DOI: 10.1002/ejic.200600509

Synthesis and Properties of Organometallic Pt^{II} and Pt^{IV} Complexes with Acyclic Selenoether and Telluroether Ligands and Selenoether Macrocycles

William Levason,[a] Joanna M. Manning,[a] Paul Pawelzyk,[a] and Gillian Reid*[a]

Keywords: Selenoether / Telluroether / Platinum / Macrocycles / Organometallic complexes

The first series of planar dimethyl(selenoether)Pt^{II} complexes, $[PtMe_2L]$ [L = $MeSe(CH_2)_nSeMe$ (n = 2 or 3), o-$C_6H_4(CH_2SeMe)_2$, [8]aneSe_2 (1,5-diselenacyclooctane), or [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane)], have been obtained by treatment of $[PtMe_2(SMe_2)_2]$ with L in Et_2O solution and characterised by VT ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy, electrospray MS and microanalysis. The corresponding dimethyl(telluroether)Pt^{II} complexes do not form under similar reaction conditions. The distorted octahedral $[PtMe_3I(L)]$ [L = o-$C_6H_4(CH_2SeMe)_2$, [8]aneSe_2, [16]aneSe_4 or $MeC(CH_2SeMe)_3$] form as stable complexes in good yield from reaction of $PtMe_3I$ with L in refluxing $CHCl_3$ and have been characterised similarly. These all show bidentate selenoether coordination, with fast pyramidal inversion occurring at room temperature. The distorted octahedral coordination environment at Pt^{IV} is also confirmed from a crystal structure of $[PtMe_3I\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$. Rare examples of (telluroether)Pt^{IV} complexes, $[PtMe_3I\{o\text{-}C_6H_4(CH_2TeMe)_2\}]$ and the dinuclear $[Me_3Pt(\mu^2\text{-}I)_2(\mu^2\text{-}MeTeCH_2TeMe)PtMe_3]$, have also been prepared and characterised similarly (and also by $^{125}Te\{^1H\}$ NMR spectroscopy). The [8]aneSe_2 and [16]aneSe_4 species are the first examples of alkyl Pt^{II} or Pt^{IV} complexes with (macro)cyclic selenoether coordination. Halide abstraction ($TlPF_6$) from $[PtMe_3I(\kappa^2\text{-}[16]aneSe_4)]$ affords $[PtMe_3(\kappa^3\text{-}[16]aneSe_4)]PF_6$; a rare example of a cationic Pt^{IV} selenoether. The (diselenoether)Pt^{II} complexes undergo oxidative addition of MeI to yield the corresponding Pt^{IV} species $[PtMe_3I(diselenoether)]$.

Introduction

The chemistry of the neutral ligands derived from the heavier group 16 elements, i.e. selenoethers and telluroethers, is of interest because these are less electronegative than their thioether or ether counterparts, and hence are better σ-donor ligands to transition-metal ions in medium oxidation states compared to their O- and S-donor counterparts.[1,2] The vast majority of transition-metal species involving the selenoether or telluroether ligands are based upon transition-metal halide systems, although we have also shown that homoleptic hexaselenoether or hexatelluroether coordination can be achieved under certain conditions.[3] In contrast, examples of organometallic complexes (involving ligands other than carbonyls) with selenoether and telluroether coordination are rare.[4–7] Abel and Orrell and co-workers have reported some such species based upon $PtMe_3X$ (X = Cl, Br or I) as part of their extensive investigation of the solution dynamics in complexes with dichalcogenoether ligands, in order to understand the fluxional processes occurring and to establish the invertomer populations.[8] However, the reaction chemistry of alkyl(chalcogenoether)transition-metal species has not been investigated. The only examples of dimethyl(chalcogenoether)-Pt^{II} complexes are those involving the $E(CH_2CH{=}CH_2)_2$ ligands (E = S, Se), in which both the chalcogen atom and the alkene functions are coordinated to Pt at low temperature.[9] The preparation of $[PtMeBr\{MeSe(CH_2)_2SeMe\}]$ has also been described.[10]

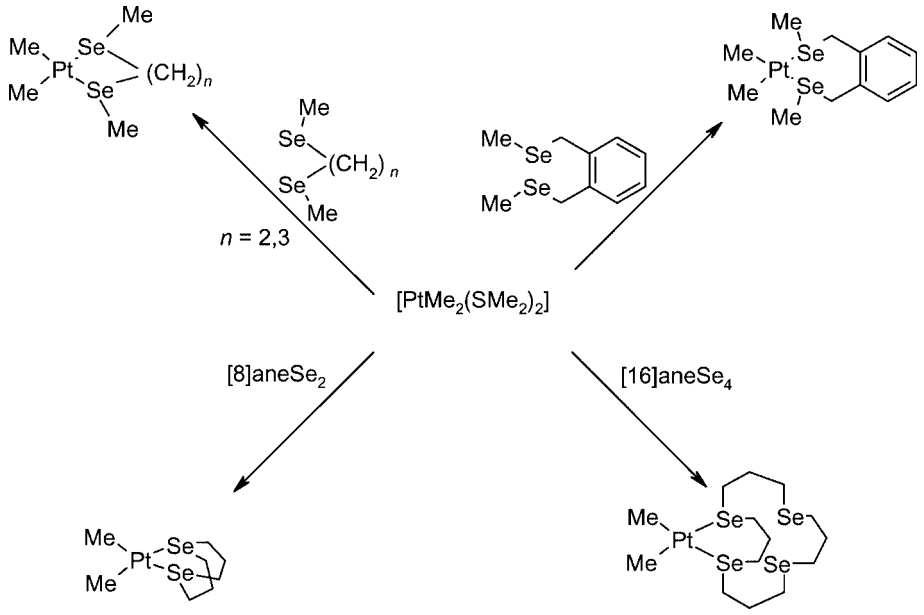
Here we describe the syntheses and spectroscopic characterisation of a series of methylplatinum(II) and methylplatinum(IV) complexes involving a selected range of acyclic di- and triseleno- and telluroether ligands and macrocyclic selenoethers incorporating between two and four chalcogen atoms and containing a range of linkages between the chalcogen atoms. The ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR shifts and coupling constants are discussed and the crystal structure of $[PtMe_3I\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$ described, together with some reaction chemistry.

Results and Discussion

Platinum(II) Complexes

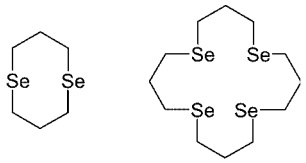
Initial attempts to prepare the dimethyl(selenoether)Pt^{II} complexes by treatment of $[PtMe_2(cod)]$ (cod = 1,5-cyclooctadiene) with the ligand in refluxing $CHCl_3$ failed. The ^1H NMR spectra of the products show that displacement of the cod is not achieved cleanly, presumably owing to the

[a] School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK



Scheme 1. Synthesis of dimethylPt^{II} complexes (note that only one of the possible stereoisomers is shown in each case).

strong σ-donor properties of the Me ligands which occupy the coordination sites *trans* to the cod. However, the (selenoether)Pt^{II} species $[PtMe_2(L\text{-}L)]$ (L-L = $MeSe(CH_2)_nSeMe$, n = 2 or 3, *o*-$C_6H_4(CH_2SeMe)_2$, [8]$aneSe_2$ or [16]$aneSe_4$) were successfully prepared (Scheme 1) by initially treating $[PtCl_2(Me_2S)_2]$ with two mol. equivs. of MeLi in cold Et_2O solution (–78 °C), followed by hydrolysis with water to give $[PtMe_2(SMe_2)_2]$ in situ. Addition of one mol. equiv. of the selenoether to this two-phase mixture and stirring at room temperature gave the products either as solutions in the Et_2O or as yellow solids at the interface. Treatment of [16]$aneSe_4$ with two mol. equivs. of the (dimethyl)Pt^{II} source under these conditions also yielded the 1:1 species $[PtMe_2([16]aneSe_4)]$, hence the product appears to be independent of the ratio used (although this may be a result of the poor solubility of the 1:1 complex which precipitates from the solution and may prevent further complexation to a second $PtMe_2$ unit). The compounds were characterised thoroughly by spectroscopic methods (IR, electrospray MS and variable temperature multinuclear NMR spectroscopy – see Table 1) and microanalysis. On the basis of the *m*/*z* values and the isotopic distributions observed, the electrospray MS show the highest mass peaks corresponding to $[PtMe(L\text{-}L)]^+$ in each case. Attempts to isolate a pure complex from reaction of $[PtMe_2(Me_2S)_2]$ with the $MeSeCH_2SeMe$ under similar conditions were not successful.



[8]$aneSe_2$ [16]$aneSe_4$

The ^1H NMR spectra of $[PtMe_2\{MeSe(CH_2)_nSeMe\}]$ (n = 2 or 3) are consistent with fast pyramidal inversion occurring in chloroform solution at room temperature. Cooling to 223 K reveals sharp resonances associated with both the *meso* and DL forms of the complexes being present in unequal amounts, resulting in two sets of PtMe, SeMe and $SeCH_2$ resonances. Similar behaviour is seen by both $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectroscopy (Table 1). When recorded at 223 K, the ^{77}Se NMR spectra show two distinct Se resonances to high frequency of the uncoordinated selenoether, with ^{195}Pt couplings of ca. 420–460 Hz. The relative intensities of the $^{77}Se\{^1H\}$ resonances for $[PtMe_2\{MeSe(CH_2)_2SeMe\}]$ are ca. 1:2, i.e. rather disparate quantities of the *meso* and DL forms, whereas a ratio of ca. 1:1 occurs for $[PtMe_2\{MeSe(CH_2)_3SeMe\}]$. The ^{195}Pt NMR spectra (223 K) show resonances for both stereoisomers at approximately –4400 ppm. These resonances are significantly to low frequency of the corresponding $[PtCl_2\{MeSe(CH_2)_nSeMe\}]$, reflecting the better σ-donating properties of the Me ligands.

In separate work we have established that incorporation of the *o*-xylyl linkage in a range of ligand types (diphosphane, distibane, ditelluroether) leads to an increased tendency towards *cis*-chelation compared to aliphatic C_4-linked analogues. Therefore, despite the seven-membered ring chelate, these turn out to be very effective ligands for a range of transition-metal ions. We have also reported recently the first series of (alkyl)Pt^{II} and (alkyl)Pt^{IV} complexes involving stibane ligands of this type.[11,12] Furthermore, complexes involving *o*-xylyl-linked wide-angle diphosphanes provide very efficient catalysts for a range of processes such as hydroformylation and hydrocyanation.[13] A number of macrocyclic thioether and selenoethers containing *o*-xylyl linkages have also been reported.[2] We were

Table 1. Selected NMR spectroscopic data.

Compound	T [K][a]	$\delta(^{77}Se$ or $^{125}Te)$	$^1J_{PtSe/Te}$/Hz	$\delta(^{195}Pt)$
Platinum(II) complexes				
$[PtMe_2\{MeSe(CH_2)_2SeMe\}]$	243	247.9 (major)	457	–4383 (major)
		250.1 (minor)	438	–4395 (minor)
$[PtMe_2\{MeSe(CH_2)_3SeMe\}]$	243	114.0 (major)	427	–4247 (major)
		102.1 (minor)	429	–4309 (minor)
$[PtMe_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$	193	169.1	526	–4308
		160.6	492	–4316
		155.9	438	
$[PtMe_2([8]aneSe_2)]$	298	140.8	323	–4318
$[PtMe_2([16]aneSe_4)]$	[b]	[b]	[b]	[b]
Platinum(IV) complexes				
$[PtMe_3I\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$	213	114.0	289	–3382
		98.7	280	–3468
		97.8	312	minor form not obsd.
		95.5 (minor)	286	
$[PtMe_3I\{o\text{-}C_6H_4(CH_2TeMe)_2\}]$	243	189.5	602	–3968
		159.9	618	–4022
		114.5	638	–4119
		110.8	537	
$[(PtMe_3I)_2(MeTeCH_2TeMe)]$	243	173.2 (major)	713	–3430 (major)
		171.1 (minor)	605	–3451 (minor)
$[PtMe_3I\{MeC(CH_2SeMe)_3\}]$	243	53.0[c]	252	–3446
		51.6[c]	160	–3543
		49.3[c]	258	–3550
		38.5[c]	252	
		37.4[c]	162	
		37.3[c]	256	
		35.1[d]	–	
		33.0[d]	–	
		29.0[d]	–	
		27.3[d]	–	
$[PtMe_3I([8]aneSe_2)]$	298	65.3	244	–3589
$[PtMe_3I([16]aneSe_4)]$	243	116.6 (2 Se, coord.)	266	–3616
		119.5 (2 Se, uncoord.)	–	
$[PtMe_3([16]aneSe_4)]PF_6$	243	70 (3 Se, coord.)	249	–3648
		138 (1 Se, uncoord.)	–	

[a] The temperature quoted is that required to clearly resolve the invertomers (see text). [b] Spectra not obtained due to very poor solubility. [c] Coordinated Se. [d] Uncoordinated Se.

therefore interested to investigate the chemistry of *o*-xylyl-linked ligands in this work. Using the wide-angle diselenoether ligand $o\text{-}C_6H_4(CH_2SeMe)_2$ in the procedure described above gives the seven-membered chelate complex $[PtMe_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$ in good yield. For square planar $[PtMe_2(L–L)]$ (L–L = bidentate chalcogenoether) two NMR distinguishable forms arise from the chirality at the coordinated chalcogen atom (*meso* and DL). The incorporation of the xylyl linker (which lies out of the square plane) may give rise to further invertomers depending upon the orientation of the SeMe groups with respect to the xylyl backbone. In our recent work on xylyl distibane complexes[11,12] several different conformations of the backbone were identified crystallographically, which serve to illustrate the effect of the backbone. The VT NMR spectroscopic data confirm *cis*-chelation in $[PtMe_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$, with two invertomers clearly identifiable, one of which, the DL form, results in two $\delta(^{77}Se)$ resonances of equal intensity (each with ^{195}Pt satellites) and one $\delta(^{195}Pt)$ resonance. The other major form is attributed to a *meso*-1 form [one $\delta(^{77}Se)$ and one $\delta(^{195}Pt)$].

The Pt^{II} complexes of the cyclic selenoethers were less soluble, although $[PtMe_2([8]aneSe_2)]$ dissolved in DMF, enabling ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra to be obtained. The $[PtMe_2([16]aneSe_4)]$ was much less soluble and hence only the ^1H NMR spectroscopic data were obtained for this compound, although the formulation was supported by microanalysis and positive ion electrospray MS measurements. The ^1H NMR spectra of these cyclic selenoether complexes show resonances associated with coordinated selenoether as well as a singlet around 0.5 ppm due to the Pt–Me groups. The Pt–H couplings (≈ 80 Hz) are in agreement with the expected values. For $[PtMe_2([8]aneSe_2)]$, the $\delta(^{13}C)$ for the Me groups is a singlet at δ = –7.6 ppm with ^{195}Pt satellites (794 Hz). The ^{77}Se NMR spectrum is a singlet at 140.8 ppm, thus there is only a very small shift from "free" $[8]aneSe_2$ (δ = 138 ppm) upon coordination, although the appearance of clear coupling to ^{195}Pt ($^1J_{PtSe}$ = 323 Hz) unambiguously confirms the assignment. This compares to $\delta(^{77}Se)$ of 194 ppm ($^1J_{PtSe}$ = 680 Hz) for the corresponding dichloro species $[PtCl_2([8]aneSe_2)]$,[14] consistent with replacement of the chloro ligands with

strong σ-donor Me groups which have a much greater *trans* influence and hence substantially reduce the Pt–Se coupling constants. The ^{195}Pt NMR shift for [$PtMe_2$([8]aneSe_2)], –4325 ppm, also compares with a value of –3825 ppm for [$PtCl_2$([8]aneSe_2)], reflecting the incorporation of the much stronger σ-donating Me ligands in the former. We note that the cyclic structure of the [8]aneSe_2 ligand eliminates the possibility of stereoisomers, hence only one form of the complex is evident. All of the dimethyl(selenoether)Pt^{II} complexes are rather unstable – the solids deteriorate with significant darkening of the powders over a period of days to weeks even when stored under N_2. Solutions in chlorocarbons are even less stable, and substantial sample degradation was clearly evident from the NMR spectra recorded after standing in solution for a few hours. Data quoted were therefore recorded from freshly prepared samples.

Attempts to prepare analogous dimethyl(ditelluroether)-Pt^{II} complexes by reaction of [$PtCl_2(SMe_2)_2$] with MeLi in situ, followed by hydrolysis and addition of either $MeTe(CH_2)_3TeMe$ or *o*-$C_6H_4(CH_2TeMe)_2$ gave dark brown, poorly soluble materials which were not the desired species. We also investigated reaction of isolated [$PtMe_2(SMe_2)_2$] with ditelluroether in anhydrous Et_2O both at room temperature and low temperature. These reactions yielded orange/brown materials whose NMR spectra show clear evidence for TeMe units, but no PtMe groups. The electrospray mass spectra from these reaction show common features consistent with diplatinum compounds involving TeMe ligands, strongly indicating significant Te–C bond fission occurs in these reactions.

Platinum(IV) Complexes

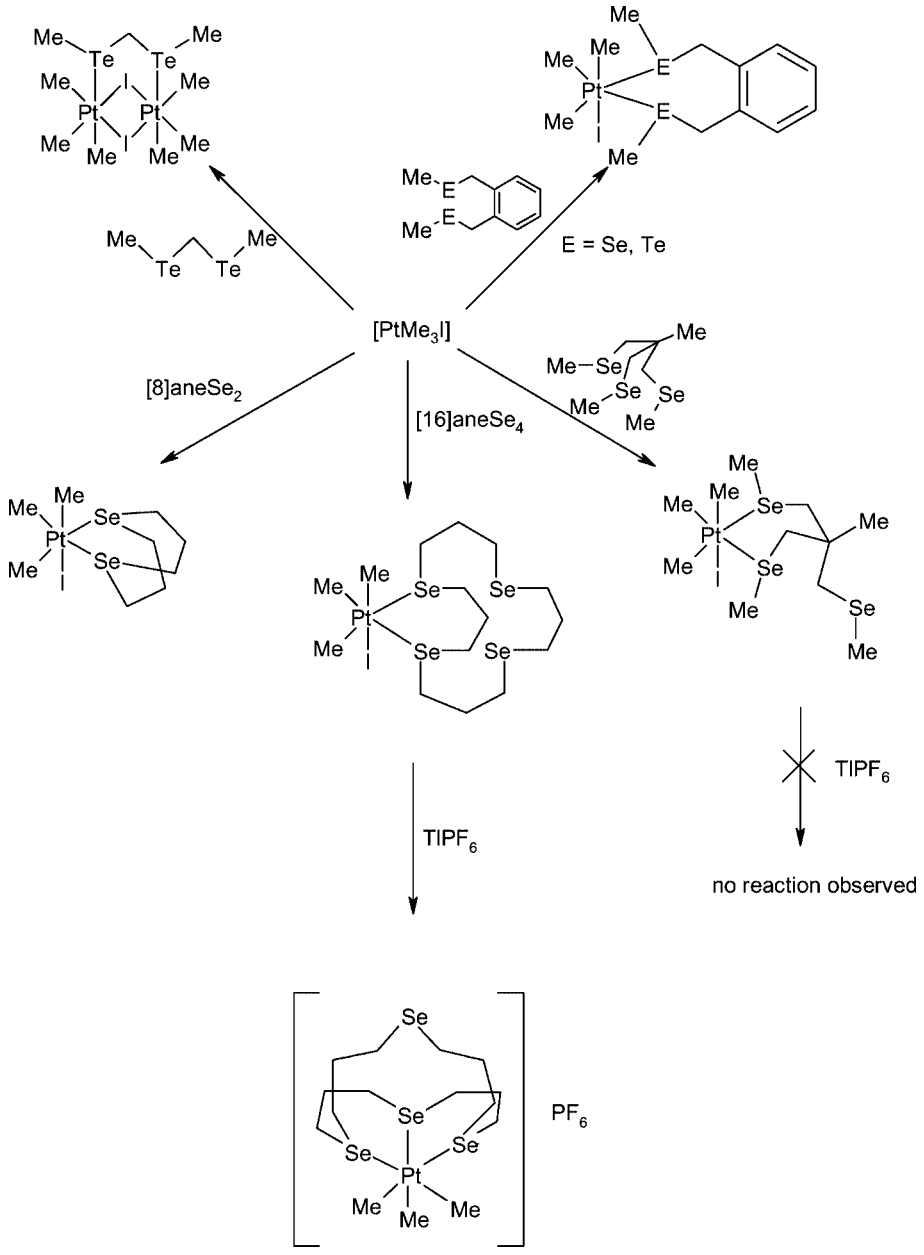
Freshly prepared solutions of the Pt^{II} complexes [$PtMe_2${*o*-$C_6H_4(CH_2SeMe)_2$}] and [$PtMe_2${$MeSe(CH_2)_3$-SeMe}] in CH_2Cl_2 were stirred overnight with excess MeI, giving light yellow solids after work-up. The ^{1}H and ^{77}Se{^{1}H} NMR spectra of solutions of these products show that oxidative addition of MeI occurs cleanly, with complete conversion of the Pt^{II} complexes to [$PtMe_3$I{*o*-$C_6H_4(CH_2SeMe)_2$}] and [$PtMe_3$I{$MeSe(CH_2)_3SeMe$}] respectively.

Six-coordinate trimethyl Pt^{IV} complexes with both selenoether and telluroether ligands, [$PtMe_3$I(L-L)] [L-L = *o*-$C_6H_4(CH_2EMe)_2$; E = Se or Te], were obtained in good yield as soluble yellow/orange powdered solids through reaction of $PtMe_3$I with one mol. equiv. of L-L in refluxing $CHCl_3$ (Scheme 2). Surprisingly, these Pt^{IV} compounds are much more stable both as solids and in solution than the Pt^{II} species described above. The formulations follow from variable temperature ^{1}H, ^{13}C{^{1}H}, ^{77}Se{^{1}H}, ^{125}Te{^{1}H} and ^{195}Pt NMR spectroscopic studies, electrospray MS and microanalyses. For bidentate chalcogenoethers coordinated to $PtMe_3$I three NMR distinguishable diastereoisomers are possible (*meso*-1, *meso*-2 and a pair of NMR indistinguishable DL enantiomers – Scheme 3) depending upon the orientations of the Me substituents relative to both the iodo and methyl ligands on Pt. The fact that the planar aromatic unit in the *o*-$C_6H_4(CH_2EMe)_2$ complexes lies out of the ME_2 plane leads to further possible stereoisomers for these particular complexes. From the NMR studies we observe that the telluroether complex is undergoing relatively slow pyramidal inversion at 298 K compared to the selenoether analogue. Cooling the solution of [$PtMe_3$I{*o*-$C_6H_4(CH_2SeMe)_2$}] leads to the observation of two significant δ(^{195}Pt) NMR resonances, while four δ(^{77}Se) NMR resonances with ^{195}Pt satellites are evident, albeit one of these is weak, indicating that one isomer (probably a rather sterically crowded *meso*-2 form) has a very low percentage population. Thus, the DL form gives rise to two δ(^{77}Se) resonances and the *meso* form gives one resonance. Figure 1 shows the low temperature ^{125}Te{^{1}H} NMR spectrum of [$PtMe_3$I{*o*-$C_6H_4(CH_2TeMe)_2$}], which clearly shows the presence of three invertomers all in significant amounts.

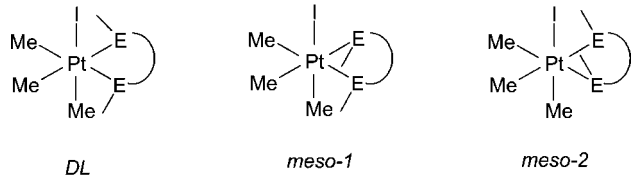
The crystal structure of [$PtMe_3$I{*o*-$C_6H_4(CH_2SeMe)_2$}] (Figure 2) confirms a distorted octahedral coordination sphere at Pt^{IV} derived from three facial Me groups, an iodo ligand and a chelating diselenoether, *d*(Pt–C) = 2.080(3)–2.114(4) Å, *d*(Pt–Se) = 2.5530(4), 2.5629(4) Å, *d*(Pt1–I) = 2.7663(3) Å. The seven-membered chelate ring gives rise to a Se1–Pt1–Se2 angle of 98.317(12)°, and somewhat longer Pt–Se bonds than in [$PtMe_3$I(MeSeCH=CHSeMe)] [2.525(4), 2.532(4) Å],[9] reflecting the considerable steric demands of the wide-angle diselenoether. The selenoether adopts a DL configuration in which the SeMe substituents lie on opposite sides of the $PtSe_2$ plane, and the aromatic ring is oriented towards the Me ligand opposite the sterically large iodo ligand.

Using the ditelluromethane ligand, $MeTeCH_2TeMe$, with two mol. equivs. of $PtMe_3$I gives the dinuclear [($PtMe_3I)_2$-($MeTeCH_2TeMe$)] in good yield. The spectroscopic data are in full accord with a diiodo-bridged species in which the telluroether also bridges between the Pt atoms, i.e. [$Me_3Pt(\mu^2$-I)$_2(\mu^2$-$MeTeCH_2TeMe)PtMe_3$], which leads to two NMR distinguishable invertomers.

In order to investigate the effect of ligand architecture further, reactions were also conducted using the cyclic selenoethers [8]aneSe_2 and [16]aneSe_4, as well as the tripodal $MeC(CH_2SeMe)_3$. The distorted octahedral (trimethyl)Pt^{IV} complexes, [$PtMe_3$I([8]aneSe_2)] and [$PtMe_3$I([16]aneSe_4)] were obtained in good yield by treatment of [$PtMe_3$I] with one molar equivalent of the cyclic selenoether in refluxing $CHCl_3$. The products were characterised by IR and multinuclear NMR spectroscopy, electrospray MS and microanalyses and represent the first examples of alkyl Pt^{IV} complexes with (macro)cyclic selenoether coordination. The electrospray MS show clusters of peaks with the correct *m*/*z* and isotope patterns for [$PtMe_3$(L)]$^+$ (L = [8]aneSe_2 or [16]-aneSe_4). For the [8]aneSe_2 complex an additional cluster of peaks corresponding to [PtMe([8]aneSe_2)]$^+$ is also clearly evident, presumably a result of facile reductive elimination of ethane from the parent complex in the MS experiment. The NMR spectroscopic data for these species are also summarised in Table 1. The presence of three mutually *fac*



Scheme 2. Synthesis of (trimethyl)Pt^{IV} complexes (note that only one of the possible stereoisomers is shown in each case).



Scheme 3. Diasteroisomers for [$PtMe_3I$(L–L)] (L–L = bidentate dichalcogenoether). Note that the planar phenylene unit present in the xylyl derivatives leads to further stereoisomers depending upon its orientation with respect to the rest of the molecule.

Me groups was confirmed by the ^1H and the $^{13}C\{^1H\}$ NMR spectra which show two Me singlets in a 1:2 ratio at low frequency, each with ^{195}Pt satellite couplings as expected. The Me group *trans* to I is to low frequency of Me *trans* to Se, as observed for the small number of known examples of (trimethyl)Pt^{IV} complexes with acyclic diselenoethers, and the Pt–H and Pt–C couplings are in also in accord.[7] For [$PtMe_3I$([8]aneSe_2)] we find that the coupling constants are consistently smaller than for the planar [$PtMe_2$([8]aneSe_2)] described above, as expected based upon the different coordination environments. The absence of axial symmetry in the Pt^{IV} compounds leads to inequivalencies in the macrocyclic CH_2 environments, giving rise to four distinct $\delta(CH_2)$ resonances in the $^{13}C\{^1H\}$ NMR spectrum for the [8]aneSe_2 complex. For [$PtMe_3I$([16]aneSe_4)] seven $\delta(CH_2)$ resonances are clearly evident, consistent with bidentate coordination of the tetraselenoether ligand, giving a six-coordinate Pt^{IV} species with a vertical plane of symmetry. The ^{77}Se NMR shifts for the Pt^{IV} species are

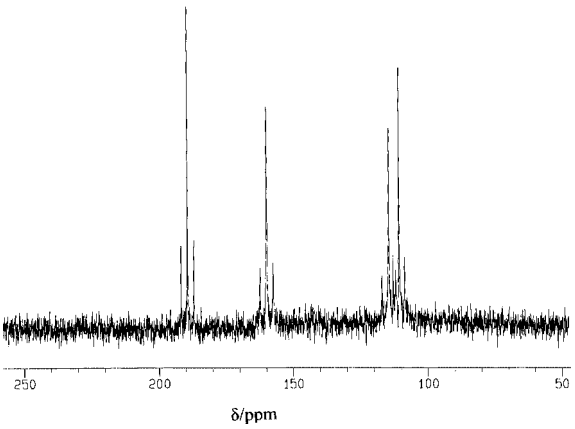


Figure 1. $^{125}Te\{^1H\}$ ($CH_2Cl_2/CDCl_3$, 243 K) spectrum of $[PtMe_3I\{o\text{-}C_6H_4(CH_2TeMe)_2\}]$ showing the presence of all three invertomers.

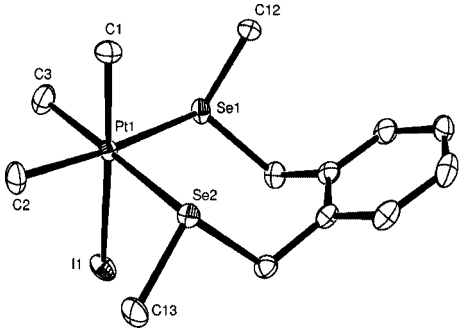


Figure 2. View of the crystal structure of $[PtMe_3I\{o\text{-}C_6H_4(CH_2SeMe)_2\}]$ with numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

substantially to low frequency of the "free" ligand values, and surprisingly even the resonance arising from the two uncoordinated Se atoms of the $[16]aneSe_4$ ring is also some 40 ppm to low frequency of $[16]aneSe_4$ itself. This suggests that the presence of the (trimethyl)Pt^{IV} fragment bound to the other two Se atoms significantly influences the electronic environment at the remote, "free" Se atoms – this may suggest that the uncoordinated Se atoms lie near to the iodo ligand.

As with all of the compounds in this study, ^{195}Pt NMR spectroscopy in principle provides an excellent and convenient direct probe of the electronic environment at platinum. Each of the Pt^{IV} compounds shows a single resonance at ca. –3600 ppm, to high frequency of that for the planar $[PtMe_2([8]aneSe_2)]$ above. The macrocycle ring size has very little influence on the ^{195}Pt chemical shift. These compare with values of –3458 and –3530 ppm for the *meso*-1 and DL forms of $[PtMe_3I\{MeSe(CH_2)_3SeMe\}]$.[7]

Treatment of $[PtMe_3I(\kappa^2\text{-}[16]aneSe_4)]$ with one mol. equiv. of $TlPF_6$ in $CHCl_3$ results in clean abstraction of the iodo ligand, giving $[PtMe_3([16]aneSe_4)]PF_6$, as a white solid. This is the first cationic (alkyl)Pt^{IV} complex with selenoether coordination. Electrospray MS shows intense peaks for the parent $[PtMe_3([16]aneSe_4)]^+$ cation, with lower intensity peaks corresponding to $[PtMe([16]aneSe_4)]^+$, i.e. loss of two Me groups (Figure 3). The generation of a Pt^{IV} cation involving a *fac*-octahedral Me_3Se_3 donor set is confirmed by NMR spectroscopy. Although the cation still has C_s local symmetry at Pt^{IV}, thus giving rise to two $\delta(^1H)$ and $\delta(^{13}C)$ resonances, this time both the chemical shift values and the Pt–H and Pt–C couplings are similar as the Me ligands are all *trans* to Se. The $^{13}C\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra for this cation–anion system show only very broad resonances at room temperature. Upon cooling the sample to 223 K, the spectra sharpen. The dynamic process probably involves "ring-whizzing", resulting in rapid interchange between the "free" and coordinated Se atoms. Abel and coworkers proposed a similar mechanism for the thioether complex $[PtMe_3(\kappa^3\text{-}[12]aneS_4)]^+$ ([12]aneS$_4$ = 1,4,7,10-tetrathiacyclododecane).[15] The occurrence of a κ^3-bonding mode for $[16]aneSe_4$ is very unusual, the only other known examples are in the carbonyl complexes *fac*-$[M(CO)_3(\kappa^3\text{-}[16]aneSe_4)]^+$ (M = Mn or Re) and *fac*-$[M'(CO)_3(\kappa^3\text{-}[16]aneSe_4)]$ (M′ = Mo or W).[16] At 223 K the $^{77}Se\{^1H\}$ NMR spectrum for $[PtMe_3([16]aneSe_4)]PF_6$ reveals two Se environments at 70 (coordinated Se) and 138 ppm ("free" Se), once again these are both to low frequency of $[16]aneSe_4$ itself (δ =158 ppm). Replacement of the iodo ligand with a third Se atom leads to a small change in the ^{195}Pt NMR spectrum, which is now a singlet at δ = –3648 ppm. The only other examples of Pt^{IV} complexes involving $[16]aneSe_4$ are the *trans*-$[PtX_2([16]aneSe_4)](PF_6)_2$ (X = Cl or Br) which we have described previously, obtained by halogen oxidation of the planar $[Pt([16]aneSe_4)](PF_6)_2$.[17] Spectroscopic studies of the yellow material obtained following treatment of the dicationic Pt^{II} species, $[Pt([16]aneSe_4)](PF_6)_2$ with excess MeI in either refluxing CH_2Cl_2 or acetone solution showed no evidence for oxidative addition of the MeI, contrasting with the halogen oxidation described above.

The successful preparation of the cationic $[PtMe_3([16]aneSe_4)]^+$ with an unusual Me_3Se_3 donor set prompted us to investigate the chemistry of the tripodal $MeC(CH_2SeMe)_3$ with $[Me_3PtI]$. The preparation of $[PtMe_3I\{MeC(CH_2SeMe)_3\}]$ was achieved in good yield and the product was characterised by electrospray MS, microanalysis, IR and VT multinuclear NMR spectroscopy. The data are consistent with bidentate coordination of the tripod selenoether at the distorted octahedral Pt^{IV} centre. For $[PtMe_3I\{\kappa^2\text{-}MeC(CH_2SeMe)_3\}]$ at room temperature both the ^1H and $^{77}Se\{^1H\}$ NMR spectra were broad and ill-defined. Upon cooling the sample to 223 K, the ^1H NMR resonances are sharp and several Pt–Me resonances are clearly evident, consistent with the presence of several invertomers (*meso*-1, *meso*-2 and DL forms, with further isomers arising depending upon the orientation of the uncoordinated arm either towards the iodo ligand or towards a Me group), and the presence of both coordinated and "free" SeMe groups. The mixture of invertomers, together with the low symmetry of the molecule make it very difficult to assign the spectra in detail. The structurally simpler (but spectroscopically still rather complicated)

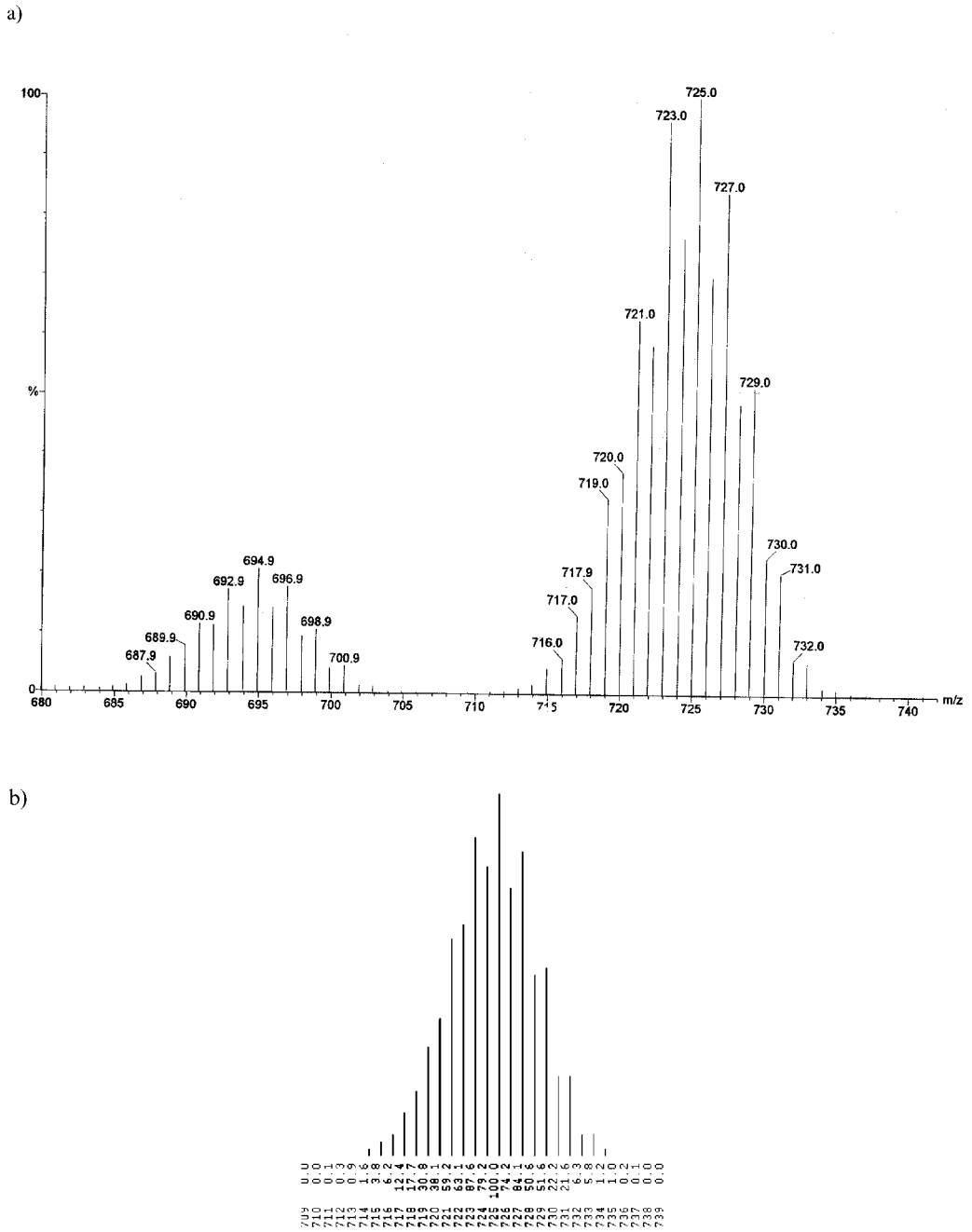


Figure 3. a) Positive ion electrospray MS (MeCN) of $[PtMe_3([16]aneSe_4)]PF_6$ (the cluster of peaks centred at m/z = 725 corresponds to $[PtMe_3([16]aneSe_4)]^+$, while that centred at m/z = 695 corresponds to $[PtMe([16]aneSe_4)]^+$). b). Simulated isotope pattern for $[PtMe_3([16]aneSe_4)]^+$.

$[PtMe_3X\{MeE(CH_2)_nEMe\}]$ (n = 2 or 3) systems have been studied in detail by Abel and co-workers by VT NMR spectroscopy and band-shape analysis.[6–8] However, the identity of the complex as $[PtMe_3I\{\kappa^2\text{-}MeC(CH_2SeMe)_3\}]$ is not in doubt.

At 223 K the $^{13}C\{^1H\}$ NMR spectrum of $[PtMe_3I\{\kappa^2\text{-}MeC(CH_2SeMe)_3\}]$ is extremely complicated owing to the presence of varying amounts of the possible invertomers, the low symmetry of the complexes and the fact that the C atoms of the Pt–Me units occur in the same region of the spectrum as the SeMe groups of the uncoordinated arm of the tripod, resulting in overlapping resonances which are not readily assigned.

The observation of three $^{195}Pt\{^1H\}$ NMR resonances at ca. –3500 ppm at 223 K is consistent with the presence of three significant, NMR distinguishable invertomers. The $^{77}Se\{^1H\}$ NMR spectrum at 223 K is also very complex, revealing three coordinated Se environments in the range 49–53 ppm, each with ^{195}Pt satellites, three further coordinated Se environments in the range 37–39 ppm with satellites, and four resonances in the range 27–35 ppm which show no ^{195}Pt coupling and hence are attributed to the Se

atoms of the uncoordinated arm of the tripod selenoether [$\delta(^{77}Se)$ for $MeC(CH_2SeMe)_3$: +24]. These data strongly suggest that the orientation of the uncoordinated arm of the tripod (either towards the iodide or towards the Me group *trans* to I) are also distinguishable by NMR spectroscopy.

Attempts to promote tridentate selenoether coordination to give $[PtMe_3\{MeC(CH_2SeMe)_3\}]^+$ through treatment of the bidentate complex with $TlPF_6$ either in refluxing MeCN or $CHCl_3$ were not successful. The NMR spectra of the resulting solutions show that $[PtMe_3I\{MeC(CH_2SeMe)_3\}]$ is still the only significant species after the reaction. This suggests that the tripodal Se_3-donor ligand is not well-suited to facial coordination on the small trimethylPt^{IV} fragment. The different reactivities of the Pt^{IV} complexes containing the tripodal Se_3-donor ligand compared to that containing the macrocyclic selenoether may be due to the different constraints of the two ligands and the different ring-strain effects.

It has been shown that $[PtMe_3I(L–L)]$ (L–L = diphosphane or distibane)[18,12] undergo clean reductive elimination of ethane upon thermolysis. We have therefore probed the thermolysis of the $[PtMe_3I\{o\text{-}C_6H_4(CH_2EMe)_2\}]$ complexes prepared in this work. The telluroether complex $[PtMe_3I\{o\text{-}C_6H_4(CH_2TeMe)_2\}]$ does not melt on heating, but undergoes decomposition at ≈ 130 °C giving a black solid. The corresponding Pt^{IV} selenoether complex melts at ca. 150 °C and then darkens slowly as the temperature is increased, indicating the onset of decomposition. A solid sample of this complex was heated at ca. 160 °C for 1 h and the residue investigated by ^1H NMR spectroscopy, which revealed loss of the PtMe and SeMe resonances. Thus, it is clear that these species do not undergo clean reductive elimination under these conditions. This may be a consequence of the well-known susceptibility of group 16 ligands to undergo dealkylation.[1]

Conclusions

We have developed routes for the synthesis of the first series of dimethyl(selenoether)Pt^{II} complexes, as well as a range of trimethyl(selenoether)Pt^{IV} complexes (including the first macrocyclic examples) and rare examples involving ditelluroethers. The Pt^{IV} species are less reactive than the Pt^{II} complexes, possibly due to the very strong ligand field imparted by the Me ligands in the Pt^{IV} species, together with the fact that these compounds are coordinatively saturated, hence providing limited possibility for metal-assisted E–C bond fission (cf. the Pt^{II} species). The donor type, ligand architecture and denticity clearly play major roles in determining the invertomer populations in these compounds. Using the macrocyclic [16]aneSe$_4$ we have been able to obtain the first cationic trialkyl(selenoether)Pt^{IV}, $[PtMe_3(\kappa^3\text{-}[16]aneSe_4)]^+$, whereas surprisingly this was not possible under similar conditions using the tripodal $MeC(CH_2SeMe)_3$. This may also be a consequence of the ligand architecture which for the tripodal Se_3 ligand results in low stability on the small Pt^{IV} centre. The new dimethyl(selenoether)Pt^{II} complexes, $[PtMe_2(L\text{-}L)]$, undergo clean and complete oxidative addition of MeI to afford the corresponding Pt^{IV} species $[PtMe_3I(L\text{-}L)]$.

Experimental Section

Infrared spectra were recorded as Nujol mulls between CsI plates with a Perkin–Elmer 983G spectrometer over the range 4000–200 cm^{-1}. Mass spectra were run by positive ion electrospray (MeCN solution) with a VG Biotech platform. ^1H NMR spectra were recorded with a Bruker AV300 spectrometer or Bruker DPX400 spectrometer. $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded with a Bruker DPX400 spectrometer operating at 100.6, 76.3, 126.3 or 85.7 MHz, respectively, and are referenced to TMS, external neat Me_2Se, external neat Me_2Te and external 1 mol·dm^{-3} $Na_2[PtCl_6]$ in water, respectively. Microanalyses were undertaken by the University of Strathclyde microanalytical service. Solvents were dried prior to use, and all preparations were undertaken using standard Schlenk techniques under N_2. The precursors $[PtCl_2(Me_2S)_2]$[19] and $[PtMe_3I]$[20] were prepared by literature methods and the selenoethers and telluroethers were prepared as described previously.[21–24]

Preparations

Pt^{II} Compounds

$[PtMe_2([8]aneSe_2)]$: A 1.6 M solution of MeLi (0.2 mL, 0.32 mmol) in Et_2O was slowly added to an ice-cold suspension of $[PtCl_2(SMe_2)_2]$ (0.050 g, 0.128 mmol) in 20 cm^3 dry Et_2O. After 5 min a further 0.1 mL MeLi (1.6 M in Et_2O, 0.16 mmol) were added and the solution was warmed to room temperature. After ca. 10 min the yellow colour disappeared and a white precipitate formed. At this stage 10 mL of H_2O and 1 equiv. of [8]aneSe$_2$ (0.031 g, 0.128 mol) were added. The mixture was stirred for 2.5 h giving a beige precipitate which was filtered off and washed with Et_2O. The solid was then dissolved in CH_2Cl_2 (10 mL), filtered and the solvent was removed in vacuo. Yield 0.075 g, 64%. $C_8H_{18}PtSe_2$ (467.2): calcd. C 20.6, H 3.9; found C 21.3, H 4.2. Electrospray MS (MeCN): found 494, 453; calcd. for $[^{195}PtMe([8]ane^{80}Se_2)(MeCN)]^+$ *m*/*z* = 495, $[^{195}PtMe([8]ane^{80}Se_2)]^+$ 454. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.5 (s, $^2J_{PtH}$ = 82 Hz, 6 H, PtMe), 2.2 (m, 4 H, $CH_2CH_2CH_2$), 2.8 (m, 8 H, $SeCH_2$) ppm. $^{13}C\{^1H\}$ NMR (DMF/$[D_6]Me_2CO$, 298 K): δ = –7.6 ($^1J_{PtC}$ = 794 Hz, 2 C, PtMe), 24.0 (4 C, $SeCH_2$), 27.3 (2 C, $CH_2CH_2CH_2$) ppm. $^{77}Se\{^1H\}$ NMR (DMF/$[D_6]Me_2CO$, 298 K): δ = 140.8 ($^1J_{PtSe}$ = 323 Hz) ppm. ^{195}Pt NMR (CH_2Cl_2/$CDCl_3$, 298 K): δ = –4318 ppm.

$[PtMe_2([16]aneSe_4)]$: Method as above using [16]aneSe$_4$. Yellow solid. Yield 61%. $C_{14}H_{30}PtSe_4$ (709.3): calcd. C 23.7, H 4.3; found C 23.1, H 4.2. Electrospray MS (MeCN): found *m*/*z* = 695; calcd. for $[^{195}PtMe([16]ane^{80}Se_4)]^+$ *m*/*z* = 700. ^1H NMR (300 MHz, $[D_6]$-DMSO, 298 K): δ = 0.48 (s, $^2J_{PtH}$ = 81 Hz, 6 H, PtMe), 1.92 (m, 8 H, $CH_2CH_2CH_2$) 2.61 (t, 16 H, $SeCH_2$) ppm.

$[PtMe_2\{MeSe(CH_2)_2SeMe\}]$: Method as above using $MeSe(CH_2)_2SeMe$. Yellow solid. Yield 41%. $C_6H_{16}PtSe_2$ (441.2): calcd. C 16.3, H 3.7; found C 15.9, H 3.3. Electrospray MS (MeCN): found *m*/*z* = 468, 453, 426, 411; calcd. for $[^{195}PtMe\{Me^{80}Se(CH_2)_2{}^{80}SeMe\}(MeCN)]^+$ *m*/*z* = 469, $[^{195}Pt\{Me^{80}Se(CH_2)_2{}^{80}SeMe\}(MeCN)]^+$ 454, $[^{195}PtMe\{Me^{80}Se(CH_2)_2{}^{80}SeMe\}]^+$ 428, $[^{195}Pt\{Me^{80}Se(CH_2)_2{}^{80}SeMe\}]^+$ 413. ^1H NMR (400 MHz, $CDCl_3$, 273 K): δ = 0.72 (s, $^2J_{PtH}$ = 84 Hz, PtMe), 0.77 (s, $^2J_{PtH}$ = 85 Hz, PtMe), 2.16 (s, $^3J_{PtH}$ = 22 Hz, SeMe), 2.36 (s, $^3J_{PtH}$ = 21 Hz,

SeMe), 2.55–3.25 (m, 4 H, $SeCH_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K): δ = –12.8 ($^1J_{PtC}$ = 760 Hz, PtMe), –12.6 (J = 735 Hz, PtMe), 9.9, 11.1 (SeMe), 29.2, 29.5 ($SeCH_2$) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 223 K): δ = 247.9 (major form, $^1J_{PtSe}$ = 457 Hz), 250.1 (minor form, J = 438 Hz) ppm. ^{195}Pt NMR ($CDCl_3$, 223 K): δ = –4383 (major), –4395 (minor) ppm.

[$PtMe_2\{MeSe(CH_2)_3SeMe\}$]: Method as above using $MeSe(CH_2)_3SeMe$. Beige solid. Yield 64%. $C_7H_{18}PtSe_2$ (455.2): calcd. C 18.5, H 4.0; found C 18.6, H 4.2. Electrospray MS (MeCN): found m/z = 482, 466, 425; calcd. for $[^{195}PtMe\{Me^{80}Se(CH_2)_3{}^{80}SeMe\}(MeCN)]^+$ m/z = 483, $[^{195}Pt\{Me^{80}Se(CH_2)_3{}^{80}SeMe\}(MeCN)]^+$ 468, $[^{195}PtMe\{Me^{80}Se(CH_2)_3{}^{80}SeMe\}]^+$ 427. ^1H NMR (400 MHz, $CDCl_3$, 248 K): δ = 0.51 (s, $^2J_{PtH}$ = 84 Hz, PtMe), 0.55 (s, J = 84 Hz, PtMe), 2.20 (br., 2 H, $CH_2CH_2CH_2$), 2.31, 2.33 (s, 6 H, SeMe), 2.83, 2.99 (m, 4 H, $SeCH_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K): δ = –8.9 ($^1J_{PtC}$ = 749 Hz, PtMe), –8.7 (J = 748 Hz, PtMe), 10.5, 10.9 (SeMe), 26.0, 26.7, 27.6 (CH_2) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 223 K): δ = 114.0 ($^1J_{PtSe}$ = 427 Hz), 102.1 (J = 429 Hz) ppm. ^{195}Pt NMR ($CDCl_3$, 223 K): δ = –4247 (major), –4309 (minor) ppm.

[$PtMe_2\{o\text{-}C_6H_4(CH_2SeMe)_2\}$]: Method as above using o-$C_6H_4(CH_2SeMe)_2$. Yellow solid. Yield 56%. $C_{12}H_{20}PtSe_2$ (517.3): calcd. C 27.9, H 3.9; found C 28.6, H 3.7. Electrospray MS (MeCN): found m/z = 506; calcd. for $[^{195}PtMe\{o\text{-}C_6H_4(CH_2{}^{80}SeMe)_2\}]^+$ m/z = 504. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.34 (s, $^2J_{PtH}$ = 83 Hz, 6 H, PtMe), 2.3 (s, 6 H, SeMe), 4.3 (br., 4 H, $SeCH_2$), 7.0–7.2 (br. m, 4 H, o-C_6H_4) ppm; (213 K): δ = 0.23 (s, $^2J_{PtH} \approx$ 80 Hz, PtMe), 0.25 (s, $J \approx$ 80 Hz, PtMe), 1.89, 2.21, 2.44 (s, SeMe), 3.8–5.0 (m, $SeCH_2$), 6.9–7.3 (m, 4 H, o-C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = –8.6 ($^1J_{PtC}$ = 779 Hz, PtMe), 11.0 (SeMe), 29.8 ($SeCH_2$), 126.0–134.5 (o-C_6H_4) ppm; (193 K): δ = –8.8 ($^1J_{PtC}$ = 760 Hz, PtMe), –8.3 (PtMe, J = 751 Hz), –7.4 (J = 763 Hz, PtMe), 10.3, 11.1, 13.2 (SeMe), 27.8, 28.6, 31.3 ($SeCH_2$), 127.4–134.6 (o-C_6H_4) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 171.6 ($^1J_{PtSe}$ = 520 Hz) ppm; (193 K): δ = 169.1 (J = 526 Hz), 160.6 (J = 492 Hz), 155.9 (J = 438 Hz) ppm. ^{195}Pt NMR ($CDCl_3$, 298 K): δ = –4275; (193 K): δ = –4308, –4316 ppm.

Platinum(IV) Compounds

[$PtMe_3I([8]aneSe_2)$]: [$PtMe_3I$] (0.10 g, 0.27 mmol) was dissolved in $CHCl_3$ (10 mL). [8]$aneSe_2$ (0.068 g, 0.28 mmol) in $CHCl_3$ (10 mL) was added slowly. The pale yellow solution was refluxed for 7 h, then stirred at room temperature overnight. The solution was concentrated in vacuo to approximately 5 mL. Diethyl ether (10 mL) was added, producing a cream-coloured solid, which was collected by filtration, washed with diethyl ether and dried in vacuo. Yield 0.075 g, 45%. $C_9H_{21}IPtSe_2$ (609.2): calcd. C 17.7, H 3.4; found C 17.8, H 3.3. Electrospray MS (MeCN): found 494, 483, 453; calcd. for $[^{195}PtMe([8]ane^{80}Se_2)(MeCN)]^+$ 495, $[^{195}PtMe_3([8]ane^{80}Se_2)]^+$ 484, $[^{195}PtMe([8]ane^{80}Se_2)]^+$ 454. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.0 (s, $^2J_{PtH}$ = 71.8 Hz, 3 H, PtMe *trans* I), 1.6 (s, J = 65.2 Hz, 6 H, PtMe *trans* Se), 2.1–3.4 (m, 12 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 3.5 ($^1J_{PtC}$ = 612 Hz, 1 C, PtMe *trans* I), 3.9 (J = 674 Hz, 2 C, PtMe *trans* Se), 20.8 (2 C), 21.4 (2 C, $SeCH_2$), 22.5 (1 C), 26.8 (1 C, CH_2CH_2) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 298 K): δ = 65 ($^1J_{PtSe}$ = 244 Hz) ppm. ^{195}Pt NMR ($CDCl_3$): δ = –3589 ppm.

[$PtMe_3I([16]aneSe_4)$]: Method as above, but using [16]$aneSe_4$. Cream solid. Yield 59%. $C_{15}H_{33}IPtSe_4.CHCl_3$ (970.6): calcd. C 19.8, H 3.5; found C 19.4, H 3.8. Electrospray MS (MeCN): found 724; calcd. for $[^{195}PtMe_3([16]ane^{80}Se_4)]^+$ 728. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.15 (s, $^2J_{PtH}$ = 71.6 Hz, 3 H, PtMe *trans* I), 1.55 (s, 6 H, PtMe *trans* Se, J = 66.5 Hz), 2.5–3.1 (m, 24 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 243 K): δ = 3.7 ($^1J_{PtC}$ = 619 Hz, 2 C, PtMe *trans* Se), 4.35 (1 C, PtMe *trans* I, 654 Hz), 22.1 (1 C), 22.7 (2 C, $SeCH_2$), 23.0 (2 C), 25.7 (2 C), 26.3 (2 C), 29.3 (2 C), 29.9 (1 C, CH_2) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 243 K): δ = 116.6 ($^1J_{PtSe}$ = 266 Hz, 1 Se), 119.5 (1 Se) ppm. ^{195}Pt NMR ($CDCl_3$, 243 K): δ = –3616 ppm.

[$PtMe_3([16]aneSe_4)]PF_6$: $TlPF_6$ (0.063 g, 0.18 mmol) was added to a solution of [$PtMe_3I$] (0.06 g, 0.163 mmol) and [16]$aneSe_4$ (0.079 g, 0.163 mmol) in $CHCl_3$ (8 mL). The reaction mixture was refluxed under N_2 for 2.5 h to give a fine yellow precipitate (TlI) and an almost colourless solution which was separated via cannula. After concentrating the solution in vacuo to ca. 2 mL, Et_2O was added to give a white solid which was collected by filtration, washed with Et_2O and dried in vacuo. Yield 0.049 g, 35%. $C_{15}H_{33}F_6PPtSe_4$ (869.3): calcd. C 20.7, H 3.8, found C 21.3, H 3.7. Electrospray MS (MeCN): found 725, 695; calcd. for $[^{195}PtMe_3([16]ane^{80}Se_4)]^+$ 728, $[^{195}PtMe([16]ane^{80}Se_4)]^+$ 698. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.06 (s, $^2J_{PtH}$ = 61 Hz, 3 H, PtMe), 1.13 (s, J = 66 Hz, 6 H, PtMe), 1.8–3.3 (br. m, 24 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CH_2Cl_2/$CDCl_3$, 298 K): very broad (223 K): δ = 2.4 ($^1J_{PtC}$ = 612 Hz, 1 C, PtMe), 3.0 (J = 647 Hz, 2 C, PtMe), 22.3–29.1 (CH_2) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 298 K): no spectrum; (223 K): δ = 138 (1 Se), 70 ($^1J_{PtSe}$ = 249 Hz, 3 Se) ppm. ^{195}Pt NMR (CH_2Cl_2/$CDCl_3$, 298 K): δ = –3648 ppm. IR (Nujol): $\tilde{\nu}$ = 840 [$\nu(PF_6^-)$], 557 [$\delta(PF_6^-)$] cm^{-1}.

[$PtMe_3I\{MeC(CH_2SeMe)_3\}$]: Method as for [$PtMe_3I([16]aneSe_4)$] above, but using $MeC(CH_2SeMe)_3$. Yellow solid. Yield 63%. $C_{11}H_{27}IPtSe_3$ (718.2): calcd. C 18.4, H 3.8, found C 18.7, H 3.5. Electrospray MS (MeCN): found m/z = 591, 561; calcd. for $[^{195}PtMe_3\{MeC(CH_2{}^{80}SeMe)_3\}]^+$ m/z = 594; $[^{195}PtMe\{MeC(CH_2{}^{80}SeMe)_3\}]^+$ 564. ^1H NMR (400 MHz, $CDCl_3$, 298 K): very broad (223 K): δ = 0.9–1.6 (overlapping resonances, PtMe, CMe), 2.0–3.7 (overlapping resonances, SeMe and $SeCH_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K): δ = 0.35–1.06 (s, PtMe *trans* I), 5.9–6.8 (s, PtMe *trans* Se), 7.8–12.4 (SeMe), 25.2–25.5 (MeC), 31.5–42.5 ($SeCH_2$) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 298 K): no spectrum; (223 K): δ = 53.0 ($^1J_{PtSe}$ = 252 Hz), 51.6 (J = 160 Hz), 49.3 (J = 258 Hz), 38.5 (J = 252 Hz), 37.4 (J = 162 Hz), 37.3 (J = 256 Hz), 35.1, 33.0, 29.0, 27.3 (uncoordinated Se) ppm. ^{195}Pt NMR ($CDCl_3$, 223 K): δ = –3446, –3543, –3550 ppm.

[$PtMe_3I\{o\text{-}C_6H_4(CH_2SeMe)_2\}$]: Method as above, but using o-$C_6H_4(CH_2SeMe)_2$. Cream solid. Yield 75%. $C_{13}H_{23}IPtSe_2{\cdot}1/2Et_2O$ (696.3): calcd. C 25.9, H 4.0, found C 26.3, H 3.8. Electrospray MS (MeCN): found 533; calcd. for $[^{195}PtMe_3\{o\text{-}C_6H_4(CH_2{}^{80}SeMe)_2\}]^+$ 534. ^1H NMR (400 MHz, $CDCl_3$, 298 K): broad (223 K): δ = 0.90 (s, $^2J_{PtH}$ = 79 Hz, PtMe), 1.12 (s, J = 70 Hz, PtMe), 1.20 (s, J = 70 Hz, PtMe), 1.22 (s, J = 70 Hz, PtMe), 1.36 (s, J = 68 Hz, PtMe), 2.3 (sh), 2.55, 2.6 (sh, 6 H, SeMe), 3.9–5.2 (m, 4 H, CH_2), 7.05–7.45 (m, 4 H, o-C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): broad (213 K): δ = 1.8 ($^1J_{PtC}$ = 628 Hz, PtMe), 2.6 (J = 622 Hz, PtMe), 5.2 (J = 616 Hz, PtMe), 5.85 (J = 624 Hz, PtMe), 6.2 (J = 660 Hz, PtMe), 13.7, 14.5, 14.69, 14.72 (SeMe), 27.7, 28.6, 34.3 (sh), 34.6 ($SeCH_2$), 126.8–139.9 (o-C_6H_4) ppm. $^{77}Se\{^1H\}$ NMR ($CDCl_3$, 298 K): not observed; (213 K): δ = 114.0 ($^1J_{PtSe}$ = 289 Hz) ppm; 98.7 (J = 280 Hz), 97.8 (J = 312 Hz), 95.5 (J = 286 Hz) (minor isomer) ppm. ^{195}Pt NMR ($CDCl_3$, 298 K): not observed; (213 K): δ = –3382, –3468 (the minor isomer is not observed) ppm.

[$PtMe_3I\{o\text{-}C_6H_4(CH_2TeMe)_2\}$]: Method as above, but using o-$C_6H_4(CH_2TeMe)_2$. Orange solid. Yield 60%. $C_{13}H_{23}IPtTe_2{\cdot}1/2Et_2O$ (793.6): calcd. C 22.7, H 3.6, found C 23.1, H 3.5. Electrospray MS (MeCN): found 629; calcd. for $[^{195}PtMe_3\{o\text{-}C_6H_4(CH_2{}^{130}TeMe)_2\}]^+$

634. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): broad (248 K): δ = 0.85–1.6 (s, PtMe), 2.1–3.1 (s, TeMe), 3.9–5.0 (m, 4 H, CH_2), 6.9–8.1 (m, 4 H, *o*-C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): broad (243 K): δ = –12.45, –12.4, –6.7, –5.7 (TeMe), 1.8 ($^1J_{PtC}$ = 638 Hz, PtMe), 2.9 (J = 635 Hz, PtMe), 3.9 (J = 687 Hz, PtMe), 4.3 (J = 607 Hz, PtMe), 7.3 (J = 592 Hz, PtMe), 10.4, 12.4, 16.7, 16.9 ($TeCH_2$), 126.5–135.3 (*o*-C_6H_4) ppm. $^{125}Te\{^1H\}$ NMR ($CDCl_3$, 243 K): δ = 189.5 ($^1J_{PtTe}$ = 602 Hz) ppm; 159.9 (J = 618 Hz), 114.5 (J = 638 Hz), 110.8 (J = 537 Hz) ppm. ^{195}Pt NMR ($CDCl_3$, 298 K): not observed; (223 K): δ = –3968, –4022, –4119 ppm.

[($PtMe_3I)_2$(MeTeCH_2TeMe)]: Method as above, but using 0.5 mol. equivs. of MeTeCH_2TeMe. Orange solid. Yield 68%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): broad (248 K): δ = 1.06 (s, $^2J_{PtH}$ = 76 Hz, PtMe), 1.14 (s, J = 72 Hz, PtMe), 1.16 (s, J = 74 Hz, PtMe), 1.22 (s, J = 76 Hz, PtMe), 2.06 (s, J = 68 Hz, PtMe), 2.07 (s, J = 68 Hz, PtMe), 2.01, 2.18 (s, TeMe), 4.46, 4.55 (m, $TeCH_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): broad (243 K): δ = –18.7 (major form, $TeCH_2$) –16.1 (minor form, $TeCH_2$), –8.5 (major form, TeMe), –7.95 (minor form, TeMe), 6.55 ($^1J_{PtC}$ = 670 Hz, PtMe), 7.0 (J = 678 Hz, PtMe), 7.7 (J = 600 Hz, PtMe), 7.8 (J = 660 Hz, PtMe), 9.1 (J = 607 Hz, PtMe) ppm. $^{125}Te\{^1H\}$ NMR ($CDCl_3$, 243 K): δ = 173.2 ($^1J_{PtTe}$ = 713 Hz) ppm. 171.1 (J = 605 Hz) ppm. ^{195}Pt NMR ($CDCl_3$, 223 K): δ = –3430 (major), –3451 (minor) ppm.

X-ray Crystallography: Selected bond lengths and angles for this species are presented in Table 2. Details of the crystallographic data collection and refinement parameters are given in Table 3. Yellow/orange single crystals of [$PtMe_3I${*o*-$C_6H_4(CH_2SeMe)_2$}] were obtained by diffusion of hexane into a solution of the complex in CH_2Cl_2. Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with graphite-monochromated Mo-K_α X-radiation (λ = 0.71073 Å). Structure solution and refinement were routine.[25,26]

CCDC-609594 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Selected bond lengths [Å] and angles [°] for [$PtMe_3I${*o*-$C_6H_4(CH_2SeMe)_2$}].

C1–Pt1	2.085(4)
C2–Pt1	2.080(3)
C3–Pt1	2.114(4)
Se1–Pt1	2.5530(4)
Se2–Pt1	2.5629(4)
I1–Pt1	2.7663(3)
C2–Pt1–C1	84.28(15)
C2–Pt1–C3	87.39(15)
C1–Pt1–C3	88.25(16)
C2–Pt1–Se1	172.68(11)
C1–Pt1–Se1	95.03(11)
C3–Pt1–Se1	85.30(10)
C2–Pt1–Se2	88.97(11)
C1–Pt1–Se2	89.06(11)
C3–Pt1–Se2	175.67(11)
Se1–Pt1–Se2	98.317(12)
C2–Pt1–I1	94.58(11)
C1–Pt1–I1	177.53(11)
C3–Pt1–I1	89.51(12)
Se1–Pt1–I1	85.815(11)
Se2–Pt1–I1	93.116(10)

Table 3. Crystallographic parameters.[a]

Complex	[$PtMe_3I${*o*-$C_6H_4(CH_2SeMe)_2$}]
Empirical formula	$C_{13}H_{23}IPtSe_2$
M	659.22
Crystal system	monoclinic
Space group	C2/*c*
a [Å]	13.3002(7)
b [Å]	11.6116(7)
c [Å]	22.5391(12)
α [°]	90
β [°]	102.788(2)
γ [°]	90
V [Å] ^{3}	3394.5(3)
Z	8
μ(Mo-K_α) [mm^{-1}]	14.356
R_{int}	0.0224
Total no. reflections	10840
Unique reflections	3861
No. of parameters	159
R_1 [$I_o > 2\sigma(I_o)$]	0.0196
R_1 [all data]	0.0215
wR_2 [$I_o > 2\sigma(I_o)$]	0.0443
wR_2 [all data]	0.0451

[a] $R_1 = \Sigma||F_o|-|F_c||_i/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_{oi}^4]^{1/2}$.

Acknowledgments

We thank the EPSRC for support (J. M. M.) and Johnson Matthey plc for generous loans of platinum salts. We also thank Dr N. Tsoureas for the crystallographic data analysis.

[1] a) E. G. Hope, W. Levason, *Coord. Chem. Rev.* **1993**, *122*, 109–170; b) W. Levason, S. D. Orchard, G. Reid, *Coord. Chem. Rev.* **2002**, *225*, 159–199; c) A. K. Singh, S. Sharma, *Coord. Chem. Rev.* **2000**, *209*, 49–98.
[2] W. Levason, G. Reid, in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, **2003**, vol. 1, 391–398 and 399–410.
[3] a) W. Levason, S. D. Orchard, G. Reid, *Chem. Commun.* **1999**, 1071–1072; b) S. D. Orchard, W. Levason, G. Reid, *Inorg. Chem.* **2000**, *39*, 3853–3859.
[4] W. Levason, S. D. Orchard, G. Reid, J. M. Street, *J. Chem. Soc., Dalton Trans.* **2000**, 2537–2543.
[5] E. W. Abel, D. G. Evans, J. R. Koe, M. B. Hursthouse, M. Mazid, *J. Chem. Soc., Dalton Trans.* **1992**, 663–667.
[6] a) E. W. Abel, K. G. Orrell, S. P. Scanlon, D. Stephenson, T. Kemmitt, W. Levason, *J. Chem. Soc., Dalton Trans.* **1991**, 591–595; b) H. B. Singh, A. V. Regina, J. P. Jasinski, E. S. Paight, R. J. Butcher, *J. Organomet. Chem.* **1994**, *466*, 283–289.
[7] a) E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, V. Sik, *J. Chem. Soc., Dalton Trans.* **1980**, 1169–1174; b) E. W. Abel, K. G. Orrell, A. W. G. Platt, *J. Chem. Soc., Dalton Trans.* **1983**, 2345–2351.
[8] a) K. G. Orrell, *Coord. Chem. Rev.* **1989**, *96*, 1–48; b) E. W. Abel, K. G. Orrell, *Prog. Inorg. Chem.* **1984**, *32*, 1–118.
[9] E. W. Abel, D. G. Evans, J. R. Koe, M. B. Hursthouse, M. Mazid, *J. Chem. Soc., Dalton Trans.* **1992**, 663–667.
[10] E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Sik, B. L. Williams, *Polyhedron* **1982**, *1*, 289–298.
[11] a) W. Levason, M. L. Matthews, G. Reid, M. Webster, *Dalton Trans.* **2004**, 51–58; b) W. Levason, M. L. Matthews, G. Reid, M. Webster, *Dalton Trans.* **2004**, 554–561.
[12] M. D. Brown, W. Levason, G. Reid, M. Webster, *Dalton Trans.* **2006**, 1667–1674.
[13] P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, P. Dierkes, *Chem. Rev.* **2000**, *100*, 2741–2770.

[14] N. R. Champness, W. Levason, J. J. Quirk, G. Reid, C. S. Frampton, *Polyhedron* **1995**, *14*, 2753–2758.
[15] E. W. Abel, P. D. Beer, I. Moss, K. G. Orrell, V. Sik, P. A. Bates, M. B. Hursthouse, *J. Organomet. Chem.* **1988**, *341*, 559–567.
[16] M. K. Davies, M. C. Durrant, W. Levason, G. Reid, R. L. Richards, *J. Chem. Soc., Dalton Trans.* **1999**, 1077–1083.
[17] W. Levason, J. J. Quirk, G. Reid, C. S. Frampton, *Inorg. Chem.* **1994**, *33*, 6120–6122.
[18] P. P. Brown, R. J. Puddephatt, C. E. E. Upton, *J. Chem. Soc., Dalton Trans.* **1974**, 2457–2465.
[19] G. S. Hill, M. J. Irwin, C. J. Levy, L. M. Rendina, R. J. Puddephatt, *Inorg. Synth.* **1998**, *32*, 149–153.
[20] J. C. Baldwin, W. C. Kaska, *Inorg. Chem.* **1975**, *14*, 2020.
[21] R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. D. Johnston, B. M. Pinto, *J. Am. Chem. Soc.* **1989**, *111*, 6582–6591.
[22] T. Kemmitt, E. G. Hope, W. Levason, *Organometallics* **1988**, *7*, 78–83.
[23] D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray, D. M. Potter, G. L. Marshall, *J. Chem. Soc., Perkin Trans. 2* **1984**, 429–434.
[24] W. Levason, B. Patel, G. Reid, A. J. Ward, *J. Organomet. Chem.* **2001**, *619*, 218–225.
[25] G. M. Sheldrick, SHELXS-97, program for crystal structure solution, University of Göttingen, Germany, **1997**.
[26] G. M. Sheldrick, SHELXL-97, program for crystal structure refinement, University of Göttingen, Germany, **1997**.

Received: May 31, 2006
Published Online: September 5, 2006

