Synthesis and Spectroscopic Studies of Palladium and Platinum Complexes of Methylene-backboned Dithio-, Diseleno- and Ditelluro-ether Ligands, $RECH_2ER$ (R = Me or Ph; E = S, Se or Te)*

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The complexes $[ML_2Cl_2]$ (M = Pd or Pt; L = $PhSCH_2SPh$, $MeSCH_2SMe$, $PhSeCH_2SePh$ or $MeSeCH_2SeMe$), which are square planar with monodentate sulfur or selenium ligands, have been prepared. In the solid state, on the basis of IR and Raman data, the palladium complexes are *trans* and the platinum *cis*, whilst in solution multinuclear NMR spectroscopy (^1H, ^{195}Pt-{^1H}, and ^{77}Se-{^1H}) reveal that both *cis* and *trans* isomers and *meso* and DL enantiomers are present, the isomer populations varying with L and M in a systematic way. The complexes $[ML_2Cl_2]$ are stable in solution for L = $PhSCH_2SPh$, but the other complexes lose L to precipitate polymeric $[(MLCl_2)_n]$ complexes. The ditelluroethers, $MeTeCH_2TeMe$ and $PhTeCH_2TePh$, form only the latter type of complex. The crystal structure of *trans*-$[Pd(PhSCH_2SPh)_2Cl_2]$ has been determined and contains a *trans* square-planar palladium atom with one co-ordinated and one free sulfur atom associated with each dithioether ligand [Pd–Cl 2.292(1) and Pd–S 2.329(1) Å].

Bidentate ligands in which the interdonor linkage is a single carbon atom including $Ph_2PCH_2PPh_2$, $Ph_2AsCH_2AsPh_2$, 2-$Ph_2PC_5H_4N$ and $PPh(CH_2PPh_2)_2$, have been widely used to prepare both homo- and hetero-bimetallic complexes.[1–3] The short interdonor linkage disfavours chelation to a single metal centre due to the ring strain, and hence promotes monodentate or bridging bonding modes. Much less effort has been devoted to the corresponding ligands containing Group 16 donor atoms, and only a limited number of complexes are known for $PhSCH_2SPh$, $MeSCH_2SMe$, $MeSCH_2SeMe$ and $PhTeCH_2TePh$.[4–7] We are currently investigating the synthesis of various heterobimetallic complexes as catalyst precursors, and during these studies investigated palladium and platinum complexes of $RECH_2ER$ (R = Ph or Me; E = S, Se or Te), as new building blocks for such complexes. Although the complexes ultimately proved too labile for our purposes, several interesting trends were observed and these are described here.

Results

The reaction of the dithio- or diseleno-ether ligands with $Na_2[PdCl_4]$, $K_2[PtCl_4]$, $[Pd(MeCN)_2Cl_2]$ or $[Pt(MeCN)_2Cl_2]$ in a 2:1 mol ratio in ethanol–CH_2Cl_2, usually yielded $[ML_2Cl_2]$ complexes, which in some cases lost ligand to form $[(MLCl_2)_n]$ materials. With the ditelluroethers $PhTeCH_2TePh$ and $MeTeCH_2TeMe$, the insoluble $[(MLCl_2)_n]$ complexes precipitated rapidly from CH_2Cl_2 solutions of $[M(MeCN)_2Cl_2]$ (M = Pd or Pt) on reaction even with a large excess of ligand, and unlike the dithio- or diseleno-ether complexes, the reaction was not reversed by warming with excess ligand. The complexes were characterised in the solid state by elemental analysis and IR and Raman spectroscopies, and the forms present in solution identified by variable-temperature multinuclear NMR spectroscopy. Due to the variation in behaviour it is convenient to discuss the ligands separately.

$PhSCH_2SPh$.—As described previously[5,6] $[ML_2Cl_2]$ complexes are readily obtained for both metals, and are stable in solution. The presence of single IR and Raman active ν(Pd–Cl) vibrations (Table 1) at similar frequencies to those[8] of *trans*-$[Pd(Me_2S)_2Cl_2]$ identified the palladium complex as the *trans* isomer, which was confirmed by X-ray crystallography (see later). However $[Pt(PhSCH_2SPh)_2Cl_2]$ has two coincident vibrations in the IR and Raman spectra consistent with a *cis* geometry.[8] Neither complex appeared to lose ligand in solution, although $[\{Pd(PhSCH_2SPh)Cl_2\}_n]$ is formed using a Pd:L ratio of 1:0.8.[5] The ^1H NMR spectra of solutions of $[ML_2Cl_2]$ in the presence of added $PhSCH_2SPh$ showed separate CH_2 resonances for free and co-ordinated ligands, demonstrating that intermolecular exchange was slow on the NMR time-scale. The ^1H NMR spectrum of *trans*-$[Pd(PhSCH_2SPh)_2Cl_2]$ in CD_2Cl_2 contained a single CH_2 resonance at 300 K, but on cooling to 213 K this resolved into a broad four line pattern. Two AB quartets are expected due to the presence of the *meso* and DL forms (Fig. 1) of the co-ordinated dithioether which interconvert by pyramidal inversion at sulfur, as described in detail for $[ML_2Cl_2]$ complexes of RCH_2SR' by Abel *et al.*[9] We did not resolve the separate patterns, presumably due to the near coincidence of the resonances. The solution NMR data for $[Pt(PhSCH_2SPh)_2Cl_2]$ are considerably more complex (Tables 2 and 3). At 300 K the ^{195}Pt-{^1H} NMR spectrum contains four lines of approximately equal intensity, which are assignable from their characteristic shifts[10] to the presence of *trans* (δ *ca.* −3320) and *cis* (δ *ca.* −3440) isomers, each appearing as a doublet due to the presence of *meso* and DL enantiomers. Pyramidal inversion is a higher energy process in platinum compared to palladium complexes,[4] and hence the resonances of the separate invertomers are resolved at ambient temperatures. Cooling the samples to 203 K caused the platinum resonance to sharpen and shift to more negative values but had no other effect. The ^1H NMR spectra at 300 K show two broad resonances in the CH_2 region probably due to *cis* and *trans* isomers, which sharpen on cooling, but even at 200 K the patterns are not clearly resolved. This is almost certainly due to the large number of lines expected from the resonances of the *cis–trans*, *meso*–DL forms with accompanying ^{195}Pt satellites.[9]

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and vibrational spectroscopic data

Complex	Analysis[a] (%) C	H	IR[b]/cm^{-1} ν(M–Cl)	Raman[c]/cm^{-1} ν(M–Cl)
$[Pd(MeSCH_2SMe)_2Cl_2]$	17.1 (18.3)	3.2 (4.1)	354	305
$[Pt(MeSCH_2SMe)_2Cl_2]$	14.9 (14.9)	2.7 (3.3)	316, 307	327, 304
$[Pd(PhSCH_2SPh)_2Cl_2]$	48.2 (48.6)	3.3 (3.7)	355	305
$[Pt(PhSCH_2SPh)_2Cl_2]$	43.2 (42.7)	3.3 (3.3)	319, 315	330 (vbr)
$[Pd(PhSeCH_2SePh)_2Cl_2]$	33.9 (37.6)	2.3 (2.9)[d]	354	303
$[Pt(PhSeCH_2SePh)_2Cl_2]$	32.8 (34.0)	2.4 (2.6)[d]	318, 312	326, 306
$[Pd(MeSeCH_2SeMe)_2Cl_2]$	12.7 (12.4)	3.0 (2.8)	353	305
$[Pt(MeSeCH_2SeMe)_2Cl_2]$	11.0 (10.7)	2.3 (2.4)	321, 312	323, 311
$[\{Pd(MeSCH_2SMe)Cl_2\}_n]$	12.5 (12.6)	2.4 (2.8)	361	310
$[\{Pt(MeSCH_2SMe)Cl_2\}_n]$	9.6 (9.6)	2.0 (2.1)	334, 321	334, 323 (sh)
$[\{Pd(PhSCH_2SPh)Cl_2\}_n]$	38.9 (38.2)	3.1 (2.9)	355[e]	—
$[\{Pd(PhSeCH_2SePh)Cl_2\}_n]$	30.4 (31.0)	2.5 (2.4)	354	314
$[\{Pt(PhSeCH_2SePh)Cl_2\}_n]$	27.8 (26.4)	1.9 (2.0)	326, 317 (sh)	327, 316
$[\{Pd(MeSeCH_2SeMe)Cl_2\}_n]$	9.4 (9.5)	1.5 (2.1)	349	298
$[\{Pt(MeSeCH_2SeMe)Cl_2\}_n]$	7.7 (7.7)	1.6 (1.7)	321 (sh), 314	322, 310
$[\{Pd(MeTeCH_2TeMe)Cl_2\}_n]$	7.9 (7.6)	1.6 (1.7)	362	*f*
$[\{Pt(MeTeCH_2TeMe)Cl_2\}_n]$	5.9 (6.4)	1.1 (1.4)	324, 316	*f*
$[\{Pd(PhTeCH_2TePh)Cl_2\}_n]$	25.6 (26.0)	1.4 (2.0)	349	305
$[\{Pt(PhTeCH_2TePh)Cl_2\}_n]$	22.9 (22.5)	2.0 (1.7)	327, 317	328, 311

[a] Calculated value in parentheses. [b] Nujol mull. [c] Powdered sample. [d] Due to the instability of these complexes in solution, repeated attempts to obtain samples with good analytical data have failed. [e] Data from ref. 5. [f] Decomposed in laser beam.

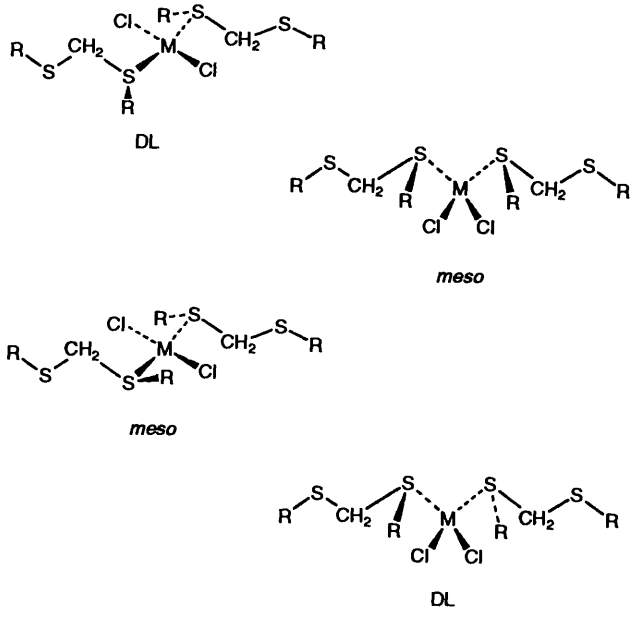

Fig. 1 The *meso* and DL enantiomers of *cis*- and *trans*-$[ML_2Cl_2]$ (L = $RSCH_2SR$)

Table 2 Selected ^1H NMR data

Complex	T/K	δ(^1H)[a]
$[Pd(PhSCH_2SPh)_2Cl_2]$	300	4.58
	213	4.6 (q)
$[Pt(PhSCH_2SPh)_2Cl_2]$	300	4.5, 4.7
	203	4.3–4.8 (m)
$[Pd(MeSCH_2SMe)_2Cl_2]$	300	4.1 (br), 2.35, 2.25
	233	4.01 (q), 2.42, 2.25
$[Pt(MeSCH_2SMe)_2Cl_2]$	300	4.1 (m), 2.64 [$^3J(^{195}Pt-^1H)$ 40], 2.37, 2.50 [$^3J(^{195}Pt-^1H)$ 32], 2.31
	233	4.1 (q),[b] 2.63 [$^3J(^{195}Pt-^1H)$ 40], 2.33, 2.48 [$^3J(^{195}Pt-^1H)$ 32], 2.28
$[Pd(PhSeCH_2SePh)_2Cl_2]$	300	4.55
	213	4.48 (m), 4.22 (m)
$[Pt(PhSeCH_2SePh)_2Cl_2]$	300	4.4 (m), 4.0 (m)
	223	4.9 (m), 4.55 (m), 4.25 (m)
$[Pd(MeSeCH_2SeMe)_2Cl_2]$	300	4.03, 2.30
	233	4.0 (q), 2.38, 2.20
$[Pt(MeSeCH_2SeMe)_2Cl_2]$	300	3.9 (q), 2.32 [$^3J(^{195}Pt-^1H)$ 35], 2.15
	213	3.9 (q), 2.35, 2.17

[a] At 360 MHz in CD_2Cl_2 relative to $SiMe_4$ at the temperature stated, signals are singlets unless indicated otherwise; *J* values in Hz. [b] Quartet overlaying another pattern.

$MeSCH_2SMe$.—This ligand was reported only to form insoluble 1 : 1 complexes with both metals,[5] but a reinvestigation reveals that 2 : 1 complexes are formed with excess ligand. These lose one equivalent of ligand on standing in solution, depositing the $[(MLCl_2)_n]$ compounds, and the solid $[ML_2Cl_2]$ complexes lose ligand on pumping in high vacuum. The ligand loss is reversible in that addition of $MeSCH_2SMe$ to suspensions of $[(MLCl_2)_n]$ in CH_2Cl_2 reform $[ML_2Cl_2]$ in solution. Ligand loss is facile and obtaining analytically pure $[ML_2Cl_2]$ compounds is difficult. The vibrational spectra (Table 1) show that $[Pd(MeSCH_2SMe)_2Cl_2]$ is *trans* and $[Pt(MeSCH_2SMe)_2Cl_2]$ *cis* in the solid state. The ^1H NMR spectrum of the palladium complex has a singlet CH_2 resonance at room temperature, but this resolves into an AB pattern at 233 K, showing pyramidal inversion is a higher energy process than in the corresponding complex of $PhSCH_2SPh$, the usual effect of replacing Me by Ph.[4] Separate resonances are seen even at room temperature for the co-ordinated and free (S)Me groups showing that 1,3 ligand switching[4] is slow on the NMR time-scale.

The $^{195}Pt-\{^1H\}$ NMR spectrum of $[Pt(MeSCH_2SMe)_2Cl_2]$ at 300 K shows only two signals at δ −3366 and −3525 assignable to *trans* and *cis* isomers respectively. This was surprising since by comparison with the complex of $PhSCH_2SPh$, four lines due to the *meso* and DL forms of each isomer were expected. On cooling to 185 K, the ^{195}Pt resonances sharpened, and very small splittings are resolved, from which we conclude that the expected splittings were lost in the line-width at room temperature. The ^1H NMR spectrum is complex even at room temperature (Fig. 2), showing a broad unresolved signal in the CH_2 region, and four Me signals, two with ^{195}Pt satellites due to the co-ordinated MeS groups, and two without due to the free MeS groups. Some free $MeSCH_2SMe$ ligand was also present in most spectra, due to partial decomposition to the 1 : 1 complex. On cooling, the

Table 3 Selected ^{195}Pt and ^{77}Se NMR data

Complex	T/K	$\delta(^{195}Pt\text{-}\{^1H\})^a$	$\delta(^{77}Se\text{-}\{^1H\})^b$
$[Pt(PhSCH_2SPh)_2Cl_2]$	300	−3319, −3331, −3437, −3450	
	203	−3330, −3346, −3465, −3488	
$[Pt(MeSCH_2SMe)_2Cl_2]$	300	−3366, −3525	
	233	−3395, −3563	
$[Pd(PhSeCH_2SePh)_2Cl_2]$	300		*ca.* 385 (vbr), *ca.* 337 (vbr), *ca.* 330 (br)
	243		388.8, 387.7, 334.6, 333.9
$[Pt(PhSeCH_2SePh)_2Cl_2]$	300	−3395, −3405, −3588, −3598	395.7, 394.8, 392.7, 391.8,[c] 331.4, 331.0, 330.6 (sh)
	243	−3408, −3420, −3593, −3615	396.0, 394.7, 389.2, 387.4,[c] 332.6 (br)
$[Pd(MeSeCH_2SeMe)_2Cl_2]$	300		*ca.* 243 (br), *ca.* 127 (br)
	233		238, 123
	193		234.7, 234.5, 120
$[Pt(MeSeCH_2SeMe)_2Cl_2]$	300	−3424	235.5, 235.3 [$^1J(^{195}Pt\text{–}^{77}Se)$ 342, 335], 118.5
	243	−3442, −3441.5	231.6, 231.3 [$^1J(^{195}Pt\text{–}^{77}Se)$ 342, 335], 113.4

[a] At 77.8 MHz in CH_2Cl_2 relative to external $[PtCl_6]^{2-}$. [b] At 68.68 MHz relative to neat external $SeMe_2$; *J* values in Hz. [c] Platinum coupling not clearly resolved.

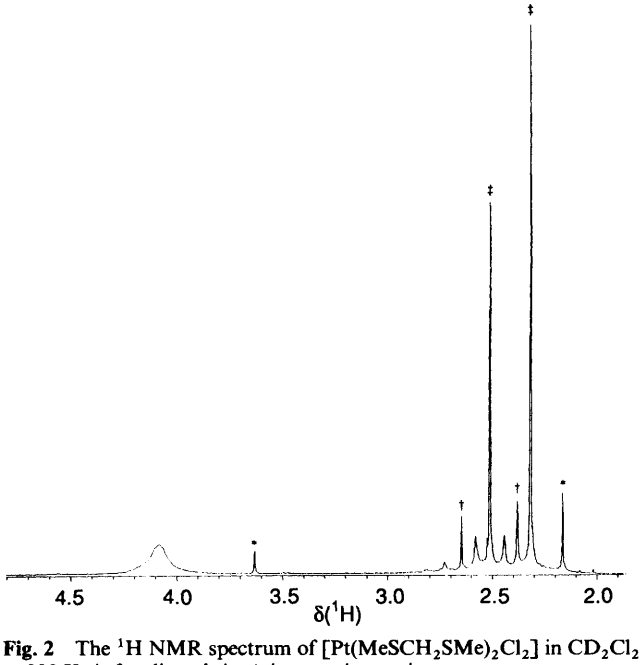

Fig. 2 The ^1H NMR spectrum of $[Pt(MeSCH_2SMe)_2Cl_2]$ in CD_2Cl_2 at 300 K: *, free ligand; †, *cis* isomer; ‡ *trans* isomer

expected[9] AB patterns of the CH_2 resonances were partially resolved. From a comparison with the ^1H NMR spectra[8] of *cis*- and *trans*-$[Pt(Me_2S)_2Cl_2]$ we assign the higher frequency MeS resonance with the larger $^3J(^1H\text{–}^{195}Pt)$ coupling to the *cis* isomer. The *trans* isomer is the more abundant form.

$PhSeCH_2SePh$.—The vibrational spectra show that the palladium complex is *trans* and the platinum *cis* in the solid state. In contrast to the dithioether analogues, solutions of these diselenoether complexes slowly deposit insoluble materials with a 1:1 M:L stoichiometry. The ^1H NMR spectrum of $[Pd(PhSeCH_2SePh)_2Cl_2]$ in CD_2Cl_2 at room temperature contained a single broad CH_2 resonance, which on cooling separated into two multiplets (Table 2). The $^{77}Se\text{-}\{^1H\}$ NMR spectrum at room temperature contained three very broad signals at δ *ca.* 385, *ca.* 337 and *ca.* 330, which on cooling resolved into five signals, two at high frequency (δ 388.8 and 387.7) assignable to the co-ordinated PhSe groups of the *meso* and DL forms of the *trans* isomer, and two at lower frequency (δ 334.6 and 333.9) due to the corresponding 'free' PhSe groups. The fifth resonance at δ 336.6 corresponds to some free ligand resulting from sample decomposition.

The ^1H NMR spectrum of the CH_2 region of $[Pt(PhSeCH_2SePh)_2Cl_2]$ at room temperature showed three broad resonances with ill defined structure, and even at 223 K the splitting remained ill defined. The ^{195}Pt data were much more useful for isomer identification. At 300 K four resonances were present, two (δ −3395, −3405) due to the *meso* and DL forms of the *trans* isomer, with two weaker features (δ −3588, −3598) due to the corresponding *cis* isomers. The *trans*:*cis* ratio was estimated as *ca.* 5:1. On cooling, the resonances shifted to low frequency and broadened (Table 3). The $^{77}Se\text{-}\{^1H\}$ NMR spectrum was difficult to obtain since considerable decomposition occurred during the long accumulation required, and in addition to a precipitate of the 1:1 complex, the spectra showed various weak features in the range δ 380–340 due to decomposition products, as well as resonances assigned to the original complex. At 300 K weak resonances at δ 395.7 and 394.8 are assigned to the *meso* and DL forms of the minor *cis* isomer, and stronger features at δ 392.7 and 391.8 to the corresponding enantiomers of the *trans* form. Several overlapping resonances at δ *ca.* 330 were due to the uncoordinated PhSe groups and to free ligand formed in the decomposition. The $^1J(^{77}Se\text{–}^{195}Pt)$ couplings were not clearly resolved. The spectrum was not appreciably different at 243 K.

$MeSeCH_2SeMe$.—The ^1H NMR spectra of *trans*-$[Pd(MeSeCH_2SeMe)_2Cl_2]$ exhibited a similar behaviour with temperature to those of the sulfur analogue. At 300 K the $^{77}Se\text{-}\{^1H\}$ NMR spectrum in CH_2Cl_2 contains broad resonances at δ *ca.* 243 and 127 assignable to the co-ordinated and free SeMe groups in the monodentate diselenoether, together with a sharper resonance at δ 115 due to free ligand. On cooling, the resonances sharpened but even at 193 K only the highest frequency resonance showed any further splitting with partial resolution of two signals at δ 234.7 and 234.5. In comparison with related complexes (see above and ref. 11), one would have expected four lines from the monodentate ligand due to the slowing of pyramidal inversion and resolution of separate resonances for the *meso* and DL forms. We conclude that the isomers have very small chemical shift differences, which cannot be clearly resolved even at low temperatures.

The platinum complex $[Pt(MeSeCH_2SeMe)_2Cl_2]$ again appears to be the *cis* isomer in the solid state from the vibrational spectral data. However in solution in CD_2Cl_2 at 300 K the ^1H NMR spectra show that only one geometric isomer is present and that pyramidal inversion is slow (Table 2). From the single broad signal in the ^{195}Pt NMR spectrum at δ −3424 (300 K) we identify this as the *trans* isomer. On cooling, the platinum resonance sharpens and at 243 K the line has narrowed sufficiently to show two closely spaced signals for the *meso* and DL invertomers. There was no evidence in the ^{195}Pt NMR spectrum for any lower frequency signal due to the *cis* isomer. Obtaining a $^{77}Se\text{-}\{^1H\}$ NMR spectrum of this complex

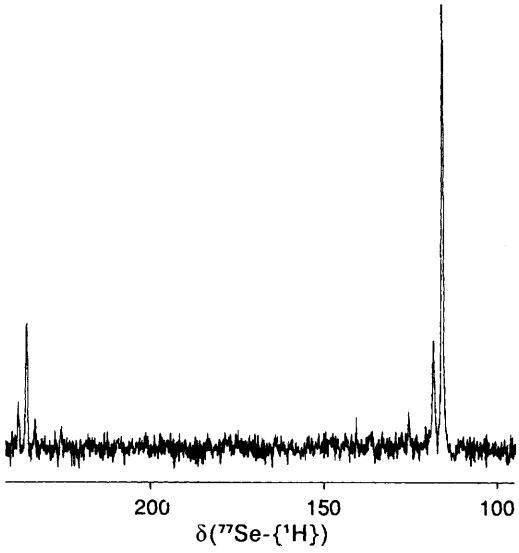

Fig. 3 The ^{77}Se-{^{1}H} NMR spectrum of $[Pt(MeSeCH_2SeMe)_2Cl_2]$ in CH_2Cl_2 at 300 K

again proved to be difficult, since considerable decomposition to $[\{Pt(MeSeCH_2SeMe)Cl_2\}_n]$ and free ligand occurred during the long accumulations, and the 1:1 complex precipitate degraded the spectral quality. The 300 K spectrum showed two very closely spaced lines with ^{195}Pt satellites at δ *ca.* 235 due to co-ordinated MeSe groups in the *meso* and DL forms of the *trans* isomer, a singlet at δ 118.5 due to the unco-ordinated SeMe groups, and a large resonance at δ 115.5 due to free ligand (Fig. 3). Cooling caused small shifts in the resonances but did not improve the resolution.

$MeTeCH_2TeMe$ *and* $PhTeCH_2TePh$.—In contrast to the analogues with sulfur or selenium donor groups the two ditelluroether ligands reacted with either $[Pd(MeCN)_2Cl_2]$ or $[Pt(MeCN)_2Cl_2]$ in CH_2Cl_2, irrespective of the M:L ratio, to precipitate $[(MLCl_2)_n]$ complexes. The ^{125}Te-{^{1}H} NMR spectrum of a mixture of $[Pt(MeCN)_2Cl_2]$ and three equivalents of $MeTeCH_2TeMe$ in CH_2Cl_2 recorded immediately after mixing, showed the resonance of the free ligand (δ 219) as the only significant feature, and we were unable to find any convincing ^{195}Pt resonance from this solution in the range δ −3000 to −4500 where a $PtTe_2Cl_2$ species would be expected.[12] Similar attempts to identify $[Pt(PhTeCH_2TePh)_2Cl_2]$ in solution were also unsuccessful. In contrast to the results with the lighter donor ligands, the isolated $[\{M(RTeCH_2TeR)Cl_2\}_n]$ did not redissolve on treatment of their suspensions in chlorocarbons with excess ligand.

Crystal Structure of $[Pd(PhSCH_2SPh)_2Cl_2]$.—The structure consists of discrete molecules with the palladium atom positioned on a centre of symmetry. Square-planar co-ordinated palladium(II) is established with *trans* monodentate co-ordinated $PhSCH_2SPh$. Selected bond lengths and angles are given in Table 4 and the molecule is shown in Fig. 4. The Pd–Cl [2.292(1) Å] and Pd–S(1) [2.329(1) Å] bond lengths may be compared with those in *trans*-$[PdL_2Cl_2]$ (L = 2,3-dihydrobenzo[*b*]thiophene)[13] [$Pd–S_{trans\text{-}S}$ 2.320(1), $Pd–Cl_{trans\text{-}Cl}$ 2.299(2) and 2.284(1) Å] and *trans*-$[PdL_2Cl_2]$ (L = $SPBu^i_3$)[14] [$Pd–S_{trans\text{-}S}$ 2.334(1) and $Pd–Cl_{trans\text{-}Cl}$ 2.297(1) Å]. The complex in the crystal is the *meso* enantiomer (*RS*/*SR*) and there are no weak contacts between the free sulfur and neighbouring molecules.

$[(MLCl_2)_n]$ *Complexes*.—Palladium complexes of this stoichiometry were obtained with all six ligands, those of $MeSCH_2SMe$, $MeSeCH_2SeMe$ and $PhSeCH_2SePh$ being formed by decomposition of the 2:1 complexes, whilst for

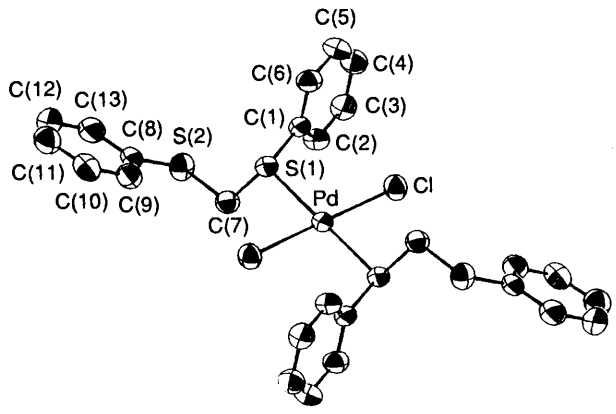

Fig. 4 Structure of $[Pd(PhSCH_2SPh)_2Cl_2]$ showing the atom labelling scheme and with thermal ellipsoids drawn at the 50% level

Table 4 Selected bond lengths (Å) and angles (°) for $[Pd(PhSCH_2SPh)_2Cl_2]$

Pd–Cl	2.292(1)	Pd–S(1)	2.329(1)
S(1)–C(1)	1.778(3)	S(2)–C(7)	1.783(4)
S(1)–C(7)	1.831(4)	S(2)–C(8)	1.769(4)
C(1)–C(2)	1.374(5)	C(8)–C(9)	1.378(6)
C(2)–C(3)	1.381(5)	C(9)–C(10)	1.385(6)
C(3)–C(4)	1.383(5)	C(10)–C(11)	1.367(6)
C(4)–C(5)	1.369(6)	C(11)–C(12)	1.379(7)
C(5)–C(6)	1.386(5)	C(12)–C(13)	1.379(6)
C(6)–C(1)	1.395(4)	C(13)–C(8)	1.389(5)
S(1)–Pd–Cl	95.3(1)	S(1)–C(7)–S(2)	113.2(2)
Pd–S(1)–C(1)	110.8(1)	Pd–S(1)–C(7)	104.5(1)
C(1)–S(1)–C(7)	102.8(2)	C(7)–S(2)–C(8)	104.4(2)
S(1)–C(1)–C(2)	123.5(3)	S(2)–C(8)–C(9)	125.9(3)
S(1)–C(1)–C(6)	116.2(3)	S(2)–C(8)–C(13)	115.1(3)
C(1)–C(2)–C(3)	120.3(3)	C(8)–C(9)–C(10)	119.7(4)
C(2)–C(3)–C(4)	119.8(4)	C(9)–C(10)–C(11)	121.2(4)
C(3)–C(4)–C(5)	119.9(4)	C(10)–C(11)–C(12)	119.4(4)
C(4)–C(5)–C(6)	121.2(4)	C(11)–C(12)–C(13)	120.0(4)
C(5)–C(6)–C(1)	118.5(4)	C(12)–C(13)–C(8)	120.7(4)
C(6)–C(1)–C(2)	120.3(3)	C(13)–C(8)–C(9)	119.0(4)

$MeTeCH_2TeMe$ and $PhTeCH_2TePh$ they were the only complexes isolated. The $[Pd(PhSCH_2SPh)_2Cl_2]$ complex did not appear to decompose spontaneously in solution, but the 1:1 complex has been made using a deficit of ligand.[5,6] The 1:1 complexes were insoluble in all solvents in which they did not decompose, which limits their characterisation. From the vibrational spectra (Table 1) the presence of single IR and Raman active Pd–Cl vibrations characteristic of terminal chlorines with a *trans* disposition, and the diffuse reflectance spectra which are consistent with planar Pd^{II}, suggest that they are *trans* planar ligand-bridged polymers. Platinum also formed 1:1 complexes with all the ligands except $PhSCH_2SPh$. The vibrational spectra fail to show ν(Pt–Cl) modes at frequencies similar to those of *trans*-$[Pt(Me_2S)_2Cl_2]$, but exhibit bands in both the IR and Raman spectra at lower frequencies, similar to those of the *cis* isomer.[8] The spectra are consistent either with a *cis*-ligand bridged polymer or the dimer structure $[Cl_2Pt(\mu\text{-}L)_2PtCl_2]$ found with some Group 15 ligands.[1,2] The complexes are completely insoluble in chlorocarbons which suggests the polymer structure is more likely.

Discussion

Comparison of the data above reveals several trends along the series of complexes. Thus the 2:1 palladium complexes are exclusively *trans* isomers both in the solid state and in solution. The solid $[PtL_2Cl_2]$ complexes appear to be *cis* isomers from the vibrational spectra {unfortunately good crystals have not so

far been obtained for $[Pt(PhSCH_2SPh)_2Cl_2]$, and the solution instability of the other complexes precluded crystal growth}, but in solution the *trans* isomers become increasingly abundant along the series $PhSCH_2SPh \longrightarrow MeSCH_2SMe \longrightarrow PhSeCH_2SePh \longrightarrow MeSeCH_2SeMe$, changing from approximately equimolar amounts of *cis*- and *trans*-forms in the first, to exclusively *trans* in the last.

The presence of chiral monodentate co-ordinated $RECH_2ER$ ligands results in *meso* and DL enantiomers for each geometric isomer (Fig. 1), and when pyramidal inversion is slow these are readily identified in the NMR spectra. The solution instability of most of the complexes, and sometimes the very small differences in the chemical shifts of the enantiomers, complicated identification of the different forms. Nonetheless the variable-temperature studies reveal the expected[4] trends in pyramidal inversion barriers namely Pd < Pt, S < Se and PhE < MeE.

The extra complexity in these systems compared with those of $RECH_2R$[4,9,11] results from their decomposition to 1:1 complexes in solution. The tendency to form $[(MLCl_2)_n]$ complexes increases in the order S ⟶ Se ⟶ Te and is greater for the methyl-substituted ligands for a fixed donor atom. This suggests that the major driving force is increased σ-donor power of the 'free' ER group in the monodentate ligand.[15,16] The insolubility of the 1:1 complexes will clearly shift any equilibrium in their favour, but the fact that $[\{M(MeECH_2EMe)Cl_2\}_n]$ (E = S or Se) are formed by prolonged pumping on the solid 2:1 complexes in high *vacuo* reveals the same trend in the absence of a solvent. It is this instability that makes the 2:1 complexes generally unsuitable starting materials for the preparation of bimetallic species.

Experimental

Proton NMR were recorded on either a Bruker AC-300 or AM-360 spectrometer and chemical shifts are reported relative to internal $SiMe_4$. The ^{77}Se NMR spectra were recorded with a Bruker AM-360 spectrometer (at 68.7 MHz) using neat $SeMe_2$ as the external reference. The ^{195}Pt NMR spectra were also recorded with a Bruker AM-360 spectrometer (at 77.8 MHz) relative to $[PtCl_6]^{2-}$ external reference. The IR spectra were recorded using a Perkin-Elmer 983 spectrometer, scanning from 4000 to 200 cm^{-1} as Nujol mulls between caesium iodide windows. Raman spectra were collected using a Perkin-Elmer 1720 Fourier-transform Raman spectrometer with Nd YAG laser at 1064 nm. Elemental analyses were obtained from the Microanalytical Laboratories, Imperial College, London.

Preparations.—$[PdCl_2(PhSCH_2SPh)_2]$. A solution of $PhSCH_2SPh$ (0.92 g, 4.0 mmol) in ethanol (40 cm^3) was treated dropwise with $Na_2[PdCl_4]$ (0.60 g, 2.0 mmol) in ethanol (15 cm^3). The mixture was stirred at room temperature for 3 h. The solution was evaporated to dryness, extracted with dichloromethane (10 cm^3), filtered and concentrated (2 cm^3) then precipitated with pentane (10 cm^3). The yellow solid was filtered off and dried *in vacuo*. Yield 1.03 g (81%).

$[PdCl_2(MeSCH_2SMe)_2]$. The salt $Na_2[PdCl_4]$ (0.29 g, 1.0 mmol) in ethanol (20 cm^3) was treated with $MeSCH_2SMe$ (0.2 cm^3, 2.0 mmol) and the mixture stirred at room temperature for 3 h. The solvent was removed and the residue extracted with dichloromethane (10 cm^3), filtered and concentrated in volume (2 cm^3). Pentane (10 cm^3) was added to afford an orange precipitate. The liquid was decanted off and the solid was briefly dried *in vacuo*. Yield 0.17 g (44%).

$[PdCl_2(MeSeCH_2SeMe)_2]$. The salt $Na_2[PdCl_4]$ (0.14 g, 0.46 mmol) in ethanol (10 cm^3) was treated with a slight excess of $MeSeCH_2SeMe$ (0.21 g, 1.03 mmol). The orange mixture was stirred for 2 h at room temperature. The solvent was removed at reduced pressure and the residue extracted with dichloromethane (5 cm^3). Two drops of ligand in dichloromethane (4 cm^3) were added to the insoluble material. This was stirred briefly and filtered. The filtrate was combined with the dichloromethane solution and concentrated. Pentane (10 cm^3) was added to precipitate the product. The liquid was decanted off and the yellow-orange solid was dried briefly *in vacuo*. Yield 0.10 g (38%).

Table 5 Atomic coordinates for $[Pd(PhSCH_2SPh)_2Cl_2]$

Atom	*x*	*y*	*z*
Pd	0.250 0	0.250 0	0.000 0
Cl	0.345 97(4)	0.388 3(2)	0.048 60(5)
S(1)	0.206 87(4)	0.402 9(1)	0.082 82(4)
S(2)	0.109 90(4)	0.733 7(2)	0.084 49(6)
C(1)	0.259 8(1)	0.578 6(6)	0.140 4(2)
C(2)	0.274 2(2)	0.780 8(6)	0.121 2(2)
C(3)	0.317 1(2)	0.905 9(6)	0.168 0(2)
C(4)	0.345 6(2)	0.827 4(8)	0.234 7(2)
C(5)	0.331 4(2)	0.625 6(8)	0.253 7(2)
C(6)	0.288 0(2)	0.498 6(7)	0.207 6(2)
C(7)	0.148 8(1)	0.589 2(6)	0.031 8(2)
C(8)	0.055 9(1)	0.547 2(6)	0.099 4(2)
C(9)	0.046 3(2)	0.340 6(7)	0.072 7(2)
C(10)	0.001 0(2)	0.213 9(7)	0.087 0(2)
C(11)	−0.034 0(2)	0.288 8(8)	0.128 2(2)
C(12)	−0.024 3(2)	0.494 8(9)	0.155 5(2)
C(13)	0.020 6(2)	0.622 7(8)	0.141 5(2)

$[PdCl_2(PhSeCH_2SePh)_2]$. The salt $Na_2[PdCl_4]$ (0.25 g, 0.85 mmol) in ethanol (25 cm^3) was treated dropwise with $PhSeCH_2SePh$ (0.57 g, 1.7 mmol) in ethanol (10 cm^3) and the mixture stirred for 2 h at room temperature. The solvent was removed at reduced pressure and the residue extracted into dichloromethane (10 cm^3). This was concentrated (2 cm^3) and precipitated with pentane (10 cm^3). The orange solid was filtered off and dried *in vacuo*. Yield 0.39 g (55%).

The platinum(II) complexes were prepared analogously using $K_2[PtCl_4]$ or $[PtCl_2(MeCN)_2]$ in aqueous ethanol–CH_2Cl_2.

The 1:1 complexes $[(MLCl_2)_n]$ typically form as precipitates in the preparation of the 2:1 $[ML_2Cl_2]$ complexes with all but $PhSCH_2SPh$. These can be separated due to their insolubility in common solvents. After extracting the 2:1 complexes into dichloromethane, the residues containing the 1:1 species are further washed with dichloromethane (10 cm^3) and dried *in vacuo*. The methyl ligand complexes can also be prepared by forcing the decomposition of the 2:1 complexes by extensive storage under vacuum. The 1:1 complexes of the tellurium ligands precipitate immediately on mixing solutions of $[M(MeCN)_2Cl_2]$ and ligand, irrespective of the ratio used.

Crystal-structure Determination of trans-$[Pd(PhSCH_2SPh)_2Cl_2]$.—Air-stable orange needle crystals were obtained by vapour diffusion from CH_2Cl_2–Et_2O. The first batch gave streaky photographic X-ray diffraction patterns but a later batch yielded one crystal of suitable quality. The density was measured by flotation (CCl_4–hexane).

Crystal data. $C_{26}H_{24}Cl_2PdS_4$, $M = 642.07$, monoclinic, space group $C2/c$, $a = 22.741(4)$, $b = 6.195(1)$, $c = 19.739(3)$ Å, $\beta = 106.15(1)°$, $U = 2671.1$ Å^3, $Z = 4$, $D_c = 1.596$ g cm^{-3}, $D_m = 1.55(2)$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 11.6 cm^{-1}, $F(000) = 1296$, $T = 295$ K.

Data collection, structure solution and refinement. Using a Stoe Stadi-4B diffractometer fitted with Mo-Kα radiation, cell dimensions were obtained from 36 centred reflections ($28 < 2\theta < 32°$) using a crystal (0.70 × 0.15 × 0.10 mm) mounted in a thin-walled glass capillary. 2929 Reflections were recorded ($5 < 2\theta < 49°$: h −26 to 25; k −1 to 7; l 0 to 23) and subsequent examination of the data indicated the space group $C2/c$ or Cc with the analysis being completed in the former centrosymmetric space group. The three standards showed no decay with time and an empirical ψ-scan absorption correction was applied. After averaging and removing systematically absent reflections there remained 2072 unique reflections ($R_{int} = 0.036$). The

structure was solved using the Patterson function to locate the heavy atoms and subsequent structure factor and electron-density syntheses readily found the C atoms. The Pd atom is on a centre of symmetry. At a later stage in the refinement the H atoms were located in the difference electron-density map and were included in the model in fixed positions. Full-matrix least-squares refinement[17] converged to $R = 0.028$ [1838 reflections with $F > 3\sigma(F)$, 152 parameters, anisotropic (Pd, Cl, S, C) and isotropic (H) atoms, $w^{-1} = \sigma^2(F) + 0.0001F^2$, maximum shift/error = 0.09, $R' = 0.034$]. The residual electron density was in the range +0.35 to −0.48 e Å^{-3}. Neutral-atom complex scattering factors were taken from SHELX 76[17] and ref. 18 (Pd) and the calculations carried out using SHELX 76[16] and ORTEP[19] on a PC. Atomic coordinates are listed in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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