_2\}_2]BF_4$	3.78	110.24(3)	This work
$[Ag\{o-C_6H_4(CH_2TeMe)_2\}_2]BF_4$	4.29, 4.40 (Ag1)	100.90(2), 105.33(2),	This work
	4.36, 4.58 (Ag2)	111.28(2), 102.41(2)	
$[W(CO)_4 \{o - C_6 H_4 (CH_2 TeMe)_2\}]$	4.14	95.69(3)	9
$[MnCl(CO)_{3}\{o-C_{6}H_{4}(CH_{2}TeMe)_{2}\}]$	3.91	96.29(3)	9
$[PtCl_2{o-C_6H_4(CH_2SPh)_2}]$	3.62 (Pt1)	106.30	22
	3.63 (Pt2)	105.66	

<sup>*a*</sup> Only ligands of the form o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>ER)<sub>2</sub> (R = aryl or alkyl) are included since in cyclic and other polydentate ligands containing the *o*-xylyl linkage the overall ligand architecture plays a major role in determining/constraining the bond angles; <sup>*b*</sup> Intraligand E  $\cdots$  E.



Fig. 9 The three conformations of the seven-membered rings formed by the  $o-C_6H_4(CH_2EMe)_2$  ligands: (i) meso-1, (ii) DL, (iii) meso-2.

and the transition metal (fast inversion on Cu(I), Ag(I), Pd(II) > Pt(II) *etc.*).<sup>1,2</sup> Furthermore, the ligands show a strong tendency for chelation despite the seven-membered chelate ring, probably attributable to the *cis*-directing effect of the *o*-xylyl units.

### Structural comparisons

In order to assess the steric consequences of the *o*-xylyl backbone in these dichalcogenoether ligand complexes, the versatility of the ligands in accommodating different coordination geometries and modes, and to allow comparisons with the corresponding Group 15 ligands  $o-C_6H_4(CH_2E'R_2)_2$  (E' = P or Sb), crystal structures of the parent dithioether,  $o-C_6H_4(CH_2SMe)_2$ , and several of the new complexes were determined. Of note are the  $E \cdots E$  distances and comparison of the E–M–E angles involved in the sevenmembered chelate rings against those not in a chelate ring—these are presented in Table 9 and discussed in detail below.

In the planar  $[Pd\{o-C_6H_4(CH_2SMe)_2\}_2]^{2+}$  and all three of the new octahedral species,  $[RuCl_2\{o-C_6H_4(CH_2SMe)_2\}_2]$  and  $[RhCl_2\{o-C_6H_4(CH_2EMe)_2\}_2]^+$ , there is an unusual distribution of bond angles subtended at the metal, with the E–M–E chelate angles always ~100°, while those not involving the chelate ring are correspondingly much more acute, ~80°. This pattern is replicated in the majority of the other structurally characterised octahedral and planar complexes with these ligands (Table 9)—the exceptions are the two carbonyl complexes  $[W(CO)_4\{o-C_6H_4(CH_2TeMe)_2\}]$ and  $[MnCl(CO)_3\{o-C_6H_4(CH_2TeMe)_2\}]$  where the  $\sigma$ -donor/ $\pi$ acceptor CO co-ligands may strongly influence the angles at the metal. A search of the crystallographic database reveals that simple bidentate coordination of the aliphatic ligands  $RE(CH_2)_n ER$  (E = S, Se, Te; n = 2 or 3) on *octahedral* metal centres typically leads to E-M-E chelate angles very close to 90°. In lower coordination species (specifically square planar) the distinction is less clear and the angles involving six-membered chelate rings can range up to 100°. The obtuse chelate angles noted in the complexes described in this work do not appear to show a dependence on the coordination number. In part this must reflect the steric requirements of the o-xylyl linker, however, it seems that this is not the only factor that is important. For example, comparison of  $[Pd\{o-C_6H_4(CH_2SMe)_2\}_2]^{2+}$  with the structure of  $[Pd{o-C_6H_4(CH_2SbMe_2)_2}_2]^{2+}$  (the distibution is expected to have similar steric requirements to the dichalcogenoethers in the present study) shows that while in the former the S-Pd-S chelate angles are 101.87(5), 102.12(5)°, the Sb-Pd-Sb chelate angle in the latter is only 91.50(2)°. This pattern of the xylyl dichalcogenoethers producing significantly wider chelate angles than the corresponding complexes of o-xylyl distibine is also maintained in e.g.  $[PtMe_3I{o-C_6H_4(CH_2SeMe)_2}] \angle Se-Pt-Se = 98.32(1)^\circ vs.$  $[PtMe_{3}I{o-C_{6}H_{4}(CH_{2}SbMe_{2})_{2}}] \angle Sb-Pt-Sb = 95.25(1)^{\circ}.^{18,19} One$ reason for this difference may be the presence of a remaining lone pair on each of the coordinated chalcogen atoms. This repulsion between the remaining lone pairs on the chelate complex may then lead to the chelate angle becoming more obtuse in the chalcogenoether species specifically. We also note that the M-E bond distances in the new complexes are not significantly different to those in similar complexes containing five- and six-membered

	$[Ag\{o-C_6H_4-(CH_2 TeMe)_2\}_2]BF_4$	<ul> <li><sup>24</sup> C<sub>20</sub>H<sub>38</sub>AgBF<sub>4</sub>Te<sub>4</sub> 973.50 Monoclinic</li> <li><i>P2</i><sub>1</sub>//a (14)</li> <li>15.8366(10)</li> <li>20.3931(15)</li> <li>16.5289(10)</li> <li>99.405(4)</li> <li>5266.4(6)</li> <li>8</li> <li>16.5289(10)</li> <li>99.405(4)</li> <li>5266.4(6)</li> <li>8</li> <li>10.0523</li> <li>0.0549</li> <li>0.0549</li> <li>0.0652</li> <li>0.0549</li> <li>0.0729</li> </ul>
	$[RhCl_2\{o-C_6H_4- (CH_2SeMe)_2\}_2]PF_6$	$\begin{array}{c} {\rm C}_{20}{\rm H}_{38}{\rm Cl}_2{\rm F}_6{\rm PRhSe}\\ 903.04\\ {\rm Monoclinic}\\ {\rm P2}_1/n~(14)\\ 12.515(2)\\ 12.0649(16)\\ 18.630(3)\\ 95.422(8)\\ 95.422(8)\\ 95.422(8)\\ 95.422(8)\\ 95.423\\ 6423\\ 6423\\ 6423\\ 311\\ 0.0672\\ 0.1308\\ 0.0878\\ 0.00878\\ 0.1016\end{array}$
	$[Cu{o-C_6H_4-(CH_2SMe)_2}_2]BF_4$	$\begin{array}{c} C_{20}H_{28}BCuF_4S_4\\ 547.01\\ Monoclinic\\ P2/n (13)\\ 10.111(3)\\ 7.746(2)\\ 15.129(4)\\ 102.987(12)\\ 1154.6(5)\\ 1154.6(5)\\ 1154.6(5)\\ 1154.6(5)\\ 1154.6(5)\\ 1154.6(5)\\ 10037\\ 2\\ 2\\ 0.0646\\ 10037\\ 139\\ 0.0779\\ 0.0778\\ 0.0778\\ 0.0884\\ 0.0884\end{array}$
	$[\{RuCl_{2}(p-cymene)\}_{2}-\{\mu-o-C_{6}H_{4}(CH_{2}SMe)_{2}\}]$	$\begin{array}{c} C_{36}H_{42}Cl_4Ru_2S_2\\ 810.70\\ Monoclinic\\ C2/c (15)\\ 13.415(2)\\ 13.415(2)\\ 13.415(2)\\ 13.4612(8)\\ 3220.7(7)\\ 124.612(8)\\ 3220.7(7)\\ 124.612(8)\\ 3220.7(7)\\ 124.612(8)\\ 31058\\ 31058\\ 31058\\ 31058\\ 31058\\ 3005\\ 0.0375\\ 0.0375\\ 0.0908\\ 0.008\\ 0.090$
	$[RuCl_2 \{o - C_6 H_4 - (CH_2 SMe)_2\}_2]$	$\begin{array}{c} C_{20}H_{28}Cl_2RuS_4\\ 568.63\\ Monoclinic\\ P2_1/c (14)\\ 8.401(2)\\ 9.182(2)\\ 15.308(3)\\ 101.282(10)\\ 1158.1(4)\\ 1158.1(4)\\ 1158.1(4)\\ 11787\\ 2\\ 2\\ 12\\ 2\\ 2645\\ 11787\\ 2645\\ 0.0345\\ 0.0267\\ 0.0607\\ 0.0667\\ 0.0663\end{array}$
	$[RhCl_2 \{o-C_6H_4-(CH_2SMe)_2\}_2]PF_6$	$\begin{array}{c} C_{30}H_{3s}Cl_2F_6PRhS_4\\ 715.44\\ Monoclinic\\ P2_4/n (14)\\ 12.356(2)\\ 12.356(2)\\ 12.356(2)\\ 12.356(2)\\ 12.356(2)\\ 12.45\\ 96.621(9)\\ 96.621(9)\\ 2711.3(9)\\ 1.245\\ 0.077\\ 0.0515\\ 0.00515\\ 0.0080\\ 0.0980\\ 0.008$
	$[Pd\{o-C_6H_4-(CH_2SMe)_2\}_2](PF_6)_2$	$\begin{array}{c} C_{30}H_{38}F_{12}P_2PdS_4\\ 793.00\\ Monoclinic\\ P24/n(14)\\ 15.614(2)\\ 9.1855(15)\\ 9.1855(15)\\ 9.1855(15)\\ 20.982(3)\\ 109.356(10)\\ 2839.3(7)\\ 109.356(10)\\ 2839.3(7)\\ 1.151\\ 0.0357\\ 29669\\ 6458\\ 352\\ 0.0357\\ 0.0574\\ 0.0665\\ 0.1469\\ 0.1521\\ 0.1521\end{array}$
phic parameters	o-C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> SMe) <sub>2</sub>	C <sub>10</sub> H <sub>14</sub> S <sub>2</sub> 198.33 Monoclinic <i>C2/c</i> (15) 15.004(3) 7.906(2) 9.4253(15) 110.785(15) 110.785(15) 110.785(15) 110.785(15) 1045.3(4) 0.454 0.0276 6475 66 0.0269 0.0314 0.0675 0.0675
Table 10   Crystallogra	Complex	Formula $M$ Crystal system $M$ Space group (no.) $a/Å$ b/Å b/Å c/Å c/Å b/Å c/Å $b/(Mo-Ka)/mm^{-1}$ $M(Mo-Ka)/mm^{-1}$ $M(Mo-Ka)/mm^{-1}$ $R(Mo-Ka)/mm^{-$

chelate rings, hence it appears that the sterically-demanding ligand backbone in the o-xylyl complexes is usually accommodated by opening the chelate angle at the metal.

# Conclusions

The preparations and characterisation of a systematic series of transition metal complexes involving three homologous o-xylyl dithio-, diseleno- and ditelluro-ether ligands are reported, together with crystal structures of seven representative examples. In addition to the bridging coordination mode observed for [{RuCl<sub>2</sub>(pcymene) $_{2}$ { $\mu$ -o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}], all four of the stereoisomeric forms of chelating  $o-C_6H_4(CH_2EMe)_2$  have been identified in this work (Fig. 9(i)-(iii), meso-1, meso-2 and DL pair), although in all of the crystal structures the plane containing the  $ME_2(CH_2)_2$ fragment is essentially planar. The studies show that these ligands tend to lead to cis-chelation producing seven-membered chelate rings. Through the structural studies we have shown that on both planar and octahedral metals the E-M-E chelate angles are consistently obtuse and usually close to 100°, significantly larger than in the corresponding complexes with  $o-C_6H_4(CH_2SbMe_2)_2$ . This is attributed to a combination of the sterically demanding o-xylyl linkage and also to minimisation of repulsion between the remaining (non-bonded) pair of electrons on the adjacent chalcogen atoms (which are not present on the Group 15 donor atoms).

# Experimental

Physical measurements: Infrared spectra were recorded as Nujol mulls between CsI discs using a Perkin-Elmer 983G spectrometer over the range 4000-180 cm<sup>-1</sup>. Mass spectra were run by electron impact on a VG-70-SE Normal geometry double focusing spectrometer or by positive ion electrospray (MeCN solution) using a VG Biotech platform. <sup>1</sup>H NMR spectra were recorded using a Bruker AV300 spectrometer.  ${}^{13}C{}^{1}H$ ,  ${}^{77}Se{}^{1}H$ , <sup>125</sup>Te{<sup>1</sup>H}, <sup>195</sup>Pt and <sup>63</sup>Cu NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 100.6, 76.3, 126.3, 85.7 or 106.1 MHz, respectively, and are referenced in ppm to TMS, external neat Me<sub>2</sub>Se, Me<sub>2</sub>Te, 1 mol dm<sup>-3</sup> Na<sub>2</sub>[PtCl<sub>6</sub>] in water or [Cu(NCMe)<sub>4</sub>]BF<sub>4</sub> in MeCN, respectively. NMR spectra were recorded at 25 °C unless otherwise stated. Microanalyses were performed by the University of Strathclyde micro-analytical service.

Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques under a N<sub>2</sub> atmosphere. The o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub> was prepared using the literature method.9

# o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>

 $= \sum ||F_{\circ}| - |F_{\circ}|| / \sum |F_{\circ}|; wR_{2} = [\sum w(F_{\circ}^{2} - F_{\circ}^{2})^{2} / \sum wF_{\circ}^{4}]^{1/2}$ 

 $\mathbb{R}^{1}$ 

Sodium (2.318 g, 0.101 mol) was added in small pieces to 200 mL liquid-ammonia cooled in a dry ice/acetone slush. Me<sub>2</sub>S<sub>2</sub> (4.54 mL, 0.050 mol) was added dropwise and the solution left under stirring at  $\sim -78$  °C until it became colourless. After evaporation of ammonia a white solid was obtained. o- $C_6H_4(CH_2Br)_2$  (13.20 g, 0.05 mmol) dissolved in ethanol (200 mL) was added to the above white solid. The mixture was refluxed for 3 h. Hydrolysis (NaCl solution, 100 mL) was followed by separation, extraction with diethyl ether and drying (MgSO<sub>4</sub>). The solvent was removed *in vacuo* to give a very pale yellow oil which crystallized on standing. Yield 8.49 g, 85%. GC-EI MS: m/z 198 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.18–7.32 (m, 4H, *o*-C<sub>6</sub>H<sub>4</sub>), 3.86 (s, 4H, CH<sub>2</sub>), 2.03 (s, 6H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  136.30 (*ipso*-C), 130.68, 127.27 (*o*-C<sub>6</sub>H<sub>4</sub>), 35.50 (CH<sub>2</sub>), 15.43 (Me).

#### o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeMe)<sub>2</sub>

Freshly ground selenium powder (12.63 g, 0.16 mol) in dry tetrahydrofuran (100 mL) was frozen in a liquid nitrogen bath. MeLi (100 mL of 1.6 M solution in diethyl ether, 0.16 mol) was added and the mixture allowed to thaw, then stirred at room temperature for 2 h. o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Br)<sub>2</sub> (21.12 g, 0.080 mol) was added and the mixture refluxed for a further 1 h. Hydrolysis (NaCl solution, 100 mL) was followed by separation, extraction with diethyl ether and drying (MgSO<sub>4</sub>). The solvent was removed by distillation under N<sub>2</sub> to give a pale yellow oil. Yield 20.33 g, 87%. GC-EI MS: m/z 294 (M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.30 (br, 4H, o-C<sub>6</sub>H<sub>4</sub>), 4.05 (s, <sup>2</sup>J<sub>SeH</sub> = 13 Hz, 4H, CH<sub>2</sub>), 2.05 (s, <sup>2</sup>J<sub>SeH</sub> = 10 Hz, 6H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  136.99 (*ipso*-C), 130.70, 127.68 (o-C<sub>6</sub>H<sub>4</sub>), 25.56 (<sup>1</sup>J<sub>C-Se</sub> = 75 Hz, CH<sub>2</sub>), 4.77 (<sup>1</sup>J<sub>C-Se</sub> = 75 Hz, Me). <sup>77</sup>Se{<sup>1</sup>H} NMR (neat):  $\delta$  149.

### $[PdCl_2\{o-C_6H_4(CH_2SMe)_2\}]$

PdCl<sub>2</sub> (0.16 g, 0.90 mmol) was dissolved in MeCN (20 mL). The solution was refluxed and stirred until all of the PdCl<sub>2</sub> dissolved giving a light yellow solution. To the solution o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> (0.162 g, 0.82 mmol) was added. The reaction mixture was refluxed for 2 h and filtered. The yellow filtrate was reduced to ~5 mL *in vacuo*. Cold diethyl ether (~10 mL) was added dropwise to precipitate an orange solid, which was filtered off and dried *in vacuo*. Yield 74%. Required for C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub>PdS<sub>2</sub> (375.7): C, 32.0; H, 3.8. Found: C, 31.9; H, 3.8%. <sup>1</sup>H NMR (d<sup>6</sup>-DMSO):  $\delta$  7.32–7.40 (m, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.22 (m, 4H, CH<sub>2</sub>), 2.53 (s, 6H, Me). IR (Nujol mull):  $\nu$  = 338m, 312s (PdCl) cm<sup>-1</sup>.

### $[PtCl_2\{o-C_6H_4(CH_2SMe)_2\}]$

Method as above, using PtCl<sub>2</sub>, giving a pale yellow solid. Yield 79%. Required for C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub>PtS<sub>2</sub> (464.3): C, 25.9; H, 3.0. Found: C, 25.7; H, 3.0%. <sup>1</sup>H NMR (d<sup>6</sup>-DMSO):  $\delta$  7.28–7.16, 7.30–7.44 (m, 4H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.60–4.30 (m, 4H, CH<sub>2</sub>), 2.62 (s, 6H, Me). IR (Nujol mull):  $\nu$  = 324m, 309m (PtCl) cm<sup>-1</sup>.

### $[Pd{o-C_6H_4(CH_2SMe)_2}_2](PF_6)_2$

PdCl<sub>2</sub> (0.155 g, 0.87 mmol) was dissolved in MeCN (20 mL). The solution was refluxed and stirred until all of the PdCl<sub>2</sub> dissolved. To this solution 2.1 mol equiv. of TlPF<sub>6</sub> (0.64 g, 1.83 mmol) in MeCN (~10 mL) was added. The reaction mixture was refluxed for 1 h. Finally, o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> (0.346 g, 1.74 mmol) was added and the reaction mixture was stirred overnight. The reaction mixture became turbid due to TlCl. The solution was carefully filtered through Celite and the filtrate was concentrated *in vacuo*. Addition of diethyl ether gave a yellow solid which was filtered off and dried *in vacuo*. Yield 82%. Required for C<sub>20</sub>H<sub>28</sub>F<sub>12</sub>P<sub>2</sub>PtS<sub>4</sub>·0.5Et<sub>2</sub>O (830.1): C, 31.8; H. 4.0. Found: C, 31.7; H, 3.9%. <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.39–7.52 (m, 4H, o-C<sub>6</sub>H<sub>4</sub>), 4.49 (s, 4H, CH<sub>2</sub>), 2.57 (s, 6H, Me) (resonances due to associated Et<sub>2</sub>O were also evident). IR

(Nujol mull):  $v = 844s (v(PF_6))$ , 557s ( $\delta(PF_6)$ ) cm<sup>-1</sup>. Electrospray MS (MeCN): m/z 344 [<sup>106</sup>Pd{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}(MeCN)]<sup>+</sup>, 251 [<sup>106</sup>Pd{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}]<sup>2+</sup>.

#### $[Pt{o-C_6H_4(CH_2SMe)_2}_2](PF_6)_2$

Method as above, using PtCl<sub>2</sub>, giving a cream solid. Yield 78%. Required for C<sub>20</sub>H<sub>28</sub>F<sub>12</sub>P<sub>2</sub>PtS<sub>4</sub> (881.7): C, 27.2; H, 3.2. Found: C, 27.7; H, 3.2%. IR (Nujol mull):  $\nu = 844s$  ( $\nu$ (PF<sub>6</sub>), 558s ( $\delta$ (PF<sub>6</sub>)) cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.36 (m, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.63–4.67 (m, 8H, CH<sub>2</sub>), 2.65 (s, 12H, Me). <sup>195</sup>Pt NMR (d<sup>6</sup>-acetone, 298 K): not observed; 243 K:  $\delta$  –4025 (br). Electrospray MS (MeCN): *m/z* 392 [<sup>195</sup>Pt{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}]<sup>+</sup>, 296 [<sup>195</sup>Pt{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}]<sup>+</sup>.

#### $[RhCl_2{o-C_6H_4(CH_2SMe)_2}_2]PF_6$

 $RhCl_3 \cdot 3H_2O(0.203 \text{ g}, 0.77 \text{ mmol})$  was dissolved in EtOH (20 mL). To this was added a solution of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> (0.415 g, 2.1 mmol) in EtOH (10 mL). The reaction mixture was refluxed under  $N_2$  for 3 h, followed by addition of  $NH_4PF_6$  (0.138 g, 0.85 mmol) in EtOH (5 mL). The reaction mixture changed from red to yellow and the white precipitate (NH<sub>4</sub>Cl) was filtered off. The solution was reduced in volume to  $\sim 5$  mL in vacuo. Upon addition of diethyl ether (10 mL) an orange precipitate formed which was filtered off and washed with diethyl ether  $(2 \times 10 \text{ mL})$ . The orange solid was dried in vacuo. Yield 85%. Required for C<sub>20</sub>H<sub>28</sub>Cl<sub>2</sub>F<sub>6</sub>PRhS<sub>4</sub> (715.5): C, 33.6; H, 3.9. Found: C, 33.9; H, 4.0%. <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.75–7.26 (m, 8H, o-C<sub>6</sub>H<sub>4</sub>), 4.08– 4.23 (m, 4H, CH2), 4.08-4.23 (m, 4H, CH2), 2.95, 2.89 (s, 12H, Me). IR (Nujol mull):  $v = 833s (v(PF_6)), 556s (\delta(PF_6)), 332w, 314w$ (v(RhCl)) cm<sup>-1</sup>. Electrospray MS (MeCN): m/z 569 [RhCl<sub>2</sub>{o- $C_6H_4(CH_2SMe)_2_2^{+}$ .

### $[RuCl_2\{o-C_6H_4(CH_2SMe)_2\}_2]$

To a deoxygenated solution of RuCl<sub>3</sub>·*x*H<sub>2</sub>O (0.236 g, 0.90 mmol) in ethanol (50 mL) and water (15 mL) was added o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> (0.358 g, 1.81 mmol), and the mixture was heated to reflux. At this point hypophosphorous acid (2 mL) was added to the solution. Further reflux led to a colour change to deep blue and finally yellow, and a yellow solid precipitated which was filtered off, washed with Et<sub>2</sub>O and dried *in vacuo*. Yield 65%. Required for C<sub>20</sub>H<sub>28</sub>Cl<sub>2</sub>RuS<sub>4</sub> (568.7): C, 42.2; H, 5.0. Found: C, 41.1; H, 5.0%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.1–7.3 (m, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.19 (br s, 8H, CH<sub>2</sub>), 2.08 (s, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  135.87, 133.65, 128.24 (*o*-C<sub>6</sub>H<sub>4</sub>), 36.97 (CH<sub>2</sub>), 17.35 (Me). IR (Nujol mull):  $v = 332 (v(RuCl)) \text{ cm}^{-1}$ . Electrospray MS (MeCN): *m/z* 576 [RuCl<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>]<sub>2</sub>]<sup>+</sup>.

#### $[\{RuCl_2(p-cymene)\}_2\{\mu-o-C_6H_4(CH_2SMe)_2\}]$

[Ru( $\eta^6$ -*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (0.10 g, 0.16 mmol) was dissolved in degassed CH<sub>2</sub>Cl<sub>2</sub> (10 mL). To this was added 2 mol equiv. of *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> (0.063 g, 0.32 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) dropwise. The reaction mixture was left to stir overnight. The solvent was then removed under vacuum and the pale orange solid was washed with petroleum ether (40–60 °C) and Et<sub>2</sub>O and was dried under vacuum. Layering a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex with Et<sub>2</sub>O or a toluene solution of the complex with Et<sub>2</sub>O produces

orange crystals of the title compound. Yield 30%. Required for  $C_{30}H_{42}Cl_4Ru_2S_2$  (810.7): C, 44.4; H, 5.2. Found: C, 44.7; H, 5.3%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.33 (br s, 4H, o-C<sub>6</sub> $H_4$ (CH<sub>2</sub>SMe)<sub>2</sub>), 5.50 (d, 4H, d, <sup>3</sup> $J_{HH} = 5.5$  Hz, *p*-cymene CH), 5.33 (br s, 4H, *p*-cymene CH), 4.23 (br s, 4H, CH<sub>2</sub>S), 2.94 (sept, 2H, <sup>3</sup> $J_{HH} = 7.0$  Hz, CH), 2.04 (s, 6H, *p*-cymene Me), 2.21 (s, 6H, SMe), 1.30 (d, 12H, <sup>3</sup> $J_{HH} = 7.0$  Hz, CH $Me_2$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  134.5 (aromatic quaternary C from ligand), 132.2 (aromatic CH from ligand), 128.7 (aromatic CH from ligand), 105.1 (*p*-cymene CH), 83.4 (*p*-cymene CH), 40.4 (CH<sub>2</sub>S), 30.9 (CHMe<sub>2</sub>), 22.4 (*p*-cymene Me), 18.6 (*p*-cymene Me), 18.2 (SMe).

### $[Cu{\it o-C_6H_4(CH_2SMe_2)_2}]BF_4$

[Cu(NCMe)<sub>4</sub>](BF<sub>4</sub>) (0.150 g, 0.478 mmol) was taken up in Me<sub>2</sub>CO (20 mL) and stirred. Two mol. equivs. of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> (0.192 g, 0.972 mmol) were added, and the reaction was stirred for 2 h. A white solid precipitated off, which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 82%. Required for C<sub>20</sub>H<sub>28</sub>BCuF<sub>4</sub>S<sub>4</sub> (547.0): C, 43.9; H, 5.2. Found: C, 43.6; H, 5.0%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.34 (br, 8H, o-C<sub>6</sub>H<sub>4</sub>), 4.07 (s, 8H, CH<sub>2</sub>), 2.14 (s, 12H, Me). <sup>63</sup>Cu NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  132; (273 K):  $\delta$  137. Electrospray MS (MeCN): *m/z* 459 [Cu{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>]<sub>2</sub>]<sup>+</sup>, 302 [Cu{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}(MeCN)]<sup>+</sup>, 261 [Cu{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>]<sup>+</sup>. IR (Nujol mull): v = 1045br s (*v*(BF<sub>4</sub>)) cm<sup>-1</sup>.

### $[Ag\{\textit{o-C}_6H_4(CH_2SMe)_2\}_2]BF_4$

AgBF<sub>4</sub> (0.545 g, 2.80 mmol) was taken up in MeOH (20 mL) in a foil-wrapped reaction vessel to exclude light at 0 °C. Two equivalents of o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub> (1.11 g, 5.60 mmol) were dissolved in MeOH (10 mL) and added dropwise whilst stirring, maintaining the temperature at 0 °C. After stirring for 2 h, the white precipitate was recovered by filtration, and dried *in vacuo*. Yield 87%. The solid was stored in a foil wrapped container to avoid decomposition by light. Required for C<sub>20</sub>H<sub>28</sub>AgBF<sub>4</sub>S<sub>4</sub> (591.4): C, 40.6; H, 4.8. Found: C, 39.9; H, 4.8%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.25 (br, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 3.95 (s, 8H, CH<sub>2</sub>), 2.25 (s, 12H, Me). Electrospray MS (MeCN): *m/z* 507 [<sup>109</sup>Ag{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}]<sup>+</sup>, 348 [<sup>109</sup>Ag{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}]<sup>+</sup>. IR (Nujol mull): *v* = 1049br s (*v*(BF<sub>4</sub>)) cm<sup>-1</sup>.

### $[Pt{\it o-C_6H_4(CH_2SeMe)_2}_2](PF_6)_2$

Method same as for  $[Pt\{o-C_6H_4(CH_2SMe)_2\}_2](PF_6)_2$  above giving a pale yellow solid. Yield 70%. Required for  $C_{20}H_{28}F_{12}P_2PtSe_4$ (1069.3): C, 22.5; H, 2.6. Found: C, 22.6; H, 2.5%. <sup>1</sup>H NMR (d<sup>6</sup>acetone):  $\delta$  7.17–7.45 (m, 8H,  $o-C_6H_4$ ), 4.21–4.81 (m, 8H, CH<sub>2</sub>), 2.13–2.62 (overlapping s, 12H, Me). <sup>195</sup>Pt NMR (d<sup>6</sup>-acetone, 298 K): -4687; (198 K):  $\delta$  –4560, -4772. <sup>77</sup>Se{<sup>1</sup>H} NMR (d<sup>6</sup>-acetone 298 K):  $\delta$  212, 206, 198. IR (Nujol mull):  $\nu$  = 831s ( $\nu$ (PF<sub>6</sub>)), 556s ( $\delta$ (PF<sub>6</sub>)) cm<sup>-1</sup>. Electrospray MS (MeCN): m/z 390 [<sup>195</sup>Pt{ $o-C_6H_4$ (CH<sub>2</sub>SeMe)<sub>2</sub>}<sub>2</sub>]<sup>2+</sup>.

### $[Pd{\it o-C_6H_4(CH_2SeMe)_2}_2](PF_6)_2$

Method same as for  $[Pd\{o-C_6H_4(CH_2SMe)_2\}_2](PF_6)_2$  giving a bright yellow solid. Yield 75%. Required for  $C_{20}H_{28}F_{12}P_2PdSe_4$ 

(980.6): C, 24.5; H, 2.9. Found: C, 23.9; H, 2.7%. <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.27–7.37 (m, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.37 (s, 8H, CH<sub>2</sub>), 2.36 (s, 12H, Me). <sup>77</sup>Se{<sup>1</sup>H} NMR (d<sup>6</sup>-acetone, 298 K):  $\delta$  205. IR (Nujol mull):  $\nu = 840s (\nu(PF_6))$ , 556s ( $\delta(PF_6)$ ) cm<sup>-1</sup>. Electrospray MS (MeCN): *m/z* 346 [<sup>106</sup>Pd{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeMe)<sub>2</sub>}]<sup>2+</sup>, 582 [<sup>106</sup>Pd{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeMe)<sub>2</sub>}(MeCN)(PF<sub>6</sub>)] <sup>+</sup>.

# $[RhCl_2\{\textit{o-C}_6H_4(CH_2SeMe)_2\}_2]PF_6$

Method as for  $[RhCl_2{o-C_6H_4(CH_2SMe)_2}_2]PF_6$ , using  $RhCl_3 \cdot 3H_2O$ , giving a bright orange solid. Yield 69%. Required for  $C_{20}H_{28}F_6PRhSe_4$  (903.0): C, 26.6; H, 3.1. Found: C, 26.3; H, 2.9%. IR (Nujol mull): v = 834s ( $v(PF_6)$ ), 556s ( $\delta(PF_6)$ ), 314br (v(RhCl)) cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.27–7.51 (m, 8H, o-C<sub>6</sub>H<sub>4</sub>), 4.6–4.8, 3.8–4.2 (m, 8H, CH<sub>2</sub>), 2.13–2.63 (overlapping s, 12H, Me). <sup>77</sup>Se{<sup>1</sup>H} NMR (d<sup>6</sup>-acetone): several doublet resonances in the range  $\delta$  241–213, <sup>1</sup>J(Rh–Se) = 30–45 Hz. Electrospray MS (MeCN): m/z 759 [RhCl<sub>2</sub>{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SeMe)<sub>2</sub>}]<sup>+</sup>.

# $[RuCl_2 \{o-C_6H_4(CH_2SeMe)_2\}_2]$

Method as for  $[\text{RuCl}_2\{o\text{-}C_6\text{H}_4(\text{CH}_2\text{SMe})_2\}_2]$ , giving an orange solid. Yield 60%. IR (Nujol mull): v = 308m (v(RuCl)) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.0–7.2 (m, 8H,  $o\text{-}C_6\text{H}_4$ ), 3.5–4.7 (br m, 8H, CH<sub>2</sub>), 2.5–2.8 (overlapping s, 12H, Me). <sup>77</sup>Se{<sup>1</sup>H} NMR (d<sup>6</sup>-acetone, 298 K):  $\delta$  247, 235, 219, 213 (br). Electrospray MS (MeCN): m/z 761 [<sup>102</sup>RuCl<sub>2</sub>{ $o\text{-}C_6\text{H}_4(\text{CH}_2\text{SeMe})_2\}_2$ ]<sup>+</sup>.

### $[Cu\{\textit{o-C}_6H_4(CH_2SeMe)_2\}_2]BF_4$

Method as for  $[Cu\{o-C_6H_4(CH_2SMe)_2\}_2]BF_4$ , giving a white solid. Yield 70%. Required for  $C_{20}H_{28}BCuF_4Se_4$  (734.6): C, 32.7; H, 3.8. Found: C, 33.5; H, 4.0%. <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.32 (s, 8H,  $o-C_6H_4$ ), 4.16 (s, 8H, CH<sub>2</sub>), 2.09 (s, 12H, Me). <sup>77</sup>Se{<sup>1</sup>H} NMR (acetone):  $\delta$  87. <sup>63</sup>Cu NMR (acetone):  $\delta$  –2. IR (Nujol mull):  $\nu$  = 1043s ( $\nu$ (BF<sub>4</sub>)) cm<sup>-1</sup>. Electrospray MS (MeCN): m/z 398 [<sup>63</sup>Cu{ $o-C_6H_4$ (CH<sub>2</sub>SeMe)<sub>2</sub>](MeCN)]<sup>+</sup>, 357 [<sup>63</sup>Cu{ $o-C_6H_4$ (CH<sub>2</sub>SeMe)<sub>2</sub>]<sup>+</sup>.

### $[Ag\{\textit{o-C}_6H_4(CH_2SeMe)_2\}_2]BF_4$

Method same as for  $[Ag\{o-C_6H_4(CH_2SMe)_2\}_2]BF_4$ , giving an offwhite solid. Yield 64%. Required for  $C_{20}H_{28}AgBF_4Se_4$  (778.9): C, 30.8; H, 3.6. Found: C, 31.0; H, 3.3%. IR (Nujol mull): v =1052s ( $v(BF_4)$ ) cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.37–7.38 (m, 8H,  $o-C_6H_4$ ), 4.27–4.29 (br, 8H, CH<sub>2</sub>), 2.92 (br, 12H, Me). <sup>77</sup>Se{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>, 273 K):  $\delta$  106; (233 K):  $\delta$  101. Electrospray MS (MeCN): m/z 693 [<sup>109</sup>Ag{ $o-C_6H_4$ (CH<sub>2</sub>SeMe)<sub>2</sub>}<sub>2</sub>]<sup>+</sup>.

### $[RhCl_2\{\textit{o-C}_6H_4(CH_2TeMe)_2\}_2]Cl$

To a solution of Na<sub>3</sub>RhCl<sub>6</sub>·12H<sub>2</sub>O (0.20 g, 0.333 mmol) in ethanol (50 mL) was added o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub> (0.259 g, 0.67 mmol) in ethanol (5 mL). The reaction mixture was stirred at room temperature under N<sub>2</sub> for 15 h. The EtOH was then removed *in vacuo* and the compound was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the solution filtered and Et<sub>2</sub>O added to give a brown solid. Yield 65%. Required for C<sub>20</sub>H<sub>28</sub>Cl<sub>3</sub>RhTe<sub>4</sub> (988.1): C, 24.3; H, 2.9. Found: C, 24.8; H, 2.8%. IR (Nujol mull): v = 319m, 314m (*v*(RhCl)) cm<sup>-1</sup>. Electrospray MS (MeCN): *m/z* 952 [RhCl<sub>2</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>}<sup>+</sup>.

#### $[RuCl_2{o-C_6H_4(CH_2TeMe)_2}_2]$

RuCl<sub>3</sub>·3H<sub>2</sub>O (0.142 g, 0.543 mmol) was dissolved in 2methoxyethanol (40 mL) and the ligand o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub> (0.413 g, 1.083 mmol) was added to it. The reaction mixture was stirred overnight under N<sub>2</sub>, concentrated *in vacuo* and Et<sub>2</sub>O was added to give a yellowish brown solid. Yield 67%. Required for C<sub>20</sub>H<sub>28</sub>Cl<sub>2</sub>RuTe<sub>4</sub> (950.8): C, 25.3; H, 3.0. Found: C, 25.4; H, 3.1%. Electrospray MS (MeCN): *m/z* 956 [RuCl<sub>2</sub>{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>]<sup>+</sup>.<sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.05–7.45 (m, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.30–4.93 (m, 8H, CH<sub>2</sub>), 2.21–2.42 (overlapping s, 12H, Me). IR (Nujol mull): *v* = 313, 305 (*v*(RuCl)) cm<sup>-1</sup>.

### $[Cu{o-C_6H_4(CH_2TeMe)_2}_2]BF_4$

Prepared by the literature method,<sup>9</sup> giving a yellow solid. Yield 74%. IR (Nujol mull):  $v = 1047s (v(BF_4)) \text{ cm}^{-1}$ . <sup>1</sup>H NMR (acetone):  $\delta$  7.15–7.23 (m, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.18 (s, 8H, CH<sub>2</sub>), 1.97 (s, 12H, Me). <sup>125</sup>Te{<sup>1</sup>H} NMR (acetone 298 K):  $\delta$  98 (sample precipitates on cooling the solution). <sup>63</sup>Cu NMR (acetone 298 K):  $\delta$  +16. Electrospray MS (MeCN): m/z 845 [<sup>63</sup>Cu{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>}]<sup>+</sup>, 496 [<sup>63</sup>Cu{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>}(MeCN)]<sup>+</sup>.

### $[Ag{o-C_6H_4(CH_2TeMe)_2}_2]BF_4$

Prepared by the literature method,<sup>9</sup> but using AgBF<sub>4</sub>, giving a yellow solid. Yield 73%. IR (Nujol mull):  $v = 1043s (v(BF_4)) \text{ cm}^{-1}$ . <sup>1</sup>H NMR (d<sup>6</sup>-acetone):  $\delta$  7.14–7.23 (m, 8H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.23 (s, 8H, CH<sub>2</sub>), 2.01 (s, 12H, Me). <sup>125</sup>Te{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  107; (193 K):  $\delta$  134.5 (br), 108 (br), 80 (br). Electrospray MS (MeCN): m/z 888 [<sup>107</sup>Ag{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>}]<sup>+</sup>, 890 [<sup>109</sup>Ag{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>TeMe)<sub>2</sub>}]<sup>+</sup>.

### X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 10. Crystals of the compounds were obtained by slow evaporation from CH<sub>2</sub>Cl<sub>2</sub> solution  $(o-C_6H_4(CH_2SMe)_2, [RhCl_2\{o-C_6H_4(CH_2SeMe)_2\}_2]PF_6$ and  $[Ag\{o-C_6H_4(CH_2TeMe)_2\}]BF_4$ , by layering a  $CH_2Cl_2$ solution of the compound with  $Et_2O$  ([RhCl<sub>2</sub>{o- $C_{6}H_{4}(CH_{2}SMe)_{2}_{2}PF_{6}$ ,  $[Pd\{o-C_{6}H_{4}(CH_{2}SMe)_{2}\}_{2}](PF_{6})_{2}$  and  $[RhCl_{2}{o-C_{6}H_{4}(CH_{2}SeMe)_{2}}]PF_{6})$ , by slow evaporation from MeNO<sub>2</sub> solution ( $[Cu{o-C_6H_4(CH_2SMe)_2}_2]BF_4$ ), by slow evaporation from acetone solution ([RuCl<sub>2</sub>{o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SMe)<sub>2</sub>}]) and by layering a solution of the complex in toluene with Et<sub>2</sub>O  $([{RuCl_2(p-cymene)}_2 \{\mu - o - C_6 H_4 (CH_2 SMe)_2\}])$ . Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with graphite or confocal mirror monochromated Mo-Ka X-radiation  $(\lambda = 0.71073 \text{ Å})$ . Structure solution and refinement were generally routine,<sup>20,21</sup> except for  $[Ag\{o-C_6H_4(CH_2TeMe)_2\}_2]BF_4$  for which some disorder was identified at Te6. This was modelled very satisfactorily using a split Te atom position (Te6/Te6A) with Te6A being the very minor component. The methyl carbon (C30) bonded to Te6 was clearly identified and a weak peak in the difference electron-density map was associated with C30A bonded to Te6A. Selected bond lengths and angles are given in Tables 1-8.

CCDC reference numbers 621497-621504.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613501c

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