Complexes of Trimethylplatinum(IV) Halides with Dithio- and Diseleno-ethers, Dimethyl Disulphide, and Dimethyl Diselenide

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Trimethylplatinum(IV) halides react with MeE(CH$_2$)$_n$EMe, E = S or Se, n = 2 or 3, to give mononuclear species [PtXMe$_3${MeE(CH$_2$)$_n$EMe}], X = Cl, Br, or I. Under similar conditions the ligands L–L = MeECH$_2$EMe, MeECH(Me)EMe, and MeEEMe, E = S or Se, give dinuclear complexes [(PtXMe$_3$)$_2$(L–L)] in which the S or Se donor ligand bridges the metal atoms. Structural assignments are based on ^{1}H n.m.r. solution studies.

COMPLEXES of the *fac*-trimethylplatinum(IV) cation with neutral donor ligands are of the three basic types illustrated by [{PtIMe$_3$(py)}$_2$] (py = pyridine),[1] [PtBrMe$_3$(Me$_2$AsCH$_2$CH$_2$AsMe$_2$)],[2] and [PtMe$_3$(PMe$_2$Ph)$_3$][PF$_6$],[3] in which the neutral ligand occupies respectively one, two, and three of the remaining sites around the octahedrally coordinated metal. Compounds of all three types have been isolated from bridge-cleavage reactions of [(PtXMe$_3$)$_4$], X = Cl, Br, or I. Numerous complexes with N,P, and As donors [4,5] are known, most commonly the mononuclear species [PtXMe$_3$L$_2$], in which L$_2$ is one bidentate or two unidentate ligands, and this structural type is also accessible by oxidative addition of MeX to [PtMe$_2$L$_2$].[2,6,7] Cationic species made directly from the tetramer appear to be limited to nitrogen donors, *e.g.* [PtMe$_3$L$_3$]X, L = NH$_3$, X = Cl, Br, or I;[8] L = NH$_2$Me, X = Cl or Br;[1] and [{PtMe$_3$(en)}$_2$(en)]I$_2$ (en = ethylenediamine),[9] though ionic complexes can readily be made from the PtMe$_3$$^+$ aquo-ion,[10] or *via* [PtXMe$_3$L$_2$] by removal of the halide with Ag[PF$_6$] in acetone.[3] Only a few dinuclear bridged compounds are known, all of the type [(PtXMe$_3$L)$_2$] where L is a unidentate nitrogen donor. Complexes with X = I, L = py,[1,9] 3,5-lutidine, NH$_3$, and NH$_2$Me [1] may be made directly, and thermal decomposition of the corresponding tris complexes gives L = py, X = Cl, Br, or I; L = NH$_3$, X = I;[11] L = NH$_3$, X = Cl; and L = NH$_2$Me, X = Cl or I.[9] By contrast the only reported complexes of neutral chalcogen donors with trimethylplatinum(IV) are the thiourea (L) adducts [12] [PtMe$_3$L$_3$]X, X = Cl, I, or picrate; [PtMe$_3$(NH$_3$)L$_2$]X, X = Cl or I; and [PtMe$_3$(NH$_3$)$_2$L]Cl, and the thioether complexes [PtMe$_3$(acac)(SMe$_2$)] (acac = acetylacetonate)[13] and [{PtIMe$_3$(SEt$_2$)}$_2$].[14] None with selenium or tellurium donors has been reported.

Work in this department on inversion at sulphur and selenium led us to examine the reactions of [(PtXMe$_3$)$_4$], X = Cl, Br, or I with the neutral bidentate ligands L–L = MeE(CH$_2$)$_n$EMe, E = S or Se, n = 0—3, and with MeECH(Me)EMe, E = S or Se. The expected mononuclear complexes [PtXMe$_3$(L–L)] are formed when n = 2 or 3, which have properties similar to those reported with bidentate nitrogen,[5] phosphorus,[7] and arsenic [2] donors. However, ligands having n = 0 and 1, and MeECH(Me)EMe give under similar reaction conditions the dinuclear species [(PtXMe$_3$)$_2$(L–L)], in which one pair of halide bridges is preserved (Figure 1). The bidentate S or Se donor also bridges the metal atoms, giving a new structural type in trimethylplatinum(IV) chemistry. This structure has been confirmed by an *X*-ray crystallographic study of [(PtBrMe$_3$)$_2$(MeSeSeMe)].[15] Both series of complexes show novel conformational and fluxional behaviour,[16,17] which will be analysed in detail in later papers. Here we report the preparation and properties of the compounds and their characterisation by ^{1}H n.m.r. spectroscopy.

RESULTS AND DISCUSSION

Preparations and Properties.—The complexes were made by dissolving [(PtXMe$_3$)$_4$] in hot benzene or chloroform, adding excess of ligand, and either refluxing (sulphur ligands) or stirring at room temperature (selenium ligands), usually for 1—2 h, the main exception being the ligand MeSSMe for which prolonged refluxing led to reduction to the metal. Concentration of the solution, addition of light petroleum, and recrystallisation of the precipitated solid gave the products in high yield. The compounds are white or yellow crystalline solids, which are readily soluble in organic solvents. They are stable both in air and in solution. Analytical data, and molar mass measurements on representative complexes (Table 1), support the formulations of the two series of complexes shown in Figure 1.

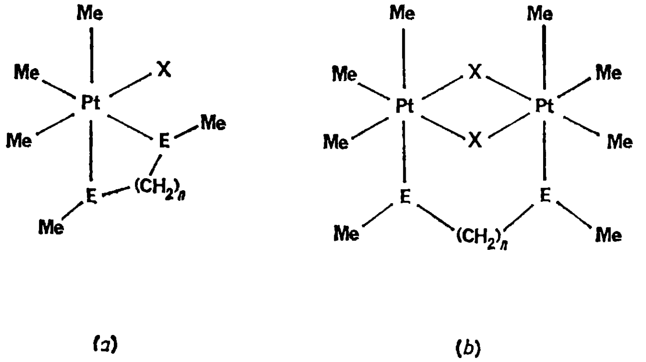

FIGURE 1 Structures of the mononuclear complexes (*a*) [PtXMe$_3${Me(CH$_2$)$_n$EMe}], E = S or Se, X = Cl, Br, or I, n = 2 or 3, and of the dinuclear complexes (*b*) [(PtXMe$_3$)$_2${MeE(CH$_2$)$_n$EMe}], E = S or Se, X = Cl, Br, or I, n = 0 or 1

A notable feature for all ligands studied is the cleanness of the reactions, one product being isolated in each case. No further reaction takes place with the excess of ligand, *i.e.* there is no formation of ionic species analogous to $[\{PtMe_3(en)\}_2(en)]I_2$,[9] or of the mononuclear from the dinuclear complexes. Attempts to make dinuclear complexes from the ligands $MeE(CH_2)_nEMe$, $n = 2$ or 3, by treating $[(PtXMe_3)_4]$, X = Cl or I, with the ligand in the mol ratio 1 : 2 gave only the mononuclear species and unchanged halide. An ^1H n.m.r. study of a 1 : 2 mixture of $[(PtIMe_3)_4]$ and $MeSe(CH_2)_3SeMe$ showed almost complete reaction after 10 min refluxing in $CDCl_3$, the mononuclear $[PtIMe_3\{MeSe(CH_2)_3SeMe\}]$ and $[(PtIMe_3)_4]$ being the only detectable products. No further reaction took place after refluxing the mixture for 12 h. Similarly, a 1 : 4 mixture of $[(PtIMe_3)_4]$ with $[PtIMe_3\{MeS(CH_2)_2SMe\}]$ was unchanged after seven days at room temperature (n.m.r. evidence).

TABLE 1

Characterisation of the mononuclear complexes $[PtXMe_3(L–L)]$ and the binuclear complexes $[(PtXMe_3)_2(L–L)]$

Complex	Colour	M.p.[a] (θ_c/°C)	Analysis[b] (%) C	H	M[c] (g mol^{-1})
$[PtClMe_3\{MeS(CH_2)_2SMe\}]$	White	181—183	20.6 (21.1)	4.8 (4.8)	412 (398)
$[PtBrMe_3\{MeS(CH_2)_2SMe\}]$	Light yellow	159—163	18.4 (19.0)	4.1 (4.3)	489 (442)
$[PtIMe_3\{MeS(CH_2)_2SMe\}]$	Light yellow	126—127	16.7 (17.2)	3.8 (3.9)	
$[PtClMe_3\{MeS(CH_2)_3SMe\}]$	White	123—128	23.1 (23.3)	5.0 (5.1)	
$[PtBrMe_3\{MeS(CH_2)_3SMe\}]$	White	175—180	20.8 (21.1)	4.6 (4.6)	447 (456)
$[PtIMe_3\{MeS(CH_2)_3SMe\}]$	Yellow	175—184	18.8 (19.1)	4.3 (4.2)	
$[PtClMe_3\{MeSe(CH_2)_2SeMe\}]$	White	179—180	17.1 (17.1)	3.7 (3.9)	
$[PtBrMe_3\{MeSe(CH_2)_2SeMe\}]$	White	185—190	15.6 (15.7)	3.6 (3.6)	544 (536)
$[PtIMe_3\{MeSe(CH_2)_2SeMe\}]$	Yellow	190—205	14.3 (14.4)	3.2 (3.3)	
$[PtClMe_3\{MeSe(CH_2)_3SeMe\}]$	White	175—176	18.8 (19.0)	4.4 (4.2)	548 (506)
$[PtBrMe_3\{MeSe(CH_2)_3SeMe\}]$	Yellow	192—198	17.2 (17.5)	4.1 (3.9)	
$[PtIMe_3\{MeSe(CH_2)_3SeMe\}]$	Yellow	195—210	15.9 (16.1)	3.4 (3.5)	
$[(PtClMe_3)_2(MeSSMe)]$	White	105—108	14.7 (14.9)	3.8 (3.7)	623 (645)
$[(PtBrMe_3)_2(MeSSMe)]$	White	122—125	13.3 (13.1)	3.3 (3.3)	
$[(PtIMe_3)_2(MeSSMe)]$	Yellow	95—110	11.5 (11.6)	2.9 (2.9)	
$[(PtClMe_3)_2\{MeS(CH_2)SMe\}]$	White	200—205	16.1 (16.4)	3.9 (4.0)	625 (659)
$[(PtBrMe_3)_2\{MeS(CH_2)SMe\}]$	White	145—150	14.5 (14.4)	3.5 (3.7)	
$[(PtIMe_3)_2\{MeS(CH_2)SMe\}]$	Light yellow	129—132	12.8 (12.8)	3.0 (3.1)	
$[(PtClMe_3)_2(MeSCHMeSMe)]$	White	157—159	18.3 (17.8)	4.1 (4.2)	663 (673)
$[(PtBrMe_3)_2(MeSCHMeSMe)]$	White	157—159	15.7 (15.7)	3.3 (3.7)	780 (762)
$[(PtIMe_3)_2(MeSCHMeSMe)]$	Light yellow	120—125	13.9 (14.0)	3.2 (3.2)	
$[(PtClMe_3)_2(MeSeSeMe)]$	Yellow	150—151	12.8 (13.0)	3.3 (3.3)	730 (739)
$[(PtBrMe_3)_2(MeSeSeMe)]$	Yellow	144—146	11.4 (11.6)	3.1 (2.9)	
$[(PtIMe_3)_2(MeSeSeMe)]$	Yellow	120—125	10.3 (10.4)	2.8 (2.6)	929 (921)
$[(PtClMe_3)_2(MeSeCH_2SeMe)]$	White	180—185	14.2 (14.3)	3.8 (3.5)	722 (753)
$[(PtBrMe_3)_2(MeSeCH_2SeMe)]$	White	185—190	12.7 (12.8)	3.5 (3.1)	
$[(PtClMe_3)_2(MeSeCHMeSeMe)]$	White	188—190	15.4 (15.7)	4.0 (3.7)	710 (767)
$[(PtBrMe_3)_2(MeSeCHMeSeMe)]$	White	190—192	14.0 (14.0)	3.7 (3.3)	

[a] All complexes melt with decomposition. [b] Calculated values are given in parentheses. [c] Osmometrically in $CHCl_3$ at 37 °C.

The effect of ring size contrasts with that found in the mononuclear complexes $[PtIMe_3\{Ph_2P(CH_2)_nPPh_2\}]$ made by oxidative addition of MeI to $[PtMe_2\{Ph_2P(CH_2)_nPPh_2\}]$.[7] Stable complexes were isolated for the four- and five-membered ring chelates ($n = 1$ or 2), but the six-membered chelate ($n = 3$) was not formed. The stability of the dinuclear complexes in solution also contrasts with the behaviour of $[(PtIMe_3L)_2]$,[1] L = pyridine and 3,5-lutidine, and $[\{PtIMe_3(SEt_2)\}_2]$.[14] The *N*-donor complexes disproportionate to $[PtIMe_3L_2]$ and $[(PtIMe_3)_4]$ in $CDCl_3$, and the thioether complex gives $[(PtXMe_3)_4]$ on standing in the same solvent. The additional stability is probably attributable to the presence of a bidentate ligand which forms five- or six-membered rings including both metal atoms. Attempts to make a more sterically crowded ring system by using the ligand $MeSCMe_2SMe$ were unsuccessful, both $[(PtClMe_3)_4]$ and $[(PtIMe_3)_4]$ being recovered unchanged after refluxing for 2 h in $CHCl_3$.

*Hydrogen-*1 *N.M.R. Spectra.*—Characterisation of $Pt^{IV}Me_3$ complexes in solution by n.m.r. spectroscopy is facilitated by the almost invariable *fac* orientation of the methyl groups, so that the number of platinum methyl signals and the coupling constants $^2J(^{195}Pt–CH_3)$ give direct information on the nature of the *trans* bonds.[4,5,18] In both the mono- and di-nuclear series, a difficulty in interpretation arises as configurational isomers are possible when both ring reversal and S,Se inversion are slow.[16] Here we therefore report, for characterisation purposes, spectral parameters taken from averaged spectra when all configurational and fluxional processes are fast on the n.m.r. time scale. The temperatures chosen (Tables 2 and 3) reflect the higher inversion energies at Se compared to S, as previously observed [19] in unidentate thio- and seleno-ether complexes of Pd^{II} and Pt^{II}. The barrier energies are also much higher in the mononuclear as compared to the dinuclear complexes, and this point will be fully discussed elsewhere. Although the temperatures at which the data are recorded do differ, the normally very small variations in coupling constant with temperature make detailed comparisons a reasonable exercise, and the regularity of the trends noted supports this view.

Mononuclear Complexes.—Three signals assignable to methyl protons are seen in the intensity ratio 2 : 2 : 1 from low to high field respectively, all showing coupling to

^{195}Pt. The signal at lowest field is from the ligand methyls, and is shifted downfield compared to the free ligand in each case. There is a small but uniform variation in both δ and ^{3}J(Pt–H) with halide (Cl $<$ Br $<$ I). The ^{3}J(Pt–E–CH$_3$) couplings are somewhat larger for the sulphur ligands, which parallels the behaviour found with phosphorus- and arsenic-bonded methyl groups.[6] The methyl–platinum resonances show the 2 : 1 intensity pattern expected by comparison with analogous complexes with Group 5 donors, with the methyl groups *trans* to halide invariably at higher field. Both signals move to low field in the sequence Cl $<$ Br $<$ I. The ^{2}J values for the higher-field signal are in the expected ranges for methyls *trans* to terminal halide, and show the normal decrease from chloride to iodide.[4,5]

TABLE 2

Hydrogen-1 n.m.r. data for the mononuclear complexes [PtXMe$_3$(L–L)]

			Pt–Me *trans* to S or Se[a]		Pt–Me *trans* to X[b]		S–Me or Se–Me		
							Complex[a]		Free ligand
(L–L)	X	θ_c/°C	δ/p.p.m.	^{2}J/Hz	δ/p.p.m.	^{2}J/Hz	δ/p.p.m.	^{3}J/Hz	δ/p.p.m.
MeS(CH$_2$)$_2$SMe	Cl	45.3	1.22	69.9	0.78	73.2	2.45	12.4	2.10
	Br	26.0	1.28	69.9	0.84	72.5	2.54	13.5	
	I	64.8	1.50	71.0	0.98	69.8	2.55	14.8	
MeS(CH$_2$)$_3$SMe	Cl	r.t.[c]	1.00	68.7	0.85	72.2	2.28	13.9	2.00
	Br	r.t.[c]	1.09	69.0	0.98	71.4	2.31	14.3	
	I	r.t.[c]	1.23	69.4	1.15	70.0	2.36	14.8	
MeSe(CH$_2$)$_2$SeMe	Cl	104.3	1.31	69.8	0.76	73.1	2.26	10.9[d]	2.04[e]
	Br	104.3	1.41	70.6	0.84	72.5	2.27	11.1[d]	
	I	100.0	1.56	70.9	0.95	70.5	2.50	11.4[d]	
MeSe(CH$_2$)$_3$SeMe	Cl	63.5	1.18	69.3	0.92	72.9	2.19	10.4	2.02[f]
	Br	64.3	1.25	69.6	1.02	72.2	2.21	11.3	
	I	80.0	1.39	70.2	1.17	69.6	2.24	11.9	

[a] Signal intensity 6 H. [b] Signal intensity 3 H. [c] r.t. = Ambient temperature not measured accurately (25—28 °C). [d] Averaged values from low-temperature spectra. [e] ^{2}J(Se–CH$_3$) = 11.0 Hz. [f] ^{2}J(Se–CH$_3$) not resolved.

TABLE 3

Hydrogen-1 n.m.r. data on the dinuclear complexes [(PtXMe$_3$)$_2$(L–L)]

			Pt–Me *trans* to S or Se[a]		Pt–Me *trans* to X[b]		S–Me or Se–Me		
							Complex[a]		Free ligand
(L–L)	X	θ_c/°C	δ/p.p.m.	^{2}J/Hz	δ/p.p.m.	^{2}J/Hz	δ/p.p.m.	^{3}J/Hz	δ/p.p.m.
MeSSMe	Cl	−57.3	1.51	71.6	0.98	76.9	2.94	11.3	2.42
	Br	−47.5	1.66	71.2	1.09	74.6	2.95	11.5	
	I	−28.0	1.94	73.8	1.30	74.3	2.95	11.6	
MeS(CH$_2$)SMe	Cl	−25.0	1.57	70.8	0.93	76.7	2.52	11.7	2.04
	Br	−23.6	1.66	70.9	1.00	76.1	2.51	12.5	
	I	−21.0	1.98	72.6	1.20	74.0	2.56	12.8	
MeSCH(Me)SMe	Cl	r.t.[c]	1.57	70.3	0.86	76.9	2.46	12.1	2.05
					0.97	76.6			
	Br	r.t.[c]	1.74	71.7	0.96	75.7	2.48	12.2	
					1.08	76.0			
	I	r.t.[c]	2.06	72.2	1.14	74.4	2.47	12.2	
					1.28	74.4			
MeSeSeMe	Cl	−13.1	1.67	71.1	1.03	77.5	2.96	8.8	2.57[d]
	Br	−14.0	1.79	71.2	1.14	76.4	3.00	9.0	
	I	−1.5	1.99	73.3	1.27	74.2	3.00	10.0	
MeSe(CH$_2$)SeMe	Cl	r.t.[c]	1.56	70.6	0.87	77.1	2.33	9.5	2.07[e]
	Br	6.4	1.72	71.3	0.97	76.6	2.35	9.8	
MeSeCH(Me)SeMe	Cl	r.t.[c]	1.56	71.0	0.78	76.8	2.29	9.6	2.05[e]
					0.92	76.9			
	Br	r.t.[c]	1.72	71.7	0.88	76.3	2.31	9.5	
					1.04	76.0			

[a] Signal intensity 6 H. [b] Signal intensity 12 H. [c] r.t. = Ambient temperature, not measured accurately (25—28 °C). [d] ^{2}J(Se–CH$_3$) = 12.5 Hz. [e] ^{2}J(Se–CH$_3$) = 10.7 Hz.

For the other signal, ^{2}J lies in the ranges 68.7—71.0 Hz and 69.3—70.9 Hz for methyls *trans* to S and Se respectively. The very small variation with halide (Cl $<$ Br $<$ I) is expected from the weak *cis* influence in complexes of this type.[5] The only comparable value of ^{2}J for a methyl group *trans* to a terminal neutral *S*-donor is 71.7 Hz in [PtMe$_3$(acac)(SMe$_2$)].[13] The closeness of the ^{2}J values for methyls *trans* to S and Se is interesting and unexpected. Values for methyls *trans* to comparable P and As donors show the former to be somewhat lower *e.g.* ^{2}J for [PtIMe$_3$\{Ph$_2$P(CH$_2$)$_2$PPh$_2$\}] [7] and [PtIMe$_3$\{Me$_2$As(CH$_2$)$_2$AsMe$_2$\}] [2] are 60 and 64 Hz respectively, while for the complexes [PtXMe$_3$(LMe$_2$Ph)$_2$], X = Cl, Br, or I, ^{2}J is *ca.* 57 Hz when L = P and 64 Hz when L = As.

The effect of ring size on the spectra is small but perceptible. For complexes of $MeE(CH_2)_2EMe$ the chemical-shift difference between the two methyl-platinum signals increases in the order $Cl < Br < I$. In the six-membered chelates of $MeE(CH_2)_3EMe$ the separation is much smaller, and decreases in the order $Cl > Br > I$. Further, with one exception, the coupling constants for both signals decrease as ring size increases, for all three halides and in both series of ligands. The usual correlation between ^2J and the strength of the *trans* bond[4,5] would imply a small strengthening of the Pt–S, Pt–Se, and Pt–X bonds on ring expansion. The same trend with ring size is reported in the complexes $[PtIMe_3\{Ph_2P(CH_2)_nPPh_2\}]$ and $[PtMe_2\{Ph_2P(CH_2)_nPPh_2\}]$, $n = 1$ or 2.

For the five-membered mononuclear complexes, pseudo-rotational vibration of the ring is very rapid even at *ca.* −100 °C, and an averaged planar conformation may be assumed. Four isomeric forms are then possible, depending on the position of the S and Se methyl groups with respect to the equatorial $PtMe_2E_2$ plane, and at low temperatures the n.m.r. spectra do show the presence of individual isomers whose relative populations vary markedly with halide. Figure 2 illustrates a typical case. In the six-membered ring compounds, the extra CH_2 group leads to additional conformational possibilities, and the interpretation of the low-temperature spectra is more difficult. However, in both the S and Se series the two E–Me signals are averaged to a single resonance at high temperature.

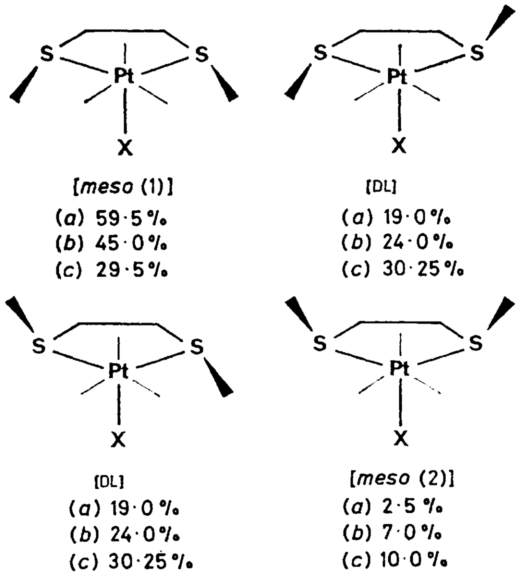

FIGURE 2 Proportions of the DL and *meso* isomers in $[PtXMe_3\{MeS(CH_2)_2SMe\}]$, (*a*) X = Cl, (*b*) X = Br, (*c*) X = I

Dinuclear Complexes.—An *X*-ray crystallographic analysis[15] of $[(PtBrMe_3)_2(MeSeSeMe)]$ reveals that it has the structure shown in Figure 1 in the solid state. Hydrogen-1 n.m.r. studies show that this structure persists in solution, and that the other dinuclear compounds are similarly constituted. Complexes of the ligands MeEEMe and $MeE(CH_2)EMe$ give high-temperature spectra (Table 3) having three platinum-coupled methyl resonances in the intensity ratio 2 : 2 : 4 from low to high field respectively. The lowest-field signal is from methyls bonded to S or Se. As with the mononuclear complexes, the expected low-field shift[20] of this signal occurs on co-ordination, and the ^3J(Pt–H) couplings are larger for the S compared to the Se compounds. The observation of only one set of 1 : 2 methyl-platinum signals shows that the two $PtMe_3$ groups are equivalent, as the proposed structure requires. The two $^2J(Pt–CH_3)$ values and signal intensities now reflect two methyls *trans* to S or Se (70.5—72.8 Hz) and four methyls *trans* to bridging halide. Both coupling constants are larger than the corresponding values for the mononuclear complexes (ΣJ = 220—226 Hz compared to 209—214 Hz), which implies a small decrease in the Pt–S and Pt–Se bond strengths and a more marked drop in Pt–X bond strength with the change from terminal to bridging halides. A similar effect appears in the spectra of the complexes $[PtIMe_3L_2]$ and $[(PtIMe_3L)_2]$, L = pyridine or 3,5-lutidine, the corresponding ΣJ values falling within the above ranges.[1] The reported dinuclear complex $[\{PtIMe_3(SEt_2)\}_2]$ made from the *S*-bridged species $[\{PtMe_2(SEt_2)\}_2]$ by oxidative addition of 2 mol of MeI has been assigned[14] a structure with the two Pt–S–Pt bridges preserved and terminal halides. While the preparative method and the ^2J values for the 2 : 1 platinum methyls (75 and 72 Hz respectively) make this assignment plausible, the chemical shifts (1.21 and 2.12 p.p.m. respectively) suggest the alternative structure with bridging halides and terminal SEt_2 groups which is also consistent with the ^2J values. In all adducts of trimethylplatinum(IV) halides so far reported, methyls *trans* to halide are always at highest field. Coupling from ^{195}Pt to the $S–CH_2$ protons could explain the apparent inequivalence of the ethyl groups. The dissociation of the sulphide ligand in $CHCl_3$ solution is similar to that reported[13] in $[PtMe_3(acac)(SMe_2)]$, for which ^2J for the methyl group *trans* to S is also *ca.* 72 Hz.

The spectra of the complexes of MeECH(Me)EMe show as an additional feature a non-equivalence of the two methyls *trans* to halide on each platinum atom. This arises from the loss of a plane of symmetry when the ligand CH_2 group is replaced by a CH(Me) group, though the $PtMe_3$ groups are still symmetry related. The effect of this methyl group is sufficient to separate the equatorial methyl signals by 0.12—0.16 p.p.m., though the ^2J values are practically the same. The configuration of the E–Me groups again allows the possibility of isomers, but the temperature dependence of the spectra can be fully explained only on the basis that at the lowest temperatures a single isomer is detectable, namely the DL invertomer (Figure 3) with the S or Se methyl groups *trans*, and the CHMe methyl group *trans* to the E–Pt bonds. Models show that if a second hydrogen atom is replaced by a methyl group as in $MeSCMe_2SMe$, considerable non-bonded interactions occur with the bridging halide and the equatorial platinum methyls, and it is therefore not surprising that we were unable to obtain any reaction of this ligand with $[(PtXMe_3)_4]$.

General Discussion.—Platinum(IV) has a much lower affinity for sulphur donors [21] than Pt^{II}, and comparatively few complexes of Pt^{IV} with thio- and seleno-ethers have been reported.[22,23] They are mostly of the type $[PtX_4L_2]$, where X = halide and L = SR_2 or SeR_2, and are usually made by oxidative addition [24,25] of halogen to PtX_2L_2 rather than from Pt^{IV}. Although Pt^{II} readily forms complexes with bidentate dithio- and diselenoethers,[26,27] the only compounds of Pt^{IV} with ligands of this type we are aware of are $[PtCl_4\{MeSe(CH_2)_nSeMe\}]$,[28] $n = 2$ or 3. This scarcity of compounds, together with the report that attempts to make platinum(IV) complexes of thioethers were unsuccessful,[21] contrasts with the ready formation and stability of the $Pt^{IV}Me_3$ complexes reported here, and strikingly illustrates the way in which the alkyl groups alter the normal properties of Pt^{IV}, particularly in respect of stability towards reduction.

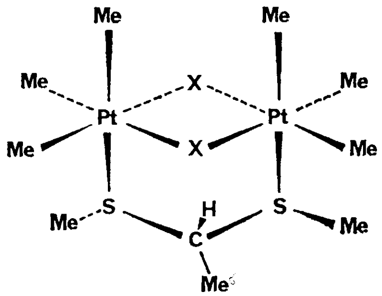

FIGURE 3 Conformation of the single isomer of the complexes $[(PtXMe_3)_2\{MeSCH(Me)SMe\}]$, X = Cl, Br, or I, which is detectable at *ca.* −90 °C

The mononuclear compounds have the ligands in their normal bidentate chelate role,[29] although they can be both bridging [26,30] and unidentate.[31] From the ^2J-(Pt–CH_3) values there appears to be little difference between the Pt–S and Pt–Se bond strengths among the 12 compounds, the sulphur series being comparable to the bidentate xanthates and dithiocarbamates (^2J = 69—72 Hz).[32] Thioether and selenoether [33] complexes of Pt^{II} show [33] ligand exchange at 70—80 °C, while the corresponding compounds with dithio- and diselenoethers [27] are kinetically stable up to 170 °C. A similar stabilising effect is apparent in the present chelate complexes (see earlier).

Contraction of the chelate ring in the ligands $MeECH_2$-EMe and MeECH(Me)EMe was of particular interest as no complexes of these ligands have been reported, and a four-membered ring complex, *cf.* $[PtIMe_3(Ph_2PCH_2$-$PPh_2)]$ was a possibility. The stability of the preferred dinuclear halide-bridged structure is remarkable, as are the varieties of conformational and fluxional processes available to it.[15] Preservation of the E–E bonds in the reactions of MeSSMe and MeSeSeMe is notable, there being no evidence of bond cleavage [34] and loss of halide to give $[\{PtMe_3(EMe)\}_n]$, but this is not unexpected in view of the high oxidation state of the metal. The recently proved ability of organodisulphides and diselenides to act as bridging ligands,[15,20,35] and in particular the close similarity between $[(PtBrMe_3)_2(MeSeSeMe)]$ [5] and the Re^I complex $[\{ReBr(CO)_3\}_2(MeSSMe)]$ [20] in the solid state, both of which have a low-spin d^6 metal, support the evidence presented from solution studies that the dichalcogen bridges are quite stable.

In all of the complexes the $PtMe_3$ group maintains its customary *fac* orientation. The selenium complexes are the first reported with this donor, and their stability implies that selenium analogues of the anionic sulphur-containing ligands [13,32] should also give very stable compounds.

EXPERIMENTAL

Dimethyl disulphide was from B.D.H. Chemicals and was used as received. Other ligands were made by literature methods as follows: bis(methylthio)methane,[36] b.p. 148—149 °C (lit.,[37] 148—150 °C); 1,1-bis(methylthio)ethane, b.p. 48 °C (16 mmHg) * [lit.,[38] 47 °C (17 mmHg)]; 2,2-bis(methylthio)propane, b.p. 58 °C (12 mmHg) [lit.,[39] 45—47 °C (12 mmHg)]; 1,2-bis(methylthio)ethane, b.p. 181 °C (lit.,[40] 181.5—183 °C); 1,3-bis(methylthio)propane, b.p. 90 °C (12 mmHg) [lit.,[41] 86.5 °C (12 mmHg)]; dimethyl diselenide, b.p. 42 °C (15 mmHg) (lit.,[42] 153 °C); bis(methylseleno)methane, b.p. 76 °C (12 mmHg) [lit.,[43] 80 °C (15 mmHg)]; 1,1-bis(methylseleno)ethane, b.p. 71 °C (12 mmHg) [lit.,[43] 72 °C (15 mmHg)]; 1,2-bis(methylseleno)ethane, b.p. 88 °C (8 mmHg) (lit.,[44] not reported); 1,3-bis(methylseleno)propane, b.p. 102 °C (8 mmHg) (lit.,[44] not reported). Trimethylplatinum iodide was made by Baldwin and Kaska's method.[45] Conversion to trimethylplatinum sulphate [46] and metathesis with the appropriate potassium halide [47] gave the trimethylplatinum halides.

Since the preparations of the complexes were very similar, representative methods are given for the chlorides of each class of complexes. The bromo- and iodo-derivatives were prepared in an analogous manner in each case. Light petroleum refers to the fraction boiling at 60—80 °C.

[1,3-Bis(methylthio)propane]chlorotrimethylplatinum(IV).—A solution of trimethylplatinum(IV) chloride (0.101 g, 0.36 mmol) † and 1,3-bis(methylthio)propane (0.059 g, 0.44 mmol) in benzene (2.5 cm^3) was refluxed for 1.75 h. Concentration of the solution to 0.25 cm^3, addition of light petroleum, and vigorous stirring gave a white solid. Recrystallisation from chloroform–light petroleum gave the white crystalline *product* (0.122 g, 82%).

[1,2-Bis(methylseleno)ethane]chlorotrimethylplatinum(IV).—An excess of 1,2-bis(methylseleno)ethane (0.062 g, 0.29 mmol) was added to a warm solution of trimethylplatinum(IV) chloride (0.066 g, 0.24 mmol) in chloroform (4 cm^3), and the mixture stirred for 5 h at room temperature. Concentration of the solution to 0.25 cm^3, addition of light petroleum, and vigorous stirring gave a white solid, which was recrystallised from chloroform–light petroleum to give 0.102 g (87%) of *product*.

Di-μ-chloro-μ-(dimethyl disulphide)-hexamethyldiplatinum(IV).—Dimethyl disulphide (0.048 g, 0.52 mmol) was added to a warm solution of trimethylplatinum(IV) chloride (0.142 g, 0.52 mmol) in chloroform (5 cm^3). The mixture was refluxed for 20 min, then stirred for 2 h at room tem-

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* Throughout this paper : 1mmHg ≈ 13.6 × 9.8 Pa.

† Based on the monomeric unit $PtXMe_3$.

perature. Solvent was removed at reduced pressure and the residue was dissolved in light petroleum. White crystals of the *complex* (0.12 g, 72%) were obtained on cooling the solution overnight at −20 °C.

μ-[*Bis*(*methylthio*)*methane*]-*di*-μ-*chloro-hexamethyldiplatinum*(IV).—A solution of trimethylplatinum(IV) chloride (0.12 g, 0.43 mmol) and bis(methylthio)methane (0.047 g, 0.43 mmol) in toluene (4 cm³) was refluxed for 1.5 h. Concentration, addition of light petroleum, and recrystallisation of the white solid from chloroform gave a white crystalline *product* (0.14 g, 98%).

μ-(*Dimethyl diselenide*)-*di*-μ-*chloro-hexamethyldiplatinum*-(IV).—A solution of trimethylplatinum(IV) chloride (0.121 g, 0.44 mmol) in chloroform (4 cm³) was refluxed with dimethyl diselenide (0.082 g, 0.44 mmol) for 1 min, then stirred at room temperature for 2 h. Concentration of the solution and addition of light petroleum gave a yellow solid, which was recrystallised by cooling a chloroform–light petroleum solution at −20 °C for 12 h (0.102 g, 63%).

μ-[1,1-*Bis*(*methylseleno*)*ethane*]-*di*-μ-*chloro-hexamethyldiplatinum*(IV).—An excess of 1,1-bis(methylseleno)ethane (0.062 g, 0.29 mmol) was added to a warm solution of trimethylplatinum(IV) chloride (0.063 g, 0.23 mmol) in chloroform (5 cm³), and the mixture stirred for 12 h at room temperature. Solvent was removed at reduced pressure and the residue was washed with light petroleum and recrystallised from chloroform–light petroleum to give the white crystalline *product* (0.072 g, 81%).

Hydrogen-1 *N.M.R. Spectra*.—These were recorded at 100 MHz using a JEOL PS/PFT-100 spectrometer equipped with a standard variable-temperature accessory. Temperature measurements were made with a calibrated copper–constantan thermocouple, and are considered accurate to ⩽1 °C. Spectra were run in $CDCl_3$ or in CD_2Cl_2–CS_2 mixtures for above and below ambient temperatures respectively.

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