Multinuclear Nuclear Magnetic Resonance Studies of Trimethylplatinum(IV) Complexes with Organochalcogen Ligands

Edward W. Abel, Keith G. Orrell,* and Andrew W. G. Platt
Department of Chemistry, University of Exeter, Exeter EX4 4QD

New preparative procedures have been developed for the formation of the platinum(IV) complexes [$PtXMe_3\{MeE(CH_2)_nE'Me\}$] (X = Cl, Br, or I; n = 2 or 3; E,E' = S or Se), and ^{195}Pt, ^{77}Se, and ^{13}C n.m.r. data obtained. Deductions on the relative stabilities of the complexes with varying ring size and chalcogen have been made on the basis of the values of $^1J(PtC)$ and $^1J(PtSe)$. These deductions are supported by chemical evidence. Correlations exist between ^{195}Pt chemical shifts and the strength of the Pt–Se bond, with weaker bonds leading to greater deshielding at the Pt nucleus.

We have recently[1-3] examined the stereochemical non-rigidity of platinum(IV) complexes of general type [$PtXMe_3\{MeE(CH_2)_nE'Me\}$] (X = Cl, Br, or I; n = 2 or 3; E,E' = S or Se). Variable-temperature ^1H n.m.r.[2,3] enabled the energy barriers of a variety of fluxional processes to be deduced. However, these complexes are rich in other magnetic nuclei apart from ^1H and we now report extensive ^{195}Pt, ^{77}Se, and ^{13}C chemical shift and coupling constant data which characterise the low temperature ' static ' structures of these complexes.

Experimental

Materials.—Ligands were prepared as described previously,[1] the sample of $MeSe(CH_2)_2SMe$ being kindly donated by Dr. B. L. Williams. The complexes were prepared as previously reported,[1-3] but in view of the considerable amounts of complex required for ^{13}C and ^{77}Se studies, ligand- and halide-exchange reactions were developed for interconverting complexes and thus minimising the quantities of starting materials required. The reactions were initially monitored on a small scale by ^1H n.m.r. and if successful adopted on a preparative scale.

It was found that five-membered ring complexes are preferentially formed over six-membered ring complexes irrespective of the nature of the chalcogen [equation (1); E^1,E^2 = S or Se]. These reactions were rapid at room temperature, the required a few hours reflux, whereas displacement of bromide by chloride necessitated refluxes of up to 12 h.

$$[PtXMe_3\{MeE^1(CH_2)_3E^1Me\}] + MeE^2(CH_2)_2E^2Me \xrightarrow{CHCl_3} [PtXMe_3\{MeE^2(CH_2)_2E^2Me\}] + MeE^1(CH_2)_3E^1Me \quad (1)$$

equilibrium being well to the right, even in the presence of excess $MeE^1(CH_2)_3E^1Me$.

For a given ring size it was invariably found that selenium ligands displace their sulphur counterparts from the complexes [equation (2)]. Similarly, dinuclear complexes of type [$(PtXMe_3)_2\{MeE^1(CH_2)_nE^1Me\}$] ($n$ = 0 or 1)[4] were smoothly converted into the mononuclear species in the presence of the appropriate ligand.

$$[PtXMe_3\{MeS(CH_2)_nSMe\}] + MeSe(CH_2)_nSeMe \xrightarrow{CHCl_3} [PtXMe_3\{MeSe(CH_2)_nSeMe\}] + MeS(CH_2)_nSMe \quad (2)$$

Halogen interchange was readily achieved by refluxing the mononuclear complex with the appropriate silver halide [equation (3); E^1 = S or Se; n = 2 or 3; X = I, X' = Br or Cl; X = Br, X' = Cl]. The replacement of iodide normally

$$[PtXMe_3\{MeE^1(CH_2)_nE^1Me\}] + AgX' \xrightarrow[CHCl_3]{reflux} [PtX'Me_3\{MeE^1(CH_2)_nE^1Me\}] + AgX \quad (3)$$

An illustrative example of a preparation involving these exchange reactions is outlined below. The complex [$PtIMe_3\{MeSe(CH_2)_3SeMe\}$] (1 g, 2 mmol) was dissolved in $CHCl_3$ (20 cm^3). AgBr (0.76 g, 4.05 mmol) and $MeSe(CH_2)_2SeMe$ (0.55 g, 2.55 mmol) were then added. The reaction vessel was protected from direct light and the solution stirred under reflux for 10 h. Filtration of the solution, extraction of the silver residues with boiling $CHCl_3$ (4 × 5 cm^3), reduction of the combined extracts and filtration to *ca.* 5 cm^3, cooling to 0 °C, and addition of light petroleum (b.p. 60—80 °C) gave a yellow-white precipitate. This was filtered off, washed with light petroleum and dried at the pump to give [$PtBrMe_3\{MeSe(CH_2)_2SeMe\}$] (0.88 g, 82.6%).

Spectra.—Selenium-77 and ^{13}C n.m.r. spectra were obtained at 19.1 and 25.1 MHz respectively on a JEOL PS/PFT-100 spectrometer in this Department using an internal deuterium lock. Temperature control was as previously described.[1] Platinum-195 spectra were obtained at 19.3 MHz on a JEOL FX 90Q spectrometer at the City of London Polytechnic. All spectra were obtained under proton broad-band decoupling conditions. $CDCl_3$ was used as the solvent throughout.

Results and Discussion

Spin–Spin Coupling Constants.—One- and two-bond couplings between platinum-195 and nuclei in the group Y in the moiety L–Pt–Y have been extensively used for measuring the relative strength of the Pt–Y and Pt–L bonds. Variations in $J(PtY)$ values reflect different *trans* influences of the ligands, L.[5,6] Ligands with greater *trans* influences cause smaller $J(PtY)$ values corresponding to a decrease in Pt–Y bond strength and an increase in the Pt–L strength. Couplings of ^{195}Pt to ^1H,[5,7,8] ^{31}P,[9,10] and ^{13}C[11,12] have been reported previously in this context. In most studies to date it has been assumed that the coupling is dominated by the Fermi contact term and expressed by equation (4),[10] where γ_{Pt} and γ_Y are

$$J(PtY) \propto \gamma_{Pt}\gamma_Y(\Delta E)^{-1}\alpha_{Pt}^2\alpha_Y^2|\psi_{Pt(6s)}(0)|^2|\psi_{Y(ns)}(0)|^2 \quad (4)$$

gyromagnetic ratios, ΔE is an average singlet–triplet excitation energy, α_{Pt}^2 and α_Y^2 are respectively the *s* characters of the Pt atom and the hybrid used by Y in the Pt–Y bond, and the $|\psi(0)|^2$ terms are electron densities of the indicated orbital at the parent nucleus.

(*i*) *Dependence of* $^1J(CPt)$ *on the* trans *ligand.* These one-bond J values are collected in Tables 1 and 2. The labelling in these tables refers to that given in Figure 1, where the three distinct

Table 1. Methyl ^{13}C shifts [a] (δ/p.p.m.) and $^{13}C-^{195}Pt$ coupling constants [a] (^nJ/Hz) for $[PtXMe_3\{MeE(CH_2)_nEMe\}]$

			[*meso*-1]							[*meso*-2]						
E	n	X	p[b]	δ^1	^1J	δ^2	^1J	δ^3	^2J	p[b]	δ^1	^1J	δ^2	^1J	δ^3	^2J
Se	2	Cl	38.8	−4.7	699.4	0.4	628.7	8.1	6.1	6.5	−5.3	—	0.4	615.2	4.7	—
Se	2	Br	25.7	−1.2	696.8	0.0	629.0	10.7	6.8	11.3	−0.9	693.8	−0.4	620.1	5.9	3.4
Se	2	I	13.0[c]	5.5	654.4	−1.5	621.8	—	—	23.0	5.3	667.5	−2.6	614.2	6.0	4.5
Se	3	Cl	39.0	−4.9	679.7	3.9	631.8	8.4	—	4.0	—	—	—	—	—	—
Se	3	Br	35.0	−0.1	671.9	2.3	635.8	9.5	—	7.0	—	—	—	—	—	—
Se	3	I	32.0[c]	6.9	653.3	0.7	629.9	11.1	—	6.3	—	—	—	—	—	—
S	2	Br	45.0	0.6	674.8	−0.6	632.8	18.2	5.9	7.0	—	—	—	—	14.4	—
S	2	I	29.5	7.6	664.9	−1.9	624.1	22.0	—	10.0	—	—	—	—	14.0	—
S	3	I	51.5	8.2	668.9	0.1	629.9	18.0	—	~0	—	—	—	—	—	—

			[DL-1/2]											
E	n	X	p[b]	δ^1	^1J	δ^2	^1J	δ^3	^1J	δ^4	^2J	δ^5	^2J
Se	2	Cl	54.8	−5.9	700.6	0.6	637.8	0.6	618.6	8.6	5.4	4.4	3.9
Se	2	Br	63.0	−1.4	690.4	−0.3	622.6	−0.2	621.1	10.4	6.8	4.7	4.4
Se	2	I	64.0	5.0	669.1	−1.9	615.6	−2.1	614.2	14.9	9.3	4.9	5.9
Se	3	Cl	57.0	−5.6	695.3	3.2	642.6	2.9	640.6	8.5	—	4.7	—
Se	3	Br	58.0	−1.0	687.5	2.5	636.7	3.6	625.0	9.4	—	4.9	—
Se	3	I	61.4	5.8	666.0	0.8	625.0	2.5	616.2	11.3	—	5.0	—
S	2	Br	48.0	1.1	687.5	−0.5	634.0	−1.2	624.0	18.4	5.9	13.3	—
S	2	I	60.5	6.8	674.4	−2.6	616.5	−2.3	614.9	22.4	—	13.4	—
S	3	I	48.5	8.6	652.3	0.1	629.9	1.8	605.3	19.1	—	14.0	—

[a] Data at *ca.* −40 °C in $CDCl_3$. Shifts measured relative to $SiMe_4$. Missing data due to complexit7 of spectra, low invertomer population or, in the case of J values, to unresolved couplings (values probably <5 Hz). [b] Populations (p) from ref. 1. [c] From ^{195}Pt spectra.

Table 2. Methyl ^{13}C n.m.r. data [a] for $[PtIMe_3\{MeSe(CH_2)_nSMe\}]$

n	Isomer	p[b]	δ^1	^1J	δ^2[c]	^1J	δ^3[c]	^1J	δ^4	^2J	δ^5	^2J
2	[DL-1]	21.7	5.8	672.2	−1.0	615.7	−4.2	613.9	13.0	—	20.5	6.8
2	[DL-2]	19.3	5.8	670.9	—	—	−4.8	611.8	14.2	7.8	14.2	7.8
2	[DL-3]	14.0	6.0	681.6	—	—	−4.4	616.2	6.5	—	15.4	8.3
2	[DL-4]	45.0	6.0	671.4	−0.8	618.2	−4.3	615.2	5.3	6.0	22.0	8.8
3	[DL-1]	13[d]	—	—	—	—	—	—	—	—	—	—
3	[DL-2]	42	7.6	653.3	1.0	610.3	1.0	614.2	11.3	—	28.0	5.9
3	[DL-3]	~0	—	—	—	—	—	—	—	—	—	—
3	[DL-4]	45	6.9	664.1	1.9	631.8	−1.0	622.2	5.1	—	25.7	7.8

[a] Shifts/p.p.m. relative to $SiMe_4$. J/Hz values refer to $^{13}C-^{195}Pt$ interactions. All data measured at −40 °C. Missing data due to reasons given in footnote *a* of Table 1. [b] Populations (p) from ref. 1. [c] Assignments to C^2 and C^3 not certain. [d] From ^{195}Pt spectra.

invertomers of the homochalcogen complexes and the four distinct invertomers of the mixed S–Se complexes are depicted.

In all cases it was found that the coupling of ^{195}Pt to the carbon *trans* to halide was significantly greater than its coupling to the carbons *trans* to chalcogen. This is consistent with the relative *trans* influences of chalcogens and halides and implies a stronger Pt–C bond *trans* to halide. Data on closely related compounds are consistent with this conclusion. For example, in $[PtIMe_3\{Me_2AsC_6H_4AsMe_2\}]$ the Pt–C bond *trans* to halide is shorter than those bonds *trans* to arsenic,[13] while in $[PtIMe_3(AsMe_3)_2]$ ^1J(PtC) (*trans* I) is 623 Hz compared to ^1J(PtC) (*trans* As) of 556 Hz.[14]

The dependence of ^1J(CPt) on the nature of the halogen follows the trend expected from the *trans* influence series [5] with ^1J (*trans* Cl) $\geqslant$ ^1J (*trans* Br) > ^1J(*trans* I). Similarly, the reduction of ^1J which occurs in most cases on changing the *trans* chalcogen from S to Se is consistent with their relative *trans* influences and agrees well with the observation that the selenium ligands will displace their sulphur counterparts from complexes, indicating stronger Pt–Se compared to Pt–S bonds. Similar trends in ^2J(PtCH) values are evident in the ^1H spectra [1–3] but are not as clearly defined.

(*ii*) *Dependence of* ^1J(PtC) *on ring size.* It will be seen from Tables 1 and 2 that on increasing the complex ring size from five to six ^1J(PtC) (*trans* halide) almost invariably decreases, implying a weakening of the Pt–C bond. The opposite trend, albeit somewhat less pronounced, was usually observed for ^1J(PtC) (*trans* chalcogen) where a strengthening of the Pt–C bond and corresponding weakening of the Pt–E bonds were indicated. This supports the observed greater stability of the five- as opposed to the six-membered ring complexes (see Experimental section). The trends in the ^2J(PtCH) values [1] however run counter to this conclusion and are not as easily rationalised. Although linear correlations between ^1J(PtC) and ^2J(PtCH) values have been observed in platinum(II)–methyl complexes,[12] there is however no strong theoretical reason for such a correlation to exist, particularly since it has been established [15,16] that these one-bond and two-bond couplings are of opposite sign.

(*iii*) *Dependence of* ^1J(PtC) *on invertomer.* Whilst the magnitudes of ^1J(PtC) (*trans* X) show no clear-cut dependence on invertomer, values of ^1J(PtC) (*trans* E) were invariably somewhat greater in [*meso*-1] than [*meso*-2], implying stronger Pt–C and weaker Pt–E bonds in the former species. In the [DL-1/2] species the two magnitudes of ^1J(PtC) were used to assign the two Pt–Me (*trans* E) carbon resonances. For the mixed-

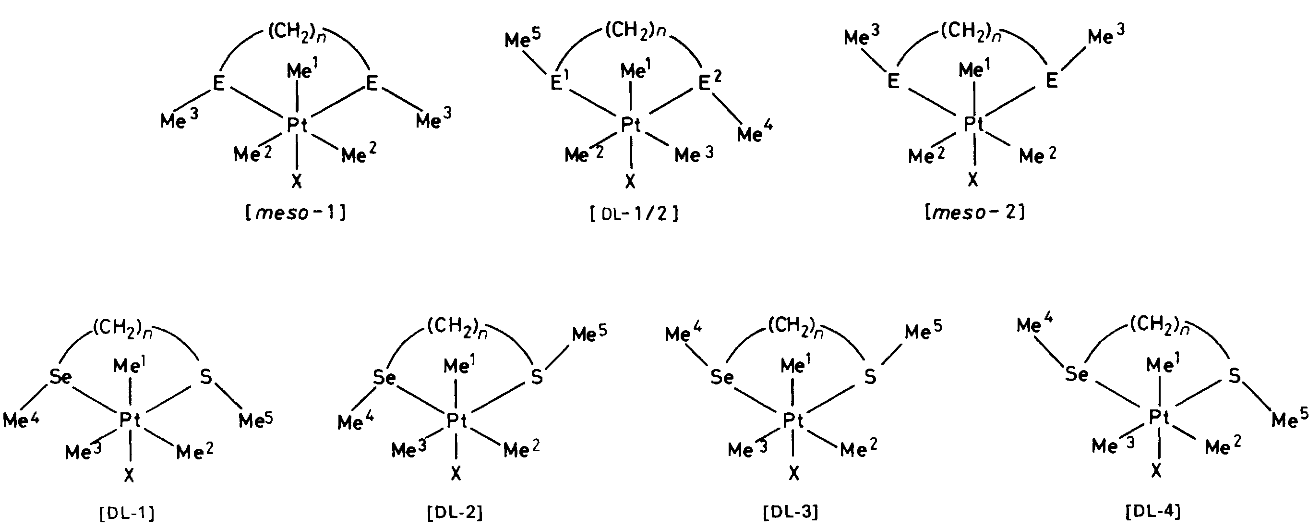


Figure 1. Chemically distinct invertomers of the homo- and hetero-chalcogen complexes [$PtXMe_3\{MeE(CH_2)_nE'Me\}$] (X = Cl, Br, or I; n = 2 or 3; E,E′ = S or Se)

Table 3. Platinum-195 and ^{77}Se n.m.r. data for [$PtXMe_3\{MeE(CH_2)_nEMe\}$]

			[*meso*-1]				[DL-1/2]						[*meso*-2]			
E	n	X	p [a]	δ_{Pt} [b]	δ_{Se} [c]	^1J [d]	p [a]	δ_{Pt} [b]	δ_{Se^1} [c]	^1J [d]	δ_{Se^2} [c]	^1J [d]	p [a]	δ_{Pt} [b]	δ_{Se} [c]	^1J [d]
Se	2	Cl	38.8	1 257.4	197.0 [e]	290.5	54.8	1 237.1	194.1	316.4	192.7	235.4	6.5	1 205.4	187.6	224.1
Se	2	Br	25.7	1 125.3	188.3	306.4	63.0	1 083.2	191.4	329.6	188.0	255.1	11.3	1 033.3	184.5	247.8
Se	2	I	13.0	934.9	177.8	321.4	64.0	865.3	181.2	343.9	181.7	263.7	23.0	795.3	178.1	255.1
Se	3	Cl	39.0	1 370.8	74.1 [f]	244.6	57.0	1 366.0	73.6	250.0	72.4	206.1	4.0	—	—	—
Se	3	Br	35.0	1 259.3	67.5	252.0	58.0	1 230.1	66.2	250.5	67.6	223.6	7.0	1 147.9	65.2	—
Se	3	I	32.0	1 063.9	55.2	260.3	61.4	992.0	52.0	252.9	58.4	240.2	6.7	—	—	—
S	2	I	29.5	1 090.0	—	—	60.5	1 025.3	—	—	—	—	10.0	957.4	—	—
S	3	I	51.5	1 213.8	—	—	48.5	1 108.0	—	—	—	—	~0	—	—	—

[a] Populations (p) from ref. 1. [b] ^{195}Pt shifts/p.p.m. (30 °C) to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz. [c] ^{77}Se shifts/p.p.m. (0 °C) to high frequency of $SeMe_2$. [d] $^1J(PtSe)$/Hz values. [e] δ_{Se}(free ligand) = 125.6 p.p.m. [f] δ_{Se}(free ligand) = 78.3 p.p.m.

chalcogen ligand complexes such assignments were more difficult, and the data given in Table 2 must be interpreted in that light.

(*iv*) $^2J(PtC)$ *values*. These data should normally reflect changes in the Pt–E bond lengths/strengths and thus trends in $^2J(PtC)$ should be the reverse of those observed for $^1J(PtC)$ (*trans* E). From the small amount of data available it appears that this is indeed generally the case for variation with ligand ring size and chalcogen, but not for the dependence on invertomer type. However, the magnitudes of these two-bond couplings are expected to be influenced by non-bonded electron interactions in a similar way to $^1J(PtSe)$ data (see below), and therefore will not directly reflect the relative strength of the Pt–E bonds.

(*v*) ^{195}Pt–^{77}Se *data. Dependence of* $^1J(PtSe)$ *on halogen.* The ^{195}Pt and, where appropriate, ^{77}Se data, are collected in Tables 3 and 4. The $^1J(PtSe)$ values have been measured previously for a number of Pt^{II} complexes [17–19] and some Pt^{IV} complexes [18] with values ranging from *ca.* 700 Hz to *ca.* −100 Hz. In the present Pt^{IV} complexes values were in the range 340—200 Hz with the signs being undetermined but almost certainly positive. The magnitude of $^1J(PtSe)$ was seen to increase with halogen such that Cl < Br < I. This trend was the same as that observed for $^2J(PtH)$ for the methyl *trans* to nitrogen in [$PtXMe_3L_2$] [5] [where L_2 = (pyridine)$_2$ or bidentate pyridine-type ligands] but opposite to the trends observed in $^1J(PtP)$ [10] and $^1J(PtC)$ [12] for Pt^{II} complexes, and in $^1J(PtSe)$ in the Pt^{IV} species [$PtX_5(SeMe_2)$]$^-$.[18] In the latter species, a very strong halogen dependence, arising from the high halogen content of these complexes, is explained in terms of the variations in hybridisation of the Pt and the *s*-orbital bond order of the metal–ligand bond.[16] The contrary trend in the $^1J(PtSe)$ values in the present Pt^{IV} complexes implies that in this case the α_{Pt}^2 and α_E^2 terms [in equation (4)] do not dominate the coupling and that changes in the average excitation energy of the electrons associated with the Pt–Se bond are equally important.

Table 4. Platinum-195 and ^{77}Se n.m.r. data [a] for [$PtIMe_3\{MeSe(CH_2)_nSMe\}$]

n	Isomer	p [b]	δ_{Pt}	δ_{Se}	$^1J(PtSe)$	δ_{Se}(free ligand)
2	[DL-1]	21.7	1 024.9	168.4	317.4	107.3
2	[DL-2]	19.3	962.1	164.4	332.5	
2	[DL-3]	14.0	891.4	164.8	239.0	
2	[DL-4]	45.0	954.2	165.1	246.1	
3	[DL-1]	42 [c]	1 128.2	—	244.3	74.6
3	[DL-2]	13	1 050.6	—	239.2	
3	[DL-3]	~0	—	—	—	
3	[DL-4]	45	1 036.9	—	224.6	

[a] Data measured at −40 °C. See Table 3 footnotes for further details. [b] Populations from ref. 2. [c] Population from ^{195}Pt spectrum.

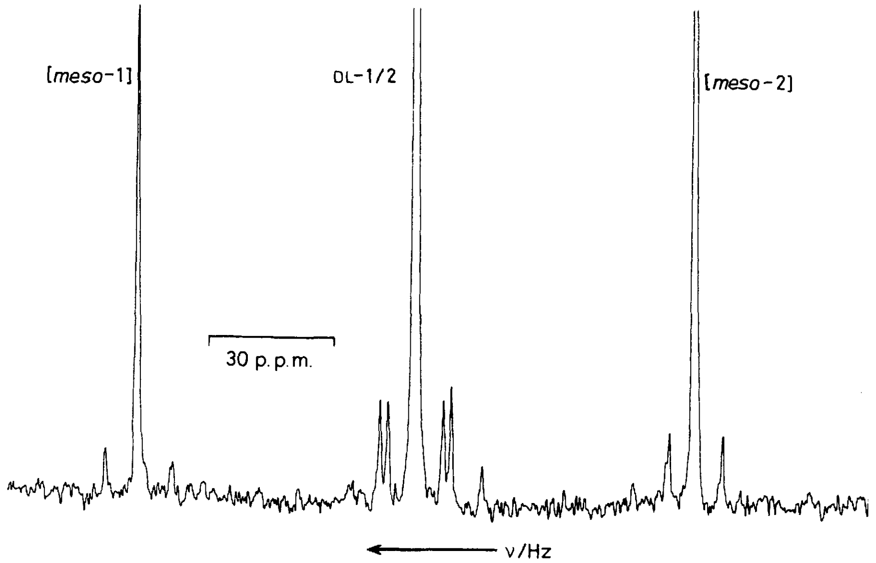


Figure 2. 19.3-MHz ^{195}Pt spectrum of [PtIMe$_3${MeSe(CH$_2$)$_2$SeMe}] at room temperature (5 000 transients), showing the three distinct invertomers

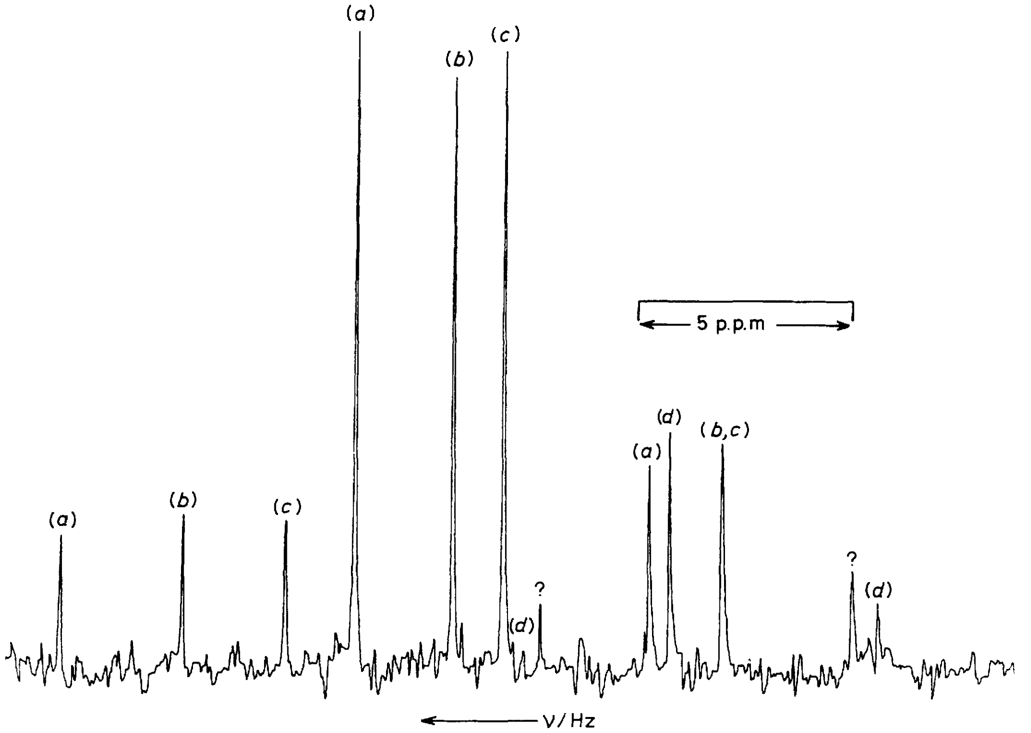


Figure 3. 19.1-MHz ^{77}Se spectrum of [PtClMe$_3${MeSe(CH$_2$)$_2$SeMe}] at -16 °C (1 126 transients). The signals (+ ^{195}Pt satellites) labelled (*a*)—(*d*) refer to the invertomers [*meso*-1] (*a*), [DL-1/2] (*b*, *c*), and [*meso*-2] (*d*)

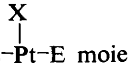
(*vi*) *Dependence of* ^1J(PtSe) *on ring size.* A considerable reduction in these values with expansion of the ligand ring is observed in Tables 3 and 4. This accords well with the corresponding increase in ^1J(PtC) (*trans* E) values and the preferred stability of the five-membered rings.

(*vii*) *Dependence of* ^1J(PtSe) *on invertomer.* The large differences in ^1J(PtSe) values within each invertomer mixture reflect the highly sensitive dependence of this coupling on the orientation of the Se methyls. The ^{195}Pt spectrum of [PtIMe$_3${MeSe(CH$_2$)$_2$SeMe}] (Figure 2) and the ^{77}Se spectrum of [PtClMe$_3${MeSe(CH$_2$)$_2$SeMe}] (Figure 3) illustrate this clearly. In the former case the DL-1/2 invertomer signal is unambiguously assigned by its *two* pairs of ^{77}Se satellite signals, whilst in the ^{77}Se spectrum the DL-1/2 species produce *two* distinct resonances. If the usual correlation between bond strengths and coupling constants is assumed, the data imply that the Pt–Se bonds in the *meso*-1 species were stronger than those in *meso*-2, which is contrary to the conclusions from the ^1J(PtC) data. However, we believe that the ^1J(PtC) data are a more reliable indicator of invertomer characteristics, since the

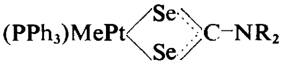
^1J(PtSe) couplings are likely to be very sensitive to non-bonded electron–electron interactions, associated with the stereochemical orientation of the Se methyl groups. Similar stereochemical effects are known profoundly to influence ^1J(PP),[20] ^1J(CH),[21] and ^2J(NH) [21,22] values. Such stereochemical factors may affect a lone pair of electrons formally situated on either of the two coupled atoms or formally situated on a third atom.[21] In the present complexes it will be the stereochemical influence of the Se lone pair which is affecting the ^1J(PtSe) values. However, in the absence of detailed structural data on individual invertomers, further interpretation is precluded.

(*viii*) *Summary of coupling constant data*. The above discussion in (*i*)—(*vii*) illustrates the value of ^1J and ^2J data as qualitative probes for elucidating structures in closely related compounds. Carbon-13 measurements are particularly informative and, in cases where the bond *trans* to the ^{13}C in question contains a nucleus of spin $\frac{1}{2}$ (*i.e.* ^{77}Se), confirmatory structural evidence is available. Care must be exercised in interpreting the ^{77}Se data due to the sensitivity of ^1J(PtSe) values to stereochemical influences of the Se lone pair. Thus, valid structural inferences can only be made by comparing the same invertomers. The interpretations of the ^1J(PtC), ^2J(PtC), and ^1J(PtSe) data are supported in most cases by independent chemical evidence, although the conclusions can vary from those deduced from ^2J(PtH) measurements.[1-3]

Chemical Shifts.—(*i*) ^{13}C *shifts*. Correlations of ^{13}C methyl shifts have previously been made with the electronegativity and number of lone pairs on the substituent.[23] Changes in the shielding of substituents have been related to the magnetic anisotropy of directly bonded metals,[24,25] the abnormally low frequency methyl shifts in $[\mathrm{PtMe(AsMe_3)_2L}]^+\mathrm{PF_6}^-$ and $[\mathrm{PtMe(PMe_2Ph)_2L}]^+\mathrm{PF_6}^-$ being rationalised on this basis.[12] However, ^{13}C data for $[(\mathrm{PtXMe_3})_4]$ [26] and $[\mathrm{PtIMe_3(AsMe_3)_2}]$ [14] do not show unusually low shifts, nor do the present complexes.

The methyl carbon shift data (Tables 1 and 2) indicate that, in the majority of cases, the Pt methyl carbons are deshielded on ring expansion, whereas there is no clear trend in the chalcogen methyl data. The variation of the ligand methyl and Pt methyl (*trans* X) carbon shifts with chalcogen follows the expected pattern for dominance of the electronegativity of the  $\mathrm{E{-}}\overset{\overset{\displaystyle \mathrm{X}}{|}}{\mathrm{Pt}}\mathrm{{-}E}$ moiety, with δ(E = S) > δ(E = Se). Shifts for the Pt methyls (*trans* E) show the reverse trend. The expected dependence on electronegativity of the halogen is followed for Pt methyl (*trans* E) carbons with δ(Cl) > δ(Br) > δ(I), but again this trend is reversed for ligand methyl and Pt methyls (*trans* X).

No correlation exists between δ(^{13}C) and ^1J(PtC), and thus there is no apparent relationship between δ(^{13}C) and the strength of the Pt–C bond.

(*ii*) ^{77}Se *shifts*. Selenium-77 chemical shifts have been measured in a variety of compounds, selenophanes [27-29] and aromatic selenides [30-34] and diselenides [35-38] receiving particular attention. Co-ordination shifts can be appreciable. Selenium co-ordinated to $\mathrm{Pt^{II}}$ in  $(\mathrm{PPh_3})\mathrm{MePt}\left\langle\begin{smallmatrix}\mathrm{Se}\\ \mathrm{Se}\end{smallmatrix}\right\rangle\mathrm{C{-}NR_2}$ (I) shows low-frequency shifts of up to 200 p.p.m. relative to $\mathrm{Et_2NH_2Se_2CNR_2}$,[19] whereas ^{77}Se nuclei in *cis*- and *trans*-$[\mathrm{PtX_2(SeMe_2)_2}]$ show high-frequency shifts of *ca*. 130 p.p.m. with respect to the free ligand.[17,38] In general, it has been found that an increase in electronegativity of the substituent bound to Se causes deshielding, although where the electronegativities are similar other factors may dominate.[38]

From Table 3 it can be seen that a deshielding of 50—70 p.p.m. at Se with respect to the free-ligand shift results on the formation of a five-membered ring complex. However, a shielding of some 5—20 p.p.m. arises on the formation of six-membered rings. Arguments in terms of a higher degree of steric crowding in the six-membered ring complexes do not really explain the results, since it has previously been noted that bulky alkyl groups (R) in $[\mathrm{Pt(Se_2CNR_2)(PPh_3)Cl}]$ [19] and $\mathrm{R_2Se}$, $\mathrm{R_2Se_2}$, RSeH, and $\mathrm{RSe^-}$ [38] cause *deshielding* of Se nuclei. A more likely explanation may be in terms of the differing shielding anisotropies associated with the pseudo-planar five-membered rings and the non-planar chair conformation of the six-membered ring.[2] A single chair conformer is considered most likely to exist in these complexes and so the ring methylene groups could influence the shielding of the Se atom in a quite different way to the five-membered rings.

The dependence of δ(Se) values on invertomer is δ(*meso*-1) > δ(DL-1/2) > δ(*meso*-2) for homochalcogen complexes, but there are some exceptions to this. Nevertheless, ^{77}Se spectra always clearly distinguish the three invertomers as illustrated in Figure 3.

The variation of δ(Se) values with halogen follows the trend expected from electronegativity and/or long range ' bulky atom ' effects,[39] with the shielding decreasing in the order I > Br > Cl.

Small but measurable temperature dependencies of the ^{77}Se shifts (+0.06 to −0.01 p.p.m./°C) were observed. These were appreciably smaller and generally in the opposite direction to data quoted for diaryl diselenides [40] and complexes of type (I).[19] For the latter the temperature variation of the shifts was very sensitive to steric crowding about the Se atom, with more hindered molecules showing less temperature variation. This was explained in terms of solvent–solute interactions being very much reduced around sterically hindered atoms. A similar explanation would appear to be valid in the present complexes which have more steric crowding than the other reported examples.[19,40]

(*iii*) ^{195}Pt *shifts*. There have been many systematic studies of ^{195}Pt shifts either by direct observation [10,26,41,42] or by double-resonance techniques.[17,39,43-45] Several trends seem to be fairly well established. Replacing Cl by Br or I causes large low-frequency shifts.[17,39,44] A similar ' heavy atom ' effect has been noted for $[(\mathrm{PtXMe_3})_4]$ [26] and $[\mathrm{PtX_6}]^{2-}$,[46] although in the latter case some more recent work [47] indicates the reverse trend.

The halogen dependence of the ^{195}Pt shifts (Table 3) follows the expected ' heavy atom ' and electronegativity effects with Cl > Br > I in all cases. Similarly, a large high-frequency shift is observed on changing from Se to S, with the shifts for the mixed S–Se ligand complexes lying between those for the homochalcogen compounds. Increases in shielding caused by Se have been noted in $\mathrm{Pt^{II}}$ complexes,[39,44] and are very likely due to the same factors as halogen dependencies.

The deshielding caused by ring expansion (Tables 3 and 4) is contrary to the trend reported for $[\mathrm{PtMe_2\{Ph_2P(CH_2)_{\mathit{n}}PPh_2\}}]$ (n = 1–4).[48] In the present complexes the extent of deshielding is virtually independent of halogen and invertomer type since an excellent 1 : 1 correlation exists for ^{195}Pt shifts in analogous invertomers in five- and six-membered ring complexes. Similar, but less firm, correlations appear to exist for ^{195}Pt–^{77}Se shifts, and for ^{77}Se–^{77}Se shifts in the different ring size complexes. A good correlation was found (Figure 4) between δ(^{195}Pt) and ^1J(PtSe) for analogous invertomers in different halogen complexes, the correlations for [*meso*-1] and [DL-1/2] (Pt–Se^1) being better than [*meso*-2] and [DL-1/2] (Pt–Se^2). This suggests a definite correlation between δ(^{195}Pt) and the relative strength of Pt–Se bonds, with weaker bonds leading to greater deshielding at the Pt nucleus. This could explain the

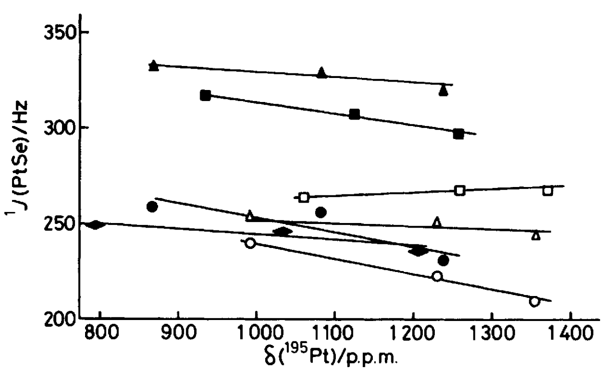


Figure 4. Graph showing the correlation between ^{195}Pt shifts and ^1J(PtSe) for analogous invertomers in different halogen complexes. ^{195}Pt shifts increase in the order I < Br < Cl (see Table 3). Key: (△, ▲) [DL-1/2] (Pt–Se^1); (□, ■) [*meso*-1]; (○, ●)[DL-1/2] (Pt–Se^2); ◆, [*meso*-2]; shaded symbols $n = 2$, unshaded symbols $n = 3$ complexes

order of shifts for individual invertomers where δ(*meso*-1) > δ(DL-1/2) > δ(*meso*-2) (see Figure 2). This result is analogous to that observed for ^{103}Rh shifts which were sensitive to the orientations of S methyl groups on the ligand.[49]

In one instance the temperature variation of ^{195}Pt shifts was measured. For all the invertomers in [PtIMe$_3${MeSe(CH$_2$)$_2$-SeMe}] the variation was ~0.3 p.p.m./°C, which is similar to values in Pt^{II} complexes.[40,44]

Isotope shifts on ^{195}Pt resonances have been previously observed[50,51] for ^{35}Cl–^{37}Cl, ^{79}Br–^{81}Br, and ^{16}O–^{18}O. In the present complexes some ^{12}C–^{13}C isotope effects were noticed in the unsymmetrical distribution of ^{13}C satellite signals about the central ^{195}Pt resonance. The shifts were always to lower frequency for higher isotopic mass, as was observed for Cl, Br, and O, and the magnitude was similar to that reported for oxygen.[51] The ^{13}C nuclei *trans* to halide produced larger shifts (up to 0.6 p.p.m.) than ^{13}C *trans* to chalcogen (~0.3 p.p.m.).

Spin–Lattice Relaxation Times.—Selenium-77 T_1 values have been measured at a variety of low temperatures for the individual invertomers of [PtXMe$_3${MeSe(CH$_2$)$_n$SeMe}] ($n = 2$, X = Cl, Br, or I; $n = 3$, X = I). Proton T_1 measurements have also been carried out for the methyl protons in some of these complexes both at low temperatures where the data refer to individual invertomers and at higher temperatures where inversion-averaged species are evident. The ^{77}Se T_1 values, based on fast inversion recovery Fourier transform experiments[52] and fittings to a two-parameter equation,[53] became larger in most cases as the temperature increased, ranging in magnitude from *ca.* 5 to 20 s over the temperature range studied with values in the order I < Br < Cl. This is compatible with a dominant chemical shielding anisotropy (c.s.a.) and/or dipolar relaxation mechanism(s). However, no significant nuclear Overhauser effects were observed implying that ^{77}Se–^{1}H dipolar relaxation is not important. Confirmation of c.s.a. relaxation as the dominant mechanism at lower temperatures has, unfortunately, not been possible to date. There is some evidence for the importance of the spin rotation mechanism at higher temperatures (>*ca.* 0 °C), and the existence of a solute–solvent (CDCl$_3$) association particularly in the case of the chloride complex. The invertomer dependencies can be rationalised in terms of the scalar coupling relaxation between ^{77}Se and the halogen X atom, but until more data are obtained and the importance of the c.s.a. mechanism is clearly established, these conclusions must remain somewhat speculative.

The methyl proton T_1 values of the complexes [PtIMe$_3${MeS(CH$_2$)$_n$SMe}] ($n = 2$ or 3) and [PtClMe$_3${MeSe(CH$_2$)$_3$-SeMe}] at above-ambient temperatures are substantially lower (by a factor of approximately one third) than for the free ligands at similar concentrations.[54] This is consistent with an increase in overall molecular correlation times on complexation, which enhances the dipolar relaxation in the platinum(IV) complexes compared to the free ligands. At lower temperatures (*ca.* −20 °C) where individual invertomers were studied, intramolecular cross-relaxation effects between platinum methyls (*trans* X) and *cis* ligand methyls were clearly in evidence. This produces appreciably shorter T_1 values for [*meso*-2] methyls than for [*meso*-1] methyls with the DL invertomer data being intermediate.

Acknowledgements

We are grateful to the S.E.R.C. for a postdoctoral research assistantship (to A. W. G. P.), and for use of the n.m.r. facilities of the City of London Polytechnic. We particularly wish to thank Dr. W. McFarlane and his staff for recording the ^{195}Pt spectra on these facilities. We also wish to thank Dr. V. Šik of this Department for assistance with some of the ^{77}Se and ^{13}C experiments.

References

1 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 1169.
2 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 1175.
3 E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Šik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1982, 583.
4 E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1980, 2208, 2220.
5 D. E. Clegg, J. R. Hall, and G. A. Swile, *J. Organomet. Chem.*, 1971, **38**, 403.
6 T. G. Appleton, H. C. Clark, and L. G. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.
7 M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1968, 3074.
8 M. J. Church and M. J. Mays, *J. Chem. Soc. A*, 1970, 1938.
9 F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 1968, 2700.
10 A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 1707.
11 B. E. Mann, *Adv. Organomet. Chem.*, 1974, **12**, 135.
12 M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, 1973, **95**, 8574.
13 G. Casalone and R. Mason, *Inorg. Chim. Acta*, 1973, **7**, 429.
14 M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1971, 1627.
15 J. D. Kennedy, W. McFarlane, R. J. Puddephatt, and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1976, 874.
16 M. A. Bennett, R. Bramley, and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 1973, 166.
17 S. J. Anderson, P. L. Goggin, and R. J. Goodfellow, *J. Chem. Soc., Dalton Trans.*, 1976, 1959.
18 P. L. Goggin, R. J. Goodfellow, and S. R. Haddock, *J. Chem. Soc., Chem. Commun.*, 1975, 176.
19 W.-H. Pan and J. P. Fackler, *J. Am. Chem. Soc.*, 1978, **100**, 5783.
20 J. P. Albrand, D. Gagnaire, and J. B. Robert, *J. Am. Chem. Soc.*, 1973, **95**, 6498.
21 W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, *J. Am. Chem. Soc.*, 1972, **94**, 8501.
22 ' NMR of Nuclei other than Protons,' eds. T. Axenrod and G. A. Webb, Wiley, New York and London, 1974, ch. 6.
23 P. Bucci, *J. Am. Chem. Soc.*, 1968, **90**, 252.
24 D. G. Cooper, R. P. Hughes, and J. Powell, *J. Am. Chem. Soc.*, 1972, **94**, 9244.
25 A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747.
26 T. G. Appleton and J. R. Hall, *Aust. J. Chem.*, 1980, **33**, 2387.

27 S. Gronowitz, I. Johnson, and A. B. Hörnfeldt, *Chem. Scr.*, 1973, **3**, 94; 1975, **8**, 8.

28 S. Gronowitz, A. Konar, and A. B. Hörnfeldt, *Chem. Scr.*, 1982, **19**, 5.

29 M. Baiwir, G. Llabres, L. Christiaens, and J. L. Piette, *Org. Magn. Reson.*, 1981, **16**, 14.

30 B. Kohne, W. Lohner, K. Praefcke, H.-J. Jakobsen, and B. Villadsen, *J. Organomet. Chem.*, 1979, **166**, 373.

31 A. Fredga, S. Gronowitz, and A. B. Hörnfeldt, *Chem. Scr.*, 1975, **8**, 15.

32 M. Baiwir, G. Llabres, L. Christiaens, and J. L. Piette, *Org. Magn. Reson.*, 1980, **14**, 293.

33 G. A. Kalabin, D. F. Kushnarev, G. A. Chmutova, and L. V. Kashurnikova, *Zh. Org. Khim.*, 1979, **15**, 24.

34 N. P. Luthra, R. B. Dunlap, and J. D. Odom, *J. Magn. Reson.*, 1982, **46**, 152.

35 S. Gronowitz, A. Konar, and A. B. Hörnfeldt, *Org. Magn. Reson.*, 1977, **9**, 213.

36 G. A. Kalabin, D. F. Kushnarev, L. M. Kataeva, L. V. Kashurnikova, and R. I. Vinokurova, *Zh. Org. Khim.*, 1978, **14**, 2478.

37 G. Llabres, M. Baiwir, L. Christiaens, and J. L. Piette, *J. Mol. Struct.*, 1981, **70**, 231.

38 W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1972, 1397.

39 W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1974, 324.

40 M. Lardon, *Ann. N.Y. Acad. Sci.*, 1972, **192**, 132.

41 J. Soulie, J. Y. Lallemand, and R. C. Rao, *Org. Magn. Reson.*, 1979, **12**, 67.

42 P. S. Pregosin, *Chimia*, 1981, **35**, 43.

43 W. McFarlane, *Chem. Commun.*, 1968, 393.

44 P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor, and I. R. H. Marshall, *J. Chem. Soc., Dalton Trans.*, 1976, 459.

45 J. D. Kennedy, W. McFarlane, R. J. Puddephatt, and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1976, 874.

46 A. V. Zelewski, *Helv. Chim. Acta*, 1968, **51**, 803.

47 J. J. Pesek and W. R. Mason, *J. Magn. Reson.*, 1977, **25**, 519.

48 S. Hietkamp, D. J. Shifkens, and K. Vrieze, *J. Organomet. Chem.*, 1979, **169**, 107.

49 W. McFarlane, *Chem. Commun.*, 1969, 700.

50 I. M. Ismail, S. J. S. Kerrison, and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1980, 1175.

51 O. Groning, T. Drakenberg, and I. L. Elding, *Inorg. Chem.*, 1982, **21**, 1820.

52 D. Canet, G. C. Levy, and I. R. Peat, *J. Magn. Reson.*, 1975, **18**, 199.

53 H. Hanssum, W. Maurer, and H. Ruterjans, *J. Magn. Reson.*, 1978, **31**, 231.

54 E. W. Abel, K. G. Orrell, and A. W. G. Platt, *Org. Magn. Reson.*, 1983, **21**, 196.

Received 22nd November 1982; *Paper* 2/1951