Structural Variety and Multiple Isomerism in 1-(Dimethylamino)propyl-2-chalcogenolate and 2-(Dimethylamino)propyl-1-chalcogenolate Complexes of Palladium(II) and Platinum(II): Synthesis, Spectroscopy and Structures

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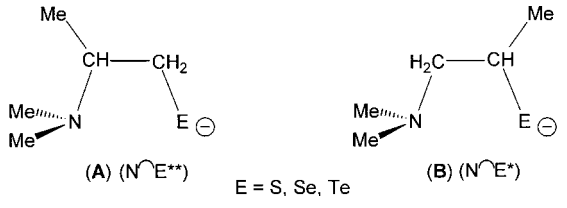
Isomeric dichalcogenides $[Me_2NCH(Me)CH_2E]_2$ $[(N^{\frown}E^{**})_2]$ and $[Me_2NCH_2CH(Me)E]_2$ $[(N^{\frown}E^{*})_2]$ (E = S, Se, Te) have been obtained by the reactions of NaSH or M'_2E_2 (M′ = Na or K) with $Me_2NCH_2CHMeCl$. The former reaction affords mainly $(N^{\frown}E^{**})_2$ (E = S) while from the latter mixtures of $(N^{\frown}E^{**})_2$ and $(N^{\frown}E^{*})_2$ [referred to as $(N^{\frown}E)_2$, E = S, Se, Te] were isolated, the ratios in the mixtures depending on the chalcogen. Reactions of $(N^{\frown}E)Na$ with $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ gave complexes $[MCl(N^{\frown}E)(PR_3)]$ (M = Pd or Pt). These chiral, mixed-ligand complexes have been characterised by elemental analysis, IR, UV/Vis and NMR (^1H, ^{13}C, ^{31}P, ^{77}Se, ^{125}Te, ^{195}Pt) spectroscopy, and, in part, by X-ray structure analysis. The complexes display a typical pattern of mutually *trans*-oriented neutral (P and N) and anionic (Cl and E) donor atoms in an approximately square-planar environment. In contrast to the platinum(II) analogues, the X-ray structures of the complexes $[PdCl(N^{\frown}E)(PMePh_2)]$ (E = S or Se) revealed both a conformational isomerism of the five-membered chelate ring and, for Se, the co-crystallisation of complexes with both the $N^{\frown}E^{*}$ and $N^{\frown}E^{**}$ isomeric ligands. The thermal behaviour of some complexes has been investigated.

Introduction

The chemistry of metal chalcogenolates continues to be an active area of research. Their emerging application as single-source precursors for low-decomposition-temperature synthesis of solid-state chalcogenide materials has provided a further momentum to this activity.[1−4] The chemistry of the heavier metal chalcogenolates is dominated by thiolate complexes, which are often isolated as non-volatile, insoluble (or sparingly soluble) polymers.[5] One of the strategies to suppress polymerisation has been to use internally functionalised ligands.[3] Among such ligands are (aminoalkyl)chalcogenolate ions $R_2N(CR_2')_nE^-$. While the chemistry of mercaptoalkylamines is now fairly well documented,[6−12] the heavier analogues containing Se and Te have been more recently developed and investigated by us.[13−17] Subtle variations in either the carbon chain length of the ligand or in the auxiliary ligands at the metal centre have led to the isolation of complexes with quite varied structural patterns. Some of these complexes also provided an opportunity to study metal-mediated donor−acceptor interactions between coordinated ligands.[14,15]

A new series of (aminoalkyl)chalcogenolate ligands with asymmetrically substituted carbon atoms in the alkyl chain was conceived for the following reasons: (i) chiral thiolate complexes such as the recently reported $[PdCl\{SCH_2CH(COOEt)NH_2\}(PPh_3)]$ are useful asymmetric homogeneous catalysts;[12,18−20] (ii) the cleavage of secondary chalcogenolates often proceeds more cleanly than that of primary or tertiary analogues;[21] (iii) the influence of electron-releasing methyl groups on donor−acceptor interactions in metal complexes can be studied.[14,15]

In this perspective, 2-[(dimethylamino)propyl]-1-chalcogenolate ($N^{\frown}E^{**}$) (**A**) and 1-[(dimethylamino)propyl]-2-chalcogenolate ($N^{\frown}E^{*}$) (**B**) ligands have been synthesised, and their chemistry with palladium(II) and platinum(II) has been explored. The results of this work are described in this paper.



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Results and Discussion

Synthesis of Dichalcogenides

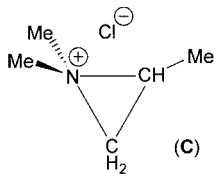
Two general reactions [Equations (1) and (2)] have been employed for the synthesis of the dichalcogenides. The disulfide formed by the reaction according to Equation (1) was isolated mainly as a single rearranged product $[Me_2NCH(Me)CH_2S]_2$ $(N^{\cap}E^{**})_2$, whereas the raction according to Equation (2) gave a mixture of $[Me_2NCH(Me)CH_2E]_2$ $(N^{\cap}E^{**})_2$ (E = S, Se, Te) and $(Me_2NCH_2CH(Me)E]_2$ $(N^{\cap}E^{*})_2$ (E = S, Se, Te). The relative amounts of $(N^{\cap}E^{**})_2$ and $(N^{\cap}E^{*})_2$ are chalcogen-dependent: the ratios were 1:2 for E = S, approx. 1:1 for E = Se, and 5:1 for E = Te (from ^{1}H NMR integration).

$$Me_2N\text{-}CH_2\text{-}CHMeCl \xrightarrow[-\ NaCl]{+\ NaSH} Me_2N\text{-}CHMe\text{-}CH_2\text{-}SH$$

$$\xrightarrow[-\ 1/2\ H_2O]{+\ 1/4\ O_2} 1/2\ (Me_2N\text{-}CHMe\text{-}CH_2S)_2 \qquad (1)$$

$$2\ Me_2N\text{-}CH_2\text{-}CHMeCl \xrightarrow[-\ NaCl\ /\ KCl]{+\ Na_2E_2\ /\ K_2Te_2} (Me_2N\text{-}CHMe\text{-}CH_2\text{-}E)_2 + (Me_2N\text{-}CH_2\text{-}CHMe\text{-}E)_2 \qquad (2)$$

Several factors have been identified which influence the product formation in nucleophilic substitution reactions of alkyl halides. In the present case, the participation of a nucleophilic neighbouring group (NMe_2) is believed to play an essential role to produce the *C*-methylaziridinium species **C** as a possible intermediate. In **C**, the less substituted carbon atom (i.e. the CH_2 group) seems to be the preferred site of attack by a nucleophile such as HS^- in the reaction according to Equation (1) as it is sterically less encumbered and electronically more positive. Accordingly, an isomerized product $[Me_2NCH(Me)CH_2S]_2$ (type **A**) could be isolated from the reaction according to Equation (1). The reaction according to Equation (2) is carried out using M_2E_2 in DMF. The nucleophiles E_2^{2-} and RE_2^- as intermediates in a solvent such as DMF may attack either of the carbon centres (CH_2 or CHMe) leading to the formation of different products. Their formation in different ratios reflects the differing nucleophilic character of anionic S, Se, or Te. Cyclic intermediates similar to **C** with various heteroatoms (e.g, N, O, S) are commonly invoked in organic reactions. The cleavage of the N−C bond in C-substituted aziridines or aziridinium ions frequently leads to isomerized products.[22]



(C)

The ^{1}H and ^{13}C NMR spectra of the disulfide obtained from reaction according to Equation (1) display only one set of resonances attributable to $[Me_2NCH(Me)CH_2S]_2$ $(N^{\cap}S^{**})_2$. However, the spectra of the dichalcogenides prepared from the reaction according to Equation (2) exhibit two sets of resonances which can be assigned to mixtures [referred to as $(N^{\cap}E)_2$].

The corresponding ^{77}Se (Figure 1) and ^{125}Te NMR spectra show eight and four lines, respectively. The molecules R_2E_2 (E = O, S, Se, Te) have a "skew" structure and can show restricted rotation about the E−E bond. For the molecules $(N^{\cap}E^{**})_2$ and $(N^{\cap}E^{*})_2$ three stereoisomers — (*R*,*R*), (*S*,*S*) and a *meso* form — are expected. Thus, each molecule is expected to display two resonances [(*R*,*R*)/(*S*,*S*) and *meso*] for the chalcogen atom in the ^{77}Se or ^{125}Te NMR spectrum. The resonances at $\delta = -791$ and -559 ppm and $\delta = -870$ and -659 ppm in the ^{125}Te NMR spectra may be assigned to molecules $(N^{\cap}Te^{*})_2$ and $(N^{\cap}Te^{**})_2$. Similarly, resonances at $\delta \approx 226$ and 357 ppm and $\delta \approx 286$ and 415 ppm in the ^{77}Se NMR spectra can be attributed to $(N^{\cap}Se^{*})_2$ and $(N^{\cap}Se^{**})_2$. However, each signal in the ^{77}Se NMR spectrum appears as two closely spaced lines (ca. 1 ppm separation). The presence of intramolecular interactions between nitrogen and selenium atoms may lead to the magnetic nonequivalence of the two selenium atoms in each molecule, resulting in two separate but closely spaced resonances. Recently, intramolecular Se···N interactions have been reported in several diselenides.[23−25] The Se···N distances of about 2.8 Å in these compounds are longer than the sum of the covalent radii, but significantly shorter than the sum of the corresponding van der Waals radii (ca. 3.5 Å).[23−25] For instance, the atomic distances Se(1)−N(1) and Se(2)−N(2) in **D** are 2.819(5) and 2.705(5) Å, respectively.[24] For the same reasons one would anticipate an analogous pattern for the ^{125}Te NMR spectrum. However, relatively large line widths [ca. 100 Hz (1 ppm)] for the ^{125}Te resonances appear to preclude a visible separation of closely spaced signals.

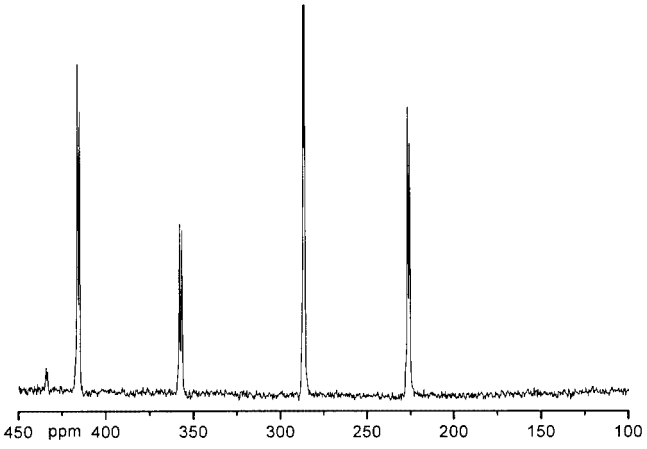
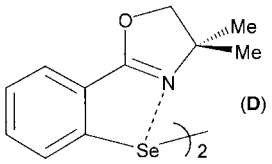
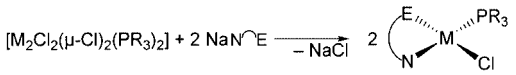


Figure 1. ^{77}Se{^{1}H} NMR spectrum of $(N^{\cap}Se)_2$ [mixture of $(N^{\cap}Se^{**})_2$ and $(N^{\cap}Se^{*})_2$] in $CDCl_3$



(D)



M = Pd or Pt; PR_3 = P*n*Bu_3, P*n*Pr_3, PEt_3, PMe_2Ph, $PMePh_2$ or PPh_3. (3)

Synthesis of Palladium(II) and Platinum(II) Complexes

Treatment of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with N∩ENa in methanol/dichloromethane readily gave coloured complexes of the general formula $[MCl(N\cap E)(PR_3)]$ [Equation (3)].

NMR Spectroscopy of Complexes $[MCl(N\cap E)(PR_3)]$

The ^1H NMR spectra (Table 1) of the thiolate complexes $[MCl(SCH_2CHMeNMe_2)(PR_3)]$ as prepared from the N∩S** (**A**) ligand display only one set of signals. The NMe_2

Table 1. ^1H and ^{31}P NMR spectroscopic data of palladium and platinum complexes $[MCl(N\cap E)(PR_3)]$[a]

	^1H	$^{31}P\{^1H\}$[b]
$[PdCl(N\cap S^{**})(P\mathit{n}Pr_3)]$	1.06 (t, J = 7.1 Hz, $PCH_2CH_2\mathit{Me}$), 1.16 (d, J = 6 Hz, $CH\mathit{Me}$), 1.60−1.67 (m, $PCH_2\mathit{CH_2}$), 1.78−1.83 (m, $PC\mathit{H_2}$), 2.51 (br., s), 2.76 (br., s) $N\mathit{Me_2}$, 2.56−2.70 (m, $SC\mathit{H_2}$), 2.86−2.96 (m, $NC\mathit{H}$)	23.8
$[PdCl(N\cap S^{**})(PEt_3)]$	1.15−1.29 (m, $PCH_2\mathit{Me}$, $NCH\mathit{Me}$), 1.83−2.00 (m, $PC\mathit{H_2}$), 2.53 (d, J = 2.5 Hz), 2.78 (d, J = 2.8 Hz) $N\mathit{Me_2}$, 2.57−2.73 (m, $SC\mathit{H_2}$), 2.92 (m, $NC\mathit{H}$)	34.5
$[PdCl(N\cap S^{**})(PMe_2Ph)]$	1.15 (d, J = 6.5 Hz $NCH\mathit{Me}$), 1.79 (d, J = 11.6 Hz), 1.83 (d, J = 11.7 Hz, $P\mathit{Me_2}$), 2.52 (d, J = 3.0 Hz), 2.80 (d, J = 3.3 Hz) $N\mathit{Me_2}$, 2.46−2.66 (m, $SC\mathit{H_2}$), 2.98 (m, $NC\mathit{H}$), 7.41−7.44 (m), 7.70−7.75 (m) $P\mathit{Ph}$	7.0
$[PdCl(N\cap S^{**})(PMePh_2)]$	1.15 (d, J = 6.5 Hz $NCH\mathit{Me}$), 2.16 (d, J = 11.4 Hz, $P\mathit{Me}$), 2.37−2.64 (m, $SC\mathit{H_2}$), 2.59 (d, J = 3.0 Hz), 2.86 (d, J = 3.3 Hz) $N\mathit{Me_2}$, 3.04 (m, $NC\mathit{H}$), 7.34−7.44 (m), 7.55−7.62 (m), 7.70−7.77 (m) $P\mathit{Ph}$	21.0
$[PdCl(N\cap S^{*})(PMePh_2)]$	1.21 (d, J = 6.5 Hz, $SCH\mathit{Me}$), 2.11 (d, J = 11 Hz, $P\mathit{Me}$) 2.70, 2.78 (d, J = 2.5 Hz, $N\mathit{Me_2}$), 2.62 (br., $SC\mathit{H_2}$), 2.74 (m, $NC\mathit{H_2}$), 3.38 (m, $C\mathit{H}S$), 7.39−7.81 (m, $P\mathit{Ph}$).	19.6
$[PdCl(N\cap S^{**})(PPh_3)]$	1.20 (d, J = 6.4 Hz $SCH\mathit{Me}$), 2.66 (d, J = 3.0 Hz), 2.93 (d, J = 3.2 Hz) $N\mathit{Me_2}$, 2.45−2.85 (m, $SC\mathit{H_2}$), 3.15 (m, $NC\mathit{H}$), 7.38−7.49, 7.71−7.78 (m, $P\mathit{Ph}$)	34.2
$[PtCl(N\cap S^{**})(P\mathit{n}Bu_3)]$	0.94 (t, J = 7.3 Hz, $PCH_2CH_2CH_2\mathit{Me}$), 1.22 (d, J = 6.5 Hz, $NCH\mathit{Me}$), 1.39−1.59 (m, $PCH_2C\mathit{H_2}C\mathit{H_2}$), 1.80−1.89 (m, $PC\mathit{H_2}$), 2.39−2.53 (m, $SC\mathit{H_2}$), 2.58, 2.88 (each d, J = 2.7 Hz, $N\mathit{Me_2}$ with Pt satellites), 2.83 (br., $NC\mathit{H}$)	−1.7 [3468]
$[PtCl(N\cap S^{**})(P\mathit{n}Pr_3)]$	1.04 (t, J = 7.3 Hz, $PCH_2CH_2\mathit{Me}$), 1.21 (d, J = 6.5 Hz, $NCH\mathit{Me}$), 1.57−1.66 (m, $PCH_2C\mathit{H_2}$), 1.78−1.87 (m, $PC\mathit{H_2}$), 2.58, 2.88 (each d, J = 2.7 Hz, $N\mathit{Me_2}$ with Pt satellites, 2.48−2.54 (m, $SC\mathit{H_2}$), 2.82 (br., $NC\mathit{H}$)	−2.4 [3472]
$[PtCl(N\cap S^{**})(PEt_3)]$	1.15 (dt, J = 7.6, 16.7 Hz, $PCH_2\mathit{Me}$), 1.22 (d, J = 6.7 Hz, $NC\mathit{H}$), 1.83−1.94 (m, $PC\mathit{H_2}$), 2.59, 2.89 (each d, J = 2.2 Hz; $J_{Pt,H}$ = 17 Hz, $N\mathit{Me_2}$), 2.82 (br., $NC\mathit{H}$), 2.43−2.54 (m, $SC\mathit{H_2}$)	6.2 [3468]
$[PtCl(N\cap S^{**})(PMe_2Ph)]$	1.22 (d, J = 6.5 Hz, $NCH\mathit{Me}$), 1.83, 1.87 (each d, J = 11 Hz, $P\mathit{Me_2}$), 2.38−2.58 (m, $SC\mathit{H_2}$), 2.62, 2.93 (each d, J = 2.9 Hz, $N\mathit{Me_2}$ with Pt satellites), 2.86 (br., $NC\mathit{H}$), 7.42, 7.74−7.81 (m, $P\mathit{Ph}$)	−18.7 [3548]
$[PtCl(N\cap S^{**})(PMePh_2)]$	1.20 (d, J = 6.5 Hz, $NCH\mathit{Me}$), 2.19 (d, J = 11 Hz, $P\mathit{Me}$), 2.64, 2.97 (each d, J = 3 Hz, $N\mathit{Me_2}$), 2.52 (m, $C\mathit{H_2}S$), $NC\mathit{H}$ merged in $N\mathit{Me_2}$, 7.40−7.70 (m, $P\mathit{Ph}$)	−4.3 [3616]
$[PdCl(N\cap Se)(PEt_3)]$	1.08−1.14 (m, $PCH_2\mathit{CH_3}$), 1.18 (d, J = 6.4 Hz, $CH\mathit{Me}$, N∩E**), 1.36 (d, J = 6.7 Hz, $CH\mathit{Me}$, N∩E*), 1.75−1.89 (m, $PC\mathit{H_2}$), 2.48, 2.51, 2.66, 2.70 (each, d, J = 2.5 Hz $J_{P,H}$, $N\mathit{Me_2}$, N∩E* + N∩E**), 2.55 ($NC\mathit{H_2}$, N∩E*, merged in $N\mathit{Me_2}$), 2.92−2.97 (m, $C\mathit{H_2}Se$, N∩E**), 3.42−3.50 (m, $C\mathit{H}Se$, N∩E*)	31.3 (s), 31.2 (s)
$[PdCl(N\cap Se)(PMe_2Ph)]$	1.19 (d, J = 6.4 Hz, $CH\mathit{Me}$, N∩E**), 1.35 (d, J = 6.6 Hz, $CH\mathit{Me}$, N∩E*), 1.79 (d, J = 13 Hz, $P\mathit{Me_2}$), 1.87 (d, J = 11.5 Hz, $P\mathit{Me_2}$), 2.53 (d, J = 3.0 Hz), 2.58 (d, J = 2.6 Hz, 2.72 (d, J = 3.5 Hz), 2.78 (d, J = 3 Hz) $N\mathit{Me_2}$, N∩E*+ N∩E**) $NC\mathit{H}$, $NC\mathit{H_2}$, merged in $N\mathit{Me_2}$, 3.01−3.08 (m, $C\mathit{H_2}Se$, N∩E**, 3.44−3.52 (m, $C\mathit{H}Se$, N∩E*), 7.40−7.43 (m), 7.66−7.73 (m) $P\mathit{Ph}$	2.5 (s)[c]

Table 1 *(continued)*

	^{1}H	^{31}P{^{1}H}[b]
[PdCl(N∩Se)(PMePh$_2$)]	1.21 (d, J = 6.4 Hz, CH*Me*, N∩E**), 1.29 (d, J = 6.6 Hz, CH*Me*, N∩E*), 2.18 (d, J = 11.3 Hz minor), 2.21 (d, J = 11.4 Hz, major, P*Me*), 2.53 (AB pattern, NCH_2), NC*H* merged with NMe_2, 2.60 (d, J = 3.1 Hz), 2.66 (d, J = 2.5 Hz), 2.77 (d, J = 3.4 Hz), 2.85 (d, J = 3.0 Hz) (NMe_2, N∩E*+ N∩E**), 3.07−3.16 (m, CH_2Se, N∩E*), 3.46 (m C*H*Se, N∩E*), 7.33−7.44 (m), 7.49−7.80 (m) P*Ph*[b]	16.7 (s)
[PdCl(N∩Se)(PPh$_3$)]	1.27 (d, J = 6.4 Hz), 1.30 (d, J = 6.5 Hz, NMe_2), 2.66, 2.92, 2.72, 2.84 (each d, J = 3 Hz) NMe_2, 2.52−2.61 (m, NC*H*), 2.95−3.30 (m, CH_2Se, NCH_2), 3.50 (m, C*H*Se) 7.19−7.80 (m, P*Ph*)	29.6, 29.8
[PtCl(N∩Se)(P*n*Bu$_3$)]	0.80 (t, J = 7.1 Hz, PCHCH$_2$CH$_2$*Me*), 1.13 (d, J = 6.3 Hz, CH*Me*, N∩E*), 1.25−1.45 (m, PCH$_2$CH_2CH_2 + doublet due to CH*Me*, N∩E*), 1.59−1.78 (m, PCH_2), 2.15, 2.40 (AB pattern, NCH_2), 2.49 (d, J = 2.4 Hz), 2.70 (d, J = 2.5 Hz), 2.74 (d, J = 2.6 Hz) ($J_{P,H}$, NMe_2, N∩E* + N∩E** merged with CH_2Se N∩E**), 3.08−3.20 (m, SeC*H*, N∩E*)	−4.0 [3431], −4.3 [3416]
[PtCl(N∩Se)(PEt$_3$)]	1.06−1.20 (m, PCH$_2$CH_3), 1.24 (d, J = 6.3 Hz, CH*Me*, N∩E**), 1.48 (d, J = 6.6 Hz, CH*Me*, N∩E*), (3:2 ratio), 1.78−1.92 (m, PCH_2), 2.25 (quadruplet, NC*H*, N∩E**), 2.49 (AB pattern, NCH_2, N∩E*), 2.61 (d, $J_{P,H}$ = 2.6, $J_{Pt,H}$ = 14.5 Hz), 2.81 (d, $J_{P,H}$ = 2.5 Hz), 2.86 (d, $J_{P,H}$ = 2.8 Hz) NMe_2, N∩E*+ N∩E**, (br., CH_2Se, N∩E**), 3.26 (m, C*H*Se, N∩E*)	4.3[d] [3435], 4.6[e] [3450]
[PtCl(N∩Se)(PMe$_2$Ph)]	1.24 (d, J = 6.4 Hz, CH*Me*, N∩E**), 1.45 (d, J = 6.7 Hz, CH*Me*, N∩E*), 1.89 (d), 1.86, 1.83 (each d, J = 11 Hz, PMe_2), 2.27 (AB, NCH_2), 2.43 (AB, NC*H* and NCH_2), 2.64, 2.66 (each d, J = 2.5 Hz), 2.88, 2.90 (each d, J = 3 Hz) (NMe_2, N∩E* + N∩E**), 3.26 (m, SeC*H*, N∩E*), 7.38−7.48 (m), 7.70−7.77 (m) P*Ph*	−22.2[d] [3476], −21.9[e] [3489]
[PdCl(N∩Te)(P*n*Pr$_3$)][f]	1.02 (t, J = 7 Hz, PCH$_2$CH$_2$*Me*), 1.25 (d, J = 6.1 Hz, CH*Me*, N∩E**), 1.52−1.63 (m, PCH$_2$CH_2 + CH*Me*, N∩E*), 1.77−1.84 (m, PCH_2), 2.15−2.21 (m, NCH_2), 2.68 (d, J = 2.7 Hz), 2.73 (d, J = 2.0 Hz) NMe_2, 2.55, 2.86 (m, NCH_2),	−6.9 [3373], −7.2 [3350]
[PdCl(N∩Te**)(PPh$_3$)][g]	1.33 (d, J = 6.0 Hz, CH*Me*), 2.63 (d, J = 3.0 Hz), 2.90 (d, J = 1.8 Hz) NMe_2, 3.10 (br., NC*H*), 3.48 (br., TeCH_2), 7.36−7.86 (m, P*Ph*)	21.6 (s)
[PdCl(N∩Te*)(PPh$_3$)][g]	1.41 (d, J = 6.8 Hz CH*Me*), 2.81 (d, J = 3.2 Hz), 2.98 (br) NMe_2, 2.70 (br., NCH_2), 3.80 (m, TeC*H*), 7.36−7.86 (m, P*Ph*)	22.4 (s)
[PtCl(N∩Te**)(PPh$_3$)]	1.12 (d, J = 6.4 Hz, CH*Me*), 2.57, 3.27 (each br, NMe_2), 3.10 (m, NC*H*), 3.21 (br., TeCH_2), 7.32−7.87 (m, P*Ph*).	8.7 [3742]
[PtCl(N∩Te*)(PPh$_3$)]	1.27 (br., CH*Me*), 2.80 (d, J = 2.9 Hz), 2.94 (d, J = 2.2 Hz) NMe_2, 2.63 (br., NCH_2), 3.90 (br., TeC*H*), 7.32−7.87 (m, P*Ph*)	0.4 [3538]

[a] Measured in CDCl3. [b] ^1J(^{195}Pt,^{31}P) in Hz in parentheses. [c] Separate signals not resolved. [d] Minor product. [e] Major product. [f] The ^{31}P NMR spectrum shows an additional small resonance at δ = −1.3 ppm ($^1J_{Pt,P}$ = 3103 Hz). [g] The ^{31}P NMR spectrum shows an impurity of [PdCl$_2$(PPh$_3$)$_2$] at δ = 23.8 ppm (ca. 10%).

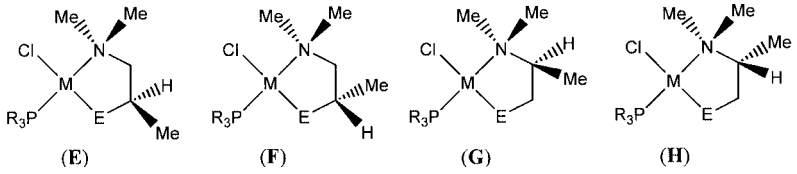
proton resonances appear as two doublets of equal intensity due to $^4J_{P,H}$ coupling. However, the spectra of those complexes synthesised with ligands obtained from the reaction according to Equation (2) show two sets of resonances for the organochalcogenolate fragments and for the phosphane methyl protons (if present). Each set of resonances can be assigned to N∩E** (**A**) and N∩E* (**B**) ligand protons. The NMe_2 proton signals for both isomers appear as two separate doublets with $^4J_{P,H} \approx 3$ Hz. The appearance of two doublets for the NMe_2 protons suggests that the methyl groups are diastereotopic in both the isomers, possibly due to the asymmetric carbon centre in the chalcogenolate moiety. In contrast, the complexes [MCl(ECH$_2$CH$_2$NMe$_2$)(PR$_3$)] show only one doublet for the NMe_2 protons.[13−15]

The ^{31}P{^{1}H} (Figure 2), ^{77}Se{^{1}H} (Figure 3) and ^{195}Pt{^{1}H} NMR spectra (Figure 4) of compounds [MCl(N∩E)(PR$_3$)] (E = Se or Te; Tables 1 and 2) and the thiolate complex [PdCl(N∩S)(PMePh$_2$)], display two sets of resonances. For the (*R*) and (*S*) forms (**E**−**H**) of each stereoisomer one set of resonances is observed. The $^1J_{Pt,P}$ coupling constants for the two resonances (from ^{31}P and ^{195}Pt NMR spectra) are of the same magnitude and are thus indicative of a similar configuration. The magnitude of $^1J_{Pt,P}$ for the platinum complexes suggests that the phosphane ligand is *trans* to the nitrogen atom. The values of $^1J_{Pt,P}$ can be compared with those observed for analogous complexes derived from achiral ligands.[13−15] The two sets of resonances in the

Table 2. $^{77}Se\{^1H\}$ and ^{195}Pt NMR spectroscopic data of selected $[MCl(N^{\cap}E)(PR_3)]$ complexes[a]

	$^{77}Se\{^1H\}$	$^{195}Pt\{^1H\}$ [$^1J^{195}_{Pt,}{}^{31}_{P}$ in Hz]
$[PdCl(N^{\cap}Se)(PEt_3)]$	201 (s), 351 (s)	–
$[PdCl(N^{\cap}Se)(PMePh_2)]$	282 (s), 425 (s)	–
$[PtCl(N^{\cap}Se)(PEt_3)]$	–	−4211 (d) [3445] (40%), −4315 (d) [3432] (60%)
$[PtCl(N^{\cap}Se)(P\mathit{n}Bu_3)]$	88 (s), 244 (s)	−4286 (d) [3426], −4182 (d) [3419]
$[PtCl(N^{\cap}Se)(PMe_2Ph)]$	113 (s), 263 (s)	−4165 (d) [3452] (minor), −4267 (d) [3478] (major)
$[PtCl(N^{\cap}Te)(P\mathit{n}Pr_3)]$	–	−4425 (d) [3362], −4569 (d) [3371]

[a] Measured in $CDCl_3$.



^{31}P, ^{77}Se, and ^{195}Pt NMR spectra are assigned to complexes containing the $N^{\cap}E^*$ and $N^{\cap}E^{**}$ ligand moieties.

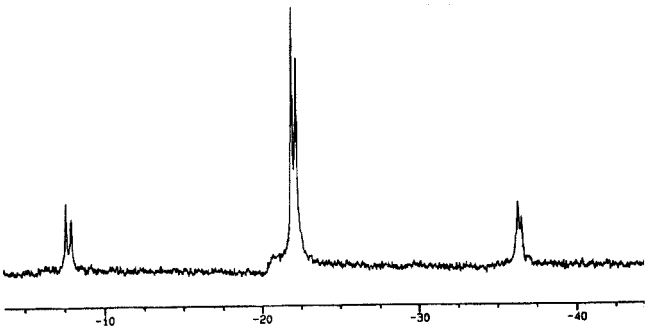


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $[PtCl(N^{\cap}Se)(PMe_2Ph)]$ in $CDCl_3$

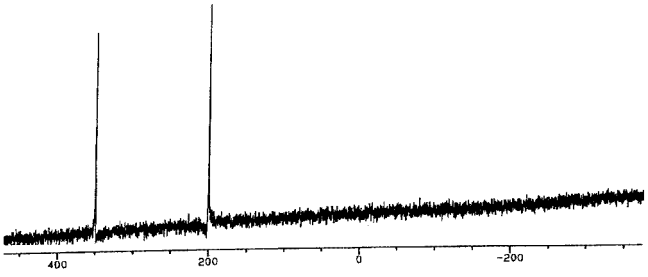


Figure 3. $^{77}Se\{^1H\}$ NMR spectrum of $[PdCl(N^{\cap}Se)(PEt_3)]$ in $CDCl_3$

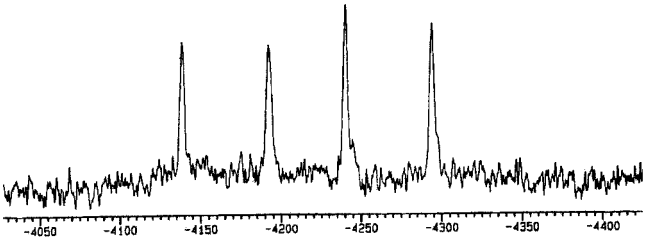


Figure 4. $^{195}Pt\{^1H\}$ NMR spectrum of $[PtCl(N^{\cap}Se)(PMe_2Ph)]$ in $CDCl_3$

Electronic Spectra

Like the analogous achiral derivatives,[14,15,27] the absorption spectra (Table 3) of the complexes $[MCl(N^{\cap}E)(PR_3)]$ display very weak long-wavelength bands. These absorptions are slightly red-shifted when compared with the corresponding achiral complexes. While the absorptions of the platinum complexes are blue-shifted in comparison to the palladium analogues, the selenium- and especially the tellurium-containing compounds absorb at lower energies than the corresponding sulfur analogues. Replacement of a methyl substituent by a phenyl group in PR_3 leads to a bathochromic shift.

Table 3. UV/Vis absorption data for $[MCl(N^{\cap}E)(PR_3)]$ complexes in CH_2Cl_2

Complex	λ_{max} (ε)[a]
$[PdCl(N^{\cap}S^{**})(P\mathit{n}Pr_3)]$	277 (2730), 325 (1780), 407 (br., 440)
$[PdCl(N^{\cap}S^{**})(PMe_2Ph)]$	329 (2150), 462 (90)
$[PdCl(N^{\cap}S^{**})(PMePh_2)]$	331 (1980), 474 (70)
$[PdCl(N^{\cap}S)(PMePh_2)]$[b]	327 (2000), 459 (90)
$[PdCl(N^{\cap}S^{**})(PPh_3)]$	337 (3340)
$[PtCl(N^{\cap}S^{**})(PEt_3)]$	282 (3000), 325 (780)
$[PtCl(N^{\cap}S^{**})(PMe_2Ph)]$	281 (2600), 396 (80)
$[PtCl(N^{\cap}S^{**})(PMePh_2)]$	289 (2130), 404 (70)
$[PdCl(N^{\cap}Se)(PEt_3)]$	338 (1830), 476 (80)
$[PdCl(N^{\cap}Se)(PMe_2Ph)]$	339 (2780), 483 (90)
$[PdCl(N^{\cap}Se)(PMePh_2)]$	255 (2860), 345 (2580), 495 (90)
$[PtCl(N^{\cap}Se)(PEt_3)]$	284 (3980), 406 (110)
$[PtCl(N^{\cap}Se)(PMe_2Ph)]$	285 (6380), 412 (180)
$[PdCl(N^{\cap}Te)(PPh_3)]$	392 (4280), 616 (110)

[a] Wavelengths, λ_{max}, at the absorption maxima in nm; molar extinction coefficients, ε, in $M^{-1}\cdot cm^{-1}$ (in parentheses). [b] Ligand prepared by the Na_2S_2 route.

Such weak long-wavelength absorptions have been attributed for similar complexes to ligand (E) to ligand (PR_3) charge-transfer (L′LCT) transitions, based on DFT calculations.[14,15] The results presented here are fully in line with this assignment.[14,15,26]

Crystal Structure Analysis

The molecular structures of [PdCl(N∩S**)(PMePh$_2$)], [PtCl(N∩S**)(PMe$_2$Ph)], the isostructural complex [PtCl(N∩Se**)(PMe$_2$Ph)] and two molecules from a crystal of [PdCl(N∩Se)(PMePh$_2$)] were unambiguously established by single-crystal X-ray diffraction analyses.

The compounds were found to crystallise in the space group $P2_1$ with the exception of [PdCl(N∩S**)(PMePh$_2$)] ($P\bar{1}$). The quality of the obtained data was excellent for [PdCl(N∩S**)(PMePh$_2$)], [PtCl(N∩S**)(PMe$_2$Ph)] and [PtCl(N∩Se**)(PMe$_2$Ph)] and moderate for [PdCl(N∩Se)(PMePh$_2$)] (see Exp. Sect.). No significant intermolecular contacts were found in any of the crystal structures. Selected bond lengths and angles for the molecules are given in Table 4, crystallographic and refinement data are given in Table 5.

The coordination environments around the central metal atom in each molecule are approximately square-planar, defined by the P, Cl, N and E atoms. The strong donor atoms E and P are oriented *cis* to each other to avoid an unfavourable *trans* interaction. Such a configuration with *trans*-oriented neutral (P and N) and anionic (Cl and E) donor atoms has also been reported for several related achiral complexes.[13−15,26]

The five-membered chelate rings exhibit a twist conformation which, combined with the presence of the methyl substituent, gives rise to two conformations, **I** and **J**, with different configurations at the asymmetric carbon [(*R*) for **I** and (*S*) for **J**]. For three compounds — both platinum complexes and [PdCl(N∩S**)(PMePh$_2$)] — the crystals analysed contained exclusively Me$_2$NCH(Me)CH$_2$E (E = S or Se) ligands (N∩E**), whereas complexes with both isomeric ligands N∩Se* and N∩Se** had co-crystallised in [PdCl(N∩Se)(PMePh$_2$)]. The crystals of [PdCl(N∩S**)-(PMePh$_2$)] (Figures 5 and 6) contain two crystallographically independent molecules, both of which show a disorder according to the conformations **I** and **J**. The structure was best refined using 45% and 55% occupancy for the two conformers, respectively (see Figure 6). For the platinum

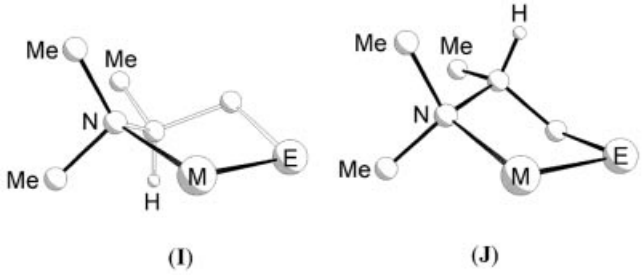


Figure 5. Molecular structure of [PdCl(N∩S**)(PMePh$_2$)]; one of two independent molecules in one possible orientation is shown (for disorder **I/J**, see text) with 30% thermal ellipsoids; H atoms have been omitted for clarity

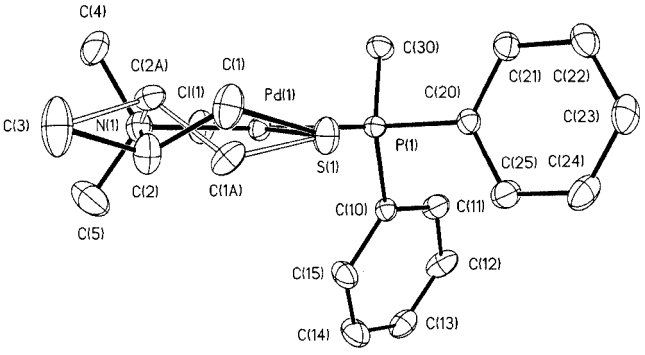
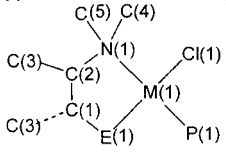


Figure 6. View of [PdCl(N∩S**)(PMePh$_2$)] showing one of two independent molecules with conformation disorder **I/J** (30% thermal ellipsoids; H atoms have been omitted for clarity)

Table 4. Selected bond lengths [Å] and bond angles [°] of complexes [MCl(N∩E)(PR$_3$)][a]

	[PdCl(N∩S**)(PMePh$_2$)] Pd1	Pd2	[PtCl(N∩S**)(PMe$_2$Ph)]	[PdCl(N∩Se)(PMePh$_2$)] Pd1(N∩E**)	Pd2(N∩E*)	[PtCl(N∩Se**)(PMe$_2$Ph)]
M−E	2.2560(10)	2.2521(11)	2.235(2)	2.323(3)	2.322(4)	2.3860(11)
M−Cl	2.3676(10)	2.3639(10)	2.403(3)	2.332(6)	2.360(8)	2.348(3)
M−P	2.2399(10)	2.2409(9)	2.247(2)	2.195(6)	2.184(6)	2.193(2)
M−N	2.172(2)	2.169(2)	2.130(9)	2.149(18)	2.127(17)	2.220(8)
N−M−P	177.58(7)	177.32(7)	176.2(3)	174.2(6)	177.7(6)	177.4(3)
N−M−Cl	93.40(7)	93.95(7)	91.1(2)	97.0(5)	93.5(6)	89.43(10)
N−M−E	87.33(7)	87.10(7)	88.6(2)	84.0(5)	87.6(6)	86.6(2)
P−M−Cl	88.60(3)	88.71(3)	86.95(10)	87.1(2)	86.8(2)	91.6(2)
Cl−M−E	177.83(3)	176.33(4)	179.40(13)	176.8(2)	176.6(2)	177.81(9)
P−M−E	90.72(3)	90.27(3)	93.29(9)	91.78(14)	92.22(18)	92.42(7)



[a] Numbering scheme employed in figures and text is shown below the table.

homologue [PtCl(N∩S**)(PMe$_2$Ph)] only one kind of molecule with conformation **J** (see Figure 7) was found in the crystal. The C(1) atom in this molecule shows some distortion according to a possible disorder. However, attempts to introduce the same disorder as observed for the palladium analogue or refining the structure in triclinic space groups failed. The C(2) atom does not show any sign of disorder; the extended thermal ellipsoid of C(1) can thus be attributed to a molecular vibration.

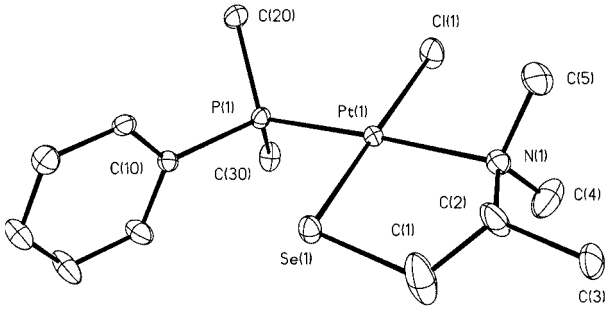


Figure 7. Molecular structure of [PtCl(N∩Se**)(PMe$_2$Ph)] with 30% thermal ellipsoids; H atoms have been omitted for clarity; the sulfur analogue [PtCl(N∩S**)(PMe$_2$Ph)] looks essentially the same

The crystals of [PtCl(N∩Se**)(PMe$_2$Ph)] also contain only one molecule, which clearly shows conformation **J** (Figure 7). In contrast, the palladium derivative [PdCl(N∩Se)(PMePh$_2$)] was found to contain both isomeric ligands N∩Se* and N∩Se**. One of the two independent molecules found in the unit cell contains the ligand Me$_2$NCH(Me)CH$_2$Se$^-$ (N∩Se**) and exhibits the disorder described by conformations **I** and **J** (Figure 8). This has also been observed for the sulfur analogue. The other complex molecule, which contains the isomeric ligand Me$_2$NCH$_2$CH(Me)Se$^-$ (N∩Se*; Figure 9), exists exclusively

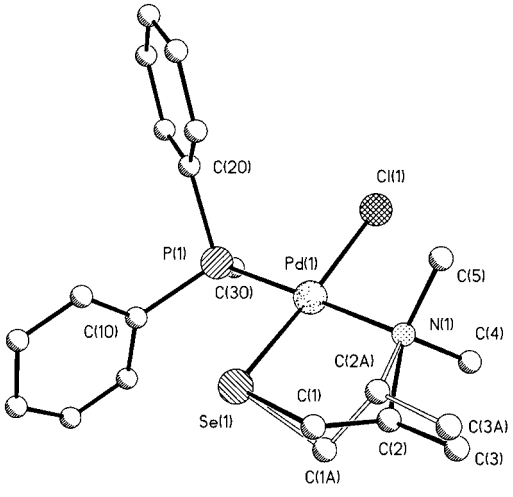


Figure 8. Molecular structure of the disordered (**I**/**J**) molecule 1 in [PdCl(N∩Se)(PMePh$_2$)] (N∩Se** isomer)

as one conformer (similar to **J**). Attempts to introduce disorder models to this molecule were unsuccessful.

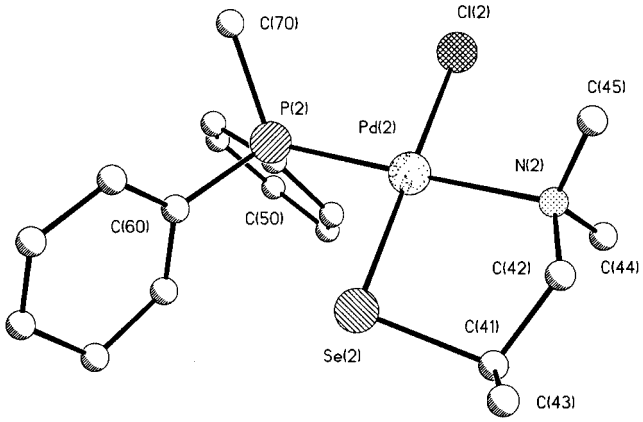


Figure 9. Molecular structure of molecule 2 in [PdCl(N∩Se)(PMePh$_2$)] (N∩Se* isomer)

The coordination planes around the metal atoms in these complexes exhibit only small tilt angles (N−M−E/Cl−M−P), ranging between 2.5 and 4.9°. The N−M−P and Cl−M−E angles are only slightly below 180° (Table 4). The metal−ligand distances are all longer for the palladium complexes than for the platinum homologues. This has also been found in related studies[14,27−29] and is attributed to the lanthanide contraction and relativistic effects.[29] The M−N and M−Cl distances are slightly longer than those reported in [M$_2$Cl$_2$(μ-Me$_2$pz)$_2$(PR$_3$)$_2$][30,31] owing to the strong *trans* influence of PR$_3$ and E (E = S or Se) donors. The M−E, M−P, M−N and M−Cl distances and various angles around the metal centre are similar to those reported for [MCl(ECH$_2$CH$_2$NMe$_2$)(PR$_3$)] complexes.[13−15,26]

In summary, it is remarkable that the two crystallised platinum complexes both contain exclusively the same conformer **J** [(*S*) enantiomer]; the two palladium derivatives are nonselective in this respect, showing disorder in the chelate ring according to both conformers in the crystal. For the selenium derivative [PtCl(N∩Se**)(PMe$_2$Ph)] multiple selectivity is observed for the molecules in the crystal: (i) regioselectivity of the ligands Se, Cl, P and N around the metal atom; (ii) the crystal contains only one regioisomer (N∩Se**) although the compound was prepared using regioisomeric mixed ligands; (iii) from the two possible conformers arising from the twist of the chelate ring only one conformer (enantiomer) is found in the crystal.

Thermal Studies

The thermal behaviour of some of the complexes has been evaluated to assess their suitability as molecular precursors for the synthesis of metal chalcogenides. The TG curve of [PdCl(N∩S**)(PMePh$_2$)] (Figure 10) shows a three-step decomposition, finally leading to Pd$_4$S at 374 °C. The first two stages are overlapping steps which account for 70% of the weight loss. This weight loss can be attributed to elimination of phosphane, organic residue and the chloride ligand with the formation of PdS. There is further loss of

sulfur at 374 °C, resulting in the formation of Pd_4S which remains stable up to 500 °C. To prepare bulk quantities, a sufficient amount of [PdCl(N∩S**)(PMePh$_2$)] (128 mg) was heated at 400 °C in a furnace and the residue (35 mg, 30 mg calcd. for Pd_4S) was annealed for 2 h. The X-ray powder pattern of this residue corresponds to that of Pd_4S[32] (JC,PDS-10-335; analysis: found C 4.7, H ca. 0.2, N ca. 0.2%). Decomposition of [PdCl(N∩Se)(PMePh$_2$)] (107 mg) at 350 °C in a furnace gave a bulk residue (35 mg, 37 mg calcd. for $Pd_{17}Se_{15}$), identified as $Pd_{17}Se_{15}$ from the XRD pattern (JC,PDS-29-1427; analysis: found C 2.6, H ca. 0.2, N ca. 0.2%). The TG curve of [PtCl(N∩S**)(PMe$_2$Ph)] shows a two-step decomposition, the first step occurring at 265 °C being attributed to the loss of the phosphane ligand by the weight loss (obsd. 26%, calcd. 28%). The second step leads to the formation of PtS at 374 °C.

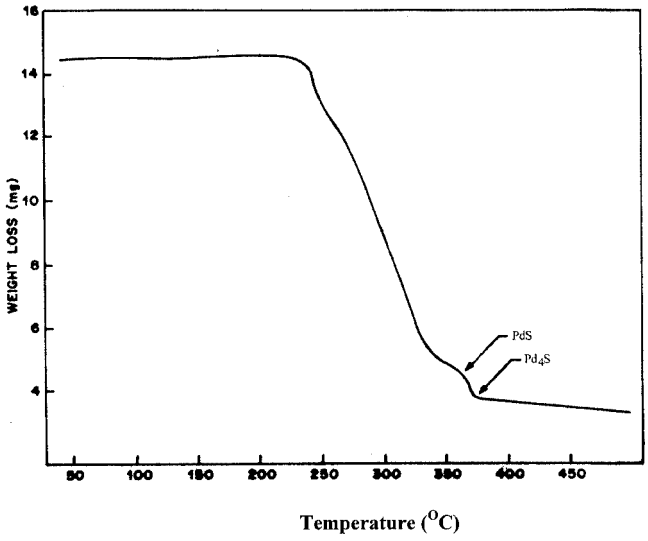


Figure 10. TG curve of [PdCl(N∩S**)(PMePh$_2$)]

Conclusion

This report illustrates how, by NMR spectroscopy and partial crystal structure analysis, the attempts to obtain aminochalcogenolate chelate ligands with an asymmetrically substituted carbon atom lead to regioisomeric dichalcogenide precursor molecules. In the chiral metal complexes [MCl(N∩E)(PR$_3$)] (M = Pt, Pd) the neutral (P and N) and charged donor atoms (Cl and E) were invariably found *trans* to each other. Further conformational isomerism in these complexes results from the twisted chelate rings. Whereas the two crystallised platinum complexes [PtCl(N∩S**)-(PMe$_2$Ph)] and [PtCl(N∩Se**)(PMe$_2$Ph)] exhibit exclusively one conformer (enantiomer), the palladium derivatives were nonselective, showing disorder in the chelate ring according to both conformers in the crystal. The regio- and enantioselectivity in the case of the selenium derivative [PtCl(N∩Se**)(PMe$_2$Ph)] is highly remarkable since the compound was prepared using a regioisomerically mixed ligand. Despite these various possibilities of constitutional, positional and conformational isomerism the isolated compounds were found to be sufficiently stable to be used as molecular precursors for metal chalcogenide phases.

Experimental Section

General: The complexes [M$_2$Cl$_2$(μ-Cl)$_2$(PR$_3$)$_2$] (M = Pd or Pt; PR$_3$ = P*n*Bu$_3$, P*n*Pr$_3$, PEt$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$) were prepared according to literature methods.[33] The phosphanes (Strem Chemicals) and Me$_2$NCH$_2$CH(Me)Cl·HCl (Fluka Chemika, Cat. No. 24367) were obtained from commercial sources. All reactions were carried out under nitrogen in dry and distilled analytical grade solvents. Microanalyses were carried out in the Analytical Chemistry Division of BARC. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{77}Se{^{1}H}, ^{125}Te{^{1}H} and ^{195}Pt{^{1}H} NMR spectra were recorded with a Bruker DPX-300 NMR spectrometer operating at 300, 75.47, 121.49, 57.24, 94.86 and 64.52 MHz, respectively. Chemical shifts are relative to the internal chloroform peak at δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C, external 85% H$_3$PO$_4$ for ^{31}P, Me$_2$Se for ^{77}Se, [Te(dtc)$_2$] (dtc = *N*,*N*-diethyldithiocarbamate) for ^{125}Te, and Na$_2$[PtCl$_6$] in D$_2$O for ^{195}Pt. A 90° pulse was used in every case. The IR spectra were recorded as Nujol mulls between CsI plates with a Bomem MB-102 FT-IR spectrometer. UV/Vis absorption spectra were recorded with a JASCO V-530 spectrometer. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 449C instrument calibrated with $CaC_2O_4.H_2O$. The TG curves were recorded at a heating rate of 10 °C·min^{-1} under a flow of argon. X-ray powder diffraction patterns were measured using Cu-K_α radiation.

Preparation of [Me$_2$NCH(Me)CH$_2$S]$_2$ [(N∩S)$_2$]:** Sodium hydrogensulfide was prepared by bubbling an excess of hydrogen sulfide into an ethanolic solution (150 mL) of sodium ethoxide (from 14.02 g Na metal) for 4 h until a pale yellow solid began to separate. Freshly distilled Me$_2$NCH$_2$CH(Me)Cl (59.34 g, 488 mmol) [obtained by neutralising an aqueous solution of Me$_2$NCH$_2$CH(Me)Cl·HCl with 10% sodium hydroxide, extracting with diethyl ether, drying with anhydrous CaCl$_2$ and distilling at 120−122 °C as a colourless liquid; ^{1}H NMR (CDCl$_3$): δ = 1.49 (d, *J* = 6.6 Hz, CH*Me*), 2.26 (s, NMe$_2$), 2.48 (doublet of AB pattern, NCH$_2$), 4.02 (m, 6.5 Hz, C*H*Cl) ppm; ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 23.2 (s, CH*Me*), 45.8 (s, N*Me*$_2$), 55.1 (s, N*C*H$_2$), 68.0 (s, *C*HCl) ppm] was added dropwise to this solution, whereupon a white precipitate formed. The reaction mixture was heated to reflux under nitrogen for 2 h, and, after cooling, the mixture was filtered. The filtrate was concentrated in vacuo, leaving behind a pale-yellow solid [Me$_2$NCH(Me)CH$_2$SH] which was found to be contaminated by disulfide. Oxygen was bubbled through an ethanol solution (50 mL) of the residue until a yellow liquid was obtained. The solvent was stripped off and the residue was distilled in vacuo at 120−125 °C/1 Torr to give a yellow oil (30.2 g, 53%). ^{1}H NMR (CDCl$_3$): δ = 1.00 (d, *J* = 6.5 Hz, CH*Me*), 2.19 (s, N*Me*$_2$), 2.52 (m, C*H*$_2$S), 2.77−2.92 (m, NC*H*) ppm. ^{13}C{^{1}H} (CDCl$_3$): δ = 12.7 (s, CH*Me*), 40.0 (s, N*Me*$_2$), 42.4 (s, N*C*H), 58.2 (*C*H$_2$S) ppm. The NMR spectra showed resonances attributable to traces (less than 1%) of [Me$_2$NCH$_2$CH(Me)S]$_2$.

Preparation of (N∩S)$_2$. [Me$_2$NCH(Me)CH$_2$S]$_2$ [(N∩S)$_2$] and [Me$_2$NCH$_2$CH(Me)S]$_2$ [(N∩S*)$_2$]:** Finely powdered yellow sulfur (3.20 g, 100 mmol) and sodium metal (2.37 g, 103 mmol) were allowed to react in liquid ammonia (100 mL) at −78 °C. The resulting yellow solution was stirred for 90 min and the ammonia

was evaporated by leaving the flask to stand at room temperature. The yellow residue (Na_2S_2) was dried under vacuum and dissolved in DMF (200 mL) with stirring. Freshly distilled $Me_2NCH_2CH(Me)Cl$ (10.5 g, 86 mmol) in DMF (100 mL) was added dropwise. The mixture was stirred at room temperature for 18 h whereupon the green colour of the solution changed to yellow. The reaction was quenched with water (300 mL) and the product was extracted with diethyl ether (3 × 60 mL). The ether extracts were dried with $CaCl_2$. The solvent was stripped off and the residue was distilled in vacuo (100−105 °C/0.5 Torr) to give a mixture of $(N^{\cap}S^{**})_2$ and $(N^{\cap}S^{*})_2$ as a yellow liquid (7.9 g, 77%). Attempts to separate the two isomers by vacuum distillation were unsuccessful. ^{1}H NMR ($CDCl_3$): δ = 1.01 [d, J = 6.5 Hz, $(N^{\cap}S^{**})_2$], 1.26 [d, J = 6.5 Hz, $(N^{\cap}S^{*})_2$] (CH*Me*) (ratio 1:2), 2.18 [s, N*Me*$_2$, $(N^{\cap}S^{*})_2$], 1.20 [s, N*Me*$_2$, $(N^{\cap}S^{**})_2$], 2.26−2.95 (m, NC*H*, C*H*$_2$S, NC*H*$_2$, C*H*S) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): $(N^{\cap}S^{*})_2$: δ = 18.6 (s, N*Me*$_2$), 43.9 (s, N*C*H$_2$), 45.3 (s, N*Me*$_2$), 64.8 (s, *C*HS) ppm; $(N^{\cap}S^{**})_2$: δ = 12.7 (s, CH*Me*), 40.1 (s, N*Me*$_2$), 42.4 (s, N*C*H), 58.2 (s, *C*H$_2$S) ppm [$(N^{\cap}S^{*})_2$ and $(N^{\cap}S^{**})_2$ in 2:1 ratio from ^{1}H NMR integration].

Preparation of $(N^{\cap}Se)_2$. $[Me_2NCH(Me)CH_2Se]_2$ $[(N^{\cap}Se^{**})_2]$ and $[Me_2NCH(Me)CH_2Se]_2$ $[(N^{\cap}Se^{*})_2]$: A mixture of $(N^{\cap}Se)_2$ was prepared (in 54% yield) in an analogous manner to the sulfur analogue as described above, from $Me_2NCH_2CH(Me)Cl$ and Na_2Se_2. The orange liquid was fractionally distilled at 130−138 °C/2 Torr. ^{1}H NMR ($CDCl_3$): δ = 1.08 [dd, J = 6.3, 2 Hz, $(N^{\cap}Se^{**})_2$], 1.47 [d, J = 6.2 Hz, $(N^{\cap}Se^{*})_2$ (CH*Me*)], 2.22 [br., NC*H*, $(N^{\cap}Se^{**})_2$], 2.24 $(N^{\cap}Se^{**})_2$, 2.25 $(N^{\cap}Se^{*})_2$ (each s, N*Me*$_2$), 2.48 [AB pattern with doublet NCH$_2$, $(N^{\cap}Se^{*})_2$], 2.89 (m, C*H*$_2$Se), 3.25 [m, CHSe, $(N^{\cap}Se^{*})_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = [$(N^{\cap}Se^{*})_2$] 20.8 (s, CH*Me*), 36.8 (N*C*H$_2$), 45.6 (N*Me*$_2$), 67.0 (Se*C*H) ppm; [$(N^{\cap}Se^{**})_2$]: δ = 13.7 (s, CH*Me*), 35.8 (N*C*H$_2$), 40.5 (N*Me*$_2$), 60.3 (Se*C*H) ppm. ^{77}Se{^{1}H} NMR ($CDCl_3$): δ = 225.4, 226.6, 286.0, 286.8, 356.5, 357.9, 415.1, 416.2 ppm.

Preparation of $(N^{\cap}Te)_2$. $[Me_2NCH(Me)CH_2Te]_2$ $[(N^{\cap}Te^{**})_2]$ and $[Me_2NCH_2CH(Me)Te]_2$ $[(N^{\cap}Te^{*})_2]$: $(N^{\cap}Te)_2$ was synthesised in a similar manner to the corresponding selenium analogue from $Me_2NCH_2CH(Me)Cl$ and K_2Te_2 (prepared from potassium and tellurium powder in liquid ammonia). The brown-red liquid was dissolved in hexane, passed through a Florisil column and dried under vacuum (yield 68%). The compound was contaminated by $(Me_2NCH_2CHMe)_2Te$; attempted vacuum distillation resulted in excessive decomposition. ^{1}H NMR ([D$_6$]acetone): δ = 1.01 [d, J = 6.5 Hz, $(N^{\cap}Te^{**})_2$], 1.66 [d, J = 6.5 Hz, $(N^{\cap}Te^{*})_2$] (CH*Me*), 2.23 [s, N*Me*$_2$, $(N^{\cap}Te^{**})_2$], 2.25 [s, N*Me*$_2$ minor, $(N^{\cap}Te^{*})_2$], 2.75 (m, C*H*), 3.12−3.49 (m, C*H*$_2$) ppm. ^{13}C NMR ([D$_6$]acetone): [$(N^{\cap}Te^{*})_2$]: δ = 14.9 (s, CH*Me*), 35.0 (s, N*C*H$_2$), 45.5 (s, N*Me*$_2$), 68.7 (s, Te*C*H) ppm; $(N^{\cap}Te^{**})_2$: δ = 13.7 (each s, CH*Me*), 31.6 (s, N*C*H), 40.4 (s, N*Me*$_2$), 61.4 (s, Te*C*H) ppm. ^{125}Te{^{1}H} NMR ([D$_6$]acetone): δ = −870 (very small), −791, −639 (very small), −559 ppm; peaks at δ = −455, −461 and −504 (integrating to about 7%) are due to partial decomposition of the ligand.

Synthesis of Palladium(II) and Platinum(II) Complexes: All preparations involving thiolate were carried out using $Me_2NCH(Me)CH_2S^-$ ($N^{\cap}S^{**}$) unless otherwise stated. For the preparation of selenolate and tellurolate complexes, $(E^{\cap}N)_2$ was employed. NMR spectroscopic data for complexes $[MCl(E^{\cap}N)(PR_3)]$ are collected in Tables 1 and 2. Yields, recrystallisation solvents and analytical data for all complexes are provided in the Supporting Information.

Thiolate Complexes: As an example for the thiolate complexes the synthesis of $[PdCl(N^{\cap}S^{**})(PMe_2Ph)]$ is described. A dichloromethane solution (40 mL) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (156 mg, 0.25 mmol) was added to a freshly prepared methanol solution of $NaSCH_2CH(Me)NMe_2$, prepared by treating $(N^{\cap}S^{**})_2$ (58 mg, 0.25 mmol) with $NaBH_4$ (19 mg, 0.51 mmol). The reaction mixture was stirred at room temperature for 4 h. After solvent evaporation in vacuo, the brown residue was extracted with dichloromethane (20 mL). The solution was passed through a Florisil column and the solvent was removed in vacuo. The residue was recrystallised from a acetone/hexane mixture to give reddish crystals. Other thiolate complexes with M = Pd and P*n*Pr$_3$, PEt$_3$, PMe$_2$Ph, PMePh$_2$ or PPh$_3$ and M = Pt and P*n*Bu$_3$, P*n*Pr$_3$, PEt$_3$, PMe$_2$Ph or PMePh$_2$ were prepared similarly.

Selenolate Complexes: As an example for the selenolate complexes the synthesis of $[PdCl(N^{\cap}Se)(PMe_2Ph)]$ is described. An acetone suspension (20 mL) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (180 mg, 0.29 mmol) was added to a freshly prepared methanol solution (5 mL) of $N^{\cap}SeNa$, prepared from $(N^{\cap}Se)_2$ (96 mg, 0.29 mmol) and $NaBH_4$ (23 mg, 0.61 mmol). The reaction mixture was stirred for 4 h. The solvents were evaporated in vacuo, the residue was washed with hexane and extracted with toluene (3 × 8 mL). The extracts were passed through a Florisil column. The solvent was reduced to 2 mL and a few drops of hexane were added which, on cooling to −5 °C, gave pink crystals (156 mg, 62%). Analogously, complexes of the type $[MCl(N^{\cap}Se)(PR_3)]$ (M = Pd with PEt$_3$, PMe$_2$Ph, PMePh$_2$ or PPh$_3$ and M = Pt with P*n*Bu$_3$, PEt$_3$, PMe$_2$Ph) were prepared.

Tellurolate Complexes: As an example for the tellurolate complexes the synthesis of $[PdCl(N^{\cap}Te)(PPh_3)]$ is described. To a freshly prepared solution of $N^{\cap}TeNa$, prepared from $(N^{\cap}Te)_2$ (127 mg, 0.30 mmol) and $NaBH_4$ (24 mg, 0.63 mmol) in methanol (10 mL), an acetone suspension (25 mL) of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ (261 mg, 0.30 mmol) was added with vigorous stirring which continued for 3 h. The solvents were removed under vacuum and the residue was washed with hexane and extracted with acetone (3 × 6 cm^3). The volume of the acetone was reduced to 8 mL which on cooling gave a brown powder (142 mg, 39% yield). $[PtCl(N^{\cap}Te)(PnPr_3)]$ and $[PtCl(N^{\cap}Te)(PPh_3)]$ were prepared similarly.

X-ray Crystallography: Single crystals of $[PdCl(N^{\cap}S^{**})(PMePh_2)]$ and $[PtCl(N^{\cap}S^{**})(PMe_2Ph)]$ were obtained at −10 °C from CH_2Cl_2/hexane and at room temperature from acetone/hexane mixtures, while single crystals of $[PdCl(N^{\cap}Se)(PMePh_2)]$ and $[PtCl(N^{\cap}Se^{**})(PMe_2Ph)]$ were obtained from toluene/hexane mixtures at room temperature and −10 °C, respectively. The X-ray data of these complexes were collected at 173(2) K or 178(2) K with Siemens (P4 or P3) or Stoe diffractometers, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and employing Wyckoff scans. Further details are given in Table 5. All structures were solved by the Patterson method using the SHELXTL package while refinement was carried out with SHELXL-97 employing full-matrix least-squares methods on F^2 with $F_o^2 = -2\sigma(F_o^2)$.[34] All non-hydrogen atoms were refined anisotropically, except for the disordered C and N atoms in the chelate ligand of $[PdCl(N^{\cap}Se^{**})(PMePh_2)]$. The same atoms had to be refined using DFIX restraints. Hydrogen atoms were introduced using appropriate riding models. Empirical absorption correction was performed using XABS2.[35] CCDC-235479 for $[PdCl(N^{\cap}S^{**})(PMePh_2)]$, -235480 for $[PtCl(N^{\cap}S^{**})(PMe_2Ph)]$, -235481 for $[PdCl(N^{\cap}Se)(PMePh_2)]$ and -235482 for $[PtCl(N^{\cap}Se^{**})(PMe_2Ph)]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union

Table 5. Crystallographic and structure refinement data of complexes [MCl(N∩E)(PR_3)]

	[PdCl(N∩S**)($PMePh_2$)]	[PtCl{N∩S**}(PMe_2Ph)]	[PdCl{N∩Se} ($PMePh_2$)]	[PtCl{N∩Se**}(PMe_2Ph)]
Empirical formula	$C_{18}H_{25}ClNPPdS$	$C_{13}H_{23}ClNPPtS$	$C_{18}H_{25}ClNPPdSe$	$C_{13}H_{23}ClNPtSe$
Formula mass	460.27	486.89	507.17	533.79
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$	$P2_1$	$P2_1$
a [Å]	11.434(2)	5.8519(12)	11.480(2)	5.8716(12)
b [Å]	13.023(3)	12.932(3)	14.025(3)	13.005(3)
c [Å]	13.932(3)	11.030(2)	12.850(3)	11.132(2)
α [°]	91.75(3)	90	90	90
β [°]	92.88(3)	98.76(3)	102.42(3)	100.24(3)
γ [°]	108.37(3)	90	90	90
V [Å^3]/Z	1964.0(7)/4	825.0(3)/2	2020.5(7)/4	836.5(3)/2
$\rho_{calcd.}$ [g·cm^{-3}]	1.557	1.960	1.667	2.119
μ [mm^{-1}]/F(000)	1.267/936	8.874/468	2.930/1008	10.802/504
Limiting indices	$-1 \le h \le 17$	$0 \le h \le 7$	$-14 \le h \le 13$	$0 \le h \le 8$
	$-16 \le k \le 15$	$0 \le k \le 17$	$-1 \le k \le 17$	$0 \le k \le 17$
	$-17 \le l \le 17$	$-15 \le l \le 14$	$0 \le l \le 15$	$-15 \le l \le 14$
Refl.collected/unique	8992/8581	2083/1910	4364/4364	2259/2086
R_{int}	0.0270	0.0214	0.0693	0.0284
Data/restr./param.	8581/0/457	1910/0/168	4364/11/407	2086/1/168
Goof on F^2	1.317	1.177	1.128	1.058
Final R_1, wR_2 indices	0.0322, 0.0735	0.0321, 0.0786	0.0715, 0.1439	0.0271, 0.0677
R_1, wR_2 (all data)	0.0443, 0.0771	0.0346, 0.0799	0.1074, 0.1619	0.0287, 0.0685
Largest diff. peak/hole [e·Å^{-3}]	0.631/−0.685	2.248/−1.553	0.998/−0.913	1.138/−0.962

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Supporting Information (see also footnote on the first page of this article): Further tables with analytical data for all new complexes and structural details of [PdCl(N∩S**)($PMePh_2$)], [PtCl(N∩S**)-(PMe_2Ph)], [PdCl(N∩Se)($PMePh_2$)] and [PtCl(N∩Se**)(PMe_2Ph)] are available. Further figures illustrating the crystal and molecular structures are also provided.

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