Platinum Metal Complexes of Potentially Chelating Alkene–Thioether and Alkene–Selenoether Ligands: Synthesis and Dynamic Nuclear Magnetic Resonance Study of $[MX_2\{MeE(CH_2)_nCH=CH_2\}]$ (M = Pt or Pd; X = Cl, Br, or I; E = S or Se; n = 2 or 3) and the *X*-Ray Structure of *cis*-Dibromo(2-thia-6-heptene)platinum(II), $[PtBr_2\{MeS(CH_2)_3CH=CH_2\}]$†

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But-3-enyl and pent-4-enyl methyl chalcogenide ligands have been found to co-ordinate to transition metals through the chalcogen atom alone in a monodentate fashion, or as bidentate ligands binding through both the chalcogen atom and the alkene moieties. The metallacycles formed on chelation have been fully characterised and an *X*-ray diffraction study of $[PtBr_2\{MeS(CH_2)_3CH=CH_2\}]$ is reported: the crystals are orthorhombic, of space group *Pbca* with $Z = 8$ in a unit cell of dimensions $a = 15.098(9)$, $b = 13.245(3)$, and $c = 10.299(2)$ Å. The principal internuclear distances are Pt–Br 2.448(4) and 2.434(4), Pt–S 2.286(7), and Pt–C 2.136(20) and 2.196(19) Å. Inversion of configuration at the co-ordinated sulphur atom is observed at moderate temperatures and has been studied by dynamic n.m.r. spectroscopy. The methyl pent-4-enyl sulphide ligand is observed to isomerise upon co-ordination to palladium(II).

There have been relatively few reports of the co-ordination chemistry of mixed alkene–thioether and -selenoether ligands. In 1968 some such ligands were prepared and the corresponding *cis*-dihalogenopalladium(II) and platinum(II) complexes were synthesised[1] and other workers[2] have investigated the temperature dependence of the fluxionality of some alkene–thioether complexes of palladium(II), but no quantitative results were reported.

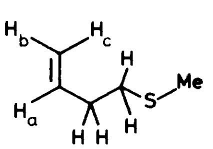
Such ligands are capable of co-ordinating to a transition metal through both the chalcogen atom and the alkene moiety and are therefore potentially chelating. Simple thioether and selenoether ligands co-ordinate fairly readily to transition-metal centres and there are numerous reports[3–5] describing the preparation and properties of such complexes. The configuration at the chalcogen atom(E) is pyramidal and the $[M]-ER_2$ moiety may undergo pyramidal atomic inversion of configuration at the chalcogen atom in a process first recorded[6,7] in 1966. Where the co-ordination chemistry of simple alkene complexes has been studied, it has been found in many cases that the alkene exhibits a conformational preference within the co-ordination sphere of the metal and may rotate in a temperature-dependent process about the axis between its centroid and the metal atom.

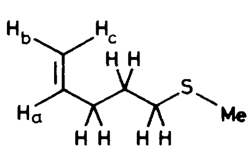
In this paper we report the synthesis, structural characterisation, and fluxional behaviour of a series of platinum and palladium metal complexes with ligands containing both chalcogenether and alkene functional groups, and we assess the extent to which these features differ from those of complexes in which these moieties are co-ordinated independently.

Table 1. Infrared data (cm^{-1})

Sample	Sample state	Alkene stretch Unco-ordinated	Alkene stretch Co-ordinated
$MeS(CH_2)_3CH=CH_2$	Liquid film	1 641	
$MeS(CH_2)_2CH=CH_2$	Liquid film	1 641	
$MeSe(CH_2)_2CH=CH_2$	Liquid film	1 641	
$[PtCl_2\{MeS(CH_2)_3CH=CH_2\}]$	Nujol mull		1 504
$[PtBr_2\{MeS(CH_2)_3CH=CH_2\}]$	KBr disc		1 497
$[PtI_2\{MeS(CH_2)_3CH=CH_2\}]$	KBr disc		1 494
$[PtCl_2\{MeS(CH_2)_2CH=CH_2\}]$	Nujol mull		1 505
$[PtBr_2\{MeS(CH_2)_2CH=CH_2\}]$	Nujol mull		1 504
$[PtI_2\{MeS(CH_2)_2CH=CH_2\}]$	Nujol mull		1 501
$[PdCl_2\{MeS(CH_2)_3CH=CH_2\}]$*	KBr disc		1 541
$[PdCl_2\{MeS(CH_2)_2CH=CH_2\}]$	KBr disc		1 530
$[PdBr_2\{MeS(CH_2)_2CH=CH_2\}]$	KBr disc		1 530
$[PtCl_2\{MeS(CH_2)_3CH=CH_2\}(2,6-Me_2C_6H_3NC)]$	KBr disc	1 641	
$[PtCl_2\{MeSe(CH_2)_2CH=CH_2\}]$	KBr disc		1 503
$[PtBr_2\{MeSe(CH_2)_2CH=CH_2\}]$	KBr disc		1 501
$[PtI_2\{MeSe(CH_2)_2CH=CH_2\}]$	KBr disc		1 497

* Ligand rearranges upon co-ordination.





Results and Discussion

Preparation and Properties of the Complexes.—The alkenyl methyl sulphide ligands $MeS(CH_2)_nCH=CH_2$ (n = 2 or 3) were prepared from the reaction of the alkenyl bromide and potassium methyl sulphide in ethanol. The selenide ligand $MeSe(CH_2)_2CH=CH_2$ was prepared by borohydride cleavage of dimethyl diselenide and reaction with the alkenyl bromide in methanol–tetrahydrofuran solution. The ligands react readily with 1 equivalent of potassium tetrachloroplatinate(II) at room temperature in aqueous ethanolic solutions left stirring over-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 2. Characterisation of the complexes

Complex	Nature	M.p./°C	Analysis^a/%	
			C	H
$[PtCl_2\{MeS(CH_2)_2CH{=}CH_2\}]$	Light yellow crystals	225.0	16.35 (16.30)	2.65 (2.70)
$[PtBr_2\{MeS(CH_2)_2CH{=}CH_2\}]$	Dark yellow crystals	202.0	13.85 (13.15)	2.20 (2.20)
$[PtI_2\{MeS(CH_2)_2CH{=}CH_2\}]$	Orange crystals	162	11.05 (10.90)	1.75 (1.80)
$[PtCl_2\{MeS(CH_2)_3CH{=}CH_2\}]$	Light yellow crystals	145	12.75 (12.75)	2.15 (2.10)
$[PtBr_2\{MeS(CH_2)_3CH{=}CH_2\}]$	Dark yellow crystals	125	15.30 (15.30)	2.60 (2.55)
$[PtI_2\{MeS(CH_2)_3CH{=}CH_2\}]$	Red crystals	110	18.85 (18.85)	3.15 (3.15)
$[PdCl_2\{MeS(CH_2)_2CH{=}CH_2\}]$	Orange powder	190 (decomp.)	21.25 (21.55)	3.40 (3.60)
$[PdBr_2\{MeS(CH_2)_2CH{=}CH_2\}]$	Red crystals	193^b	16.25 (16.30)	2.65 (2.75)
$[PdCl_2\{MeS(CH_2)_2CH{=}CHMe\}]$	Light orange crystals	153^b	23.65 (24.60)	3.80 (4.15)
$[PtCl_2\{MeSe(CH_2)_2CH{=}CH_2\}]$	Light yellow crystals	230 (decomp.)	14.70 (14.45)	2.35 (2.45)
$[PtBr_2\{MeSe(CH_2)_2CH{=}CH_2\}]$	Brown crystals	230 (decomp.)	13.00 (11.90)	2.05 (2.00)
$[PtI_2\{MeSe(CH_2)_2CH{=}CH_2\}]$	Dark orange crystals	200^b	10.00 (10.05)	1.75 (1.70)
$[PtCl_2\{MeS(CH_2)_3CH{=}CH_2\}\text{-}(2,6\text{-}Me_2C_6H_3NC)]^c$	Off-white crystals		34.00 (31.75)	3.80 (3.75)

^{a} Calculated values in parentheses. ^{b} Melts and decomposes. ^{c} N 2.80 (2.45)%.

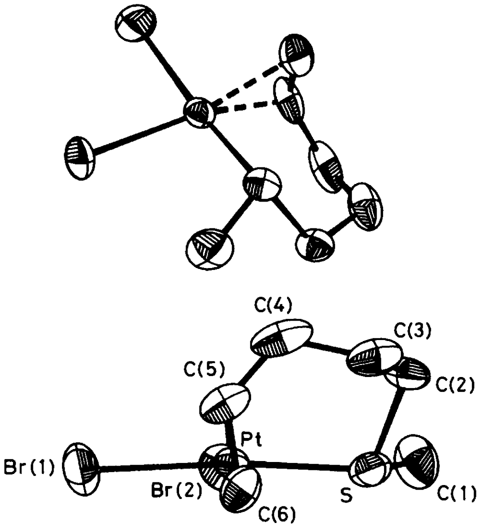


Figure. Two views of the crystal structure of $[PtBr_2\{MeS(CH_2)_3\text{-}CH{=}CH_2\}]$

Table 3. Bond lengths (Å) and angles (°) for $[PtBr_2\{MeS(CH_2)_3\text{-}CH{=}CH_2\}]$

Br(1)–Pt	2.448(4)	Br(2)–Pt	2.434(4)
S–Pt	2.286(7)	C(5)–Pt	2.196(19)
C(6)–Pt	2.136(20)	C(1)–S	1.761(19)
C(2)–S	1.799(18)	C(3)–C(2)	1.482(25)
C(4)–C(3)	1.554(28)	C(5)–C(4)	1.441(28)
C(6)–C(5)	1.418(25)		
Br(2)–Pt–Br(1)	89.2(2)	S–Pt–Br(1)	173.3(1)
S–Pt–Br(2)	94.3(2)	C(5)–Pt–Br(1)	86.0(6)
C(5)–Pt–Br(2)	155.0(4)	C(5)–Pt–S	93.2(6)
C(6)–Pt–Br(1)	90.5(6)	C(6)–Pt–Br(2)	166.6(5)
C(6)–Pt–S	84.8(6)	C(6)–Pt–C(5)	38.2(6)
C(1)–S–Pt	113.4(9)	C(2)–S–Pt	107.1(7)
C(2)–S–C(1)	99.2(10)	C(3)–C(2)–S	113.8(14)
C(4)–C(3)–C(2)	113.7(16)	C(5)–C(4)–C(3)	119.1(16)
C(4)–C(5)–Pt	113.6(15)	C(6)–C(5)–Pt	68.6(11)
C(6)–C(5)–C(4)	127.2(18)	C(5)–C(6)–Pt	73.2(11)

night, to form the pale yellow crystalline chloro-complexes. The corresponding bromo- and iodo-complexes were readily prepared by metathesis in warm acetone solution. The complexes are all crystalline, moderately soluble in organic solvents, and stable to air and water as solids and in solution. Infrared and analytical data for the complexes are reported in Tables 1 and 2 respectively. The complexes have been further characterised by variable-temperature n.m.r. spectroscopy and for *cis*-dibromo-(2-thia-6-heptene)platinum(II) $[PtBr_2\{MeS(CH_2)_3CH{=}CH_2\}]$, by single-crystal *X*-ray diffraction. Proton n.m.r. studies show that the ligands act in the bidentate mode, co-ordinating through the sulphur atom and the alkene moiety. Variable-temperature ^1H n.m.r. studies indicate the occurrence of configurational inversion at sulphur and quantitatively demonstrate the effects of different ring sizes, the different metal, and the different halogen on the energy barrier for this process (see below). In order to provide a starting point for the discussion of the variable-temperature behaviour in solution it was desirable to know the structure of the species in the solid state and therefore a single-crystal *X*-ray analysis of one member of the series was undertaken. The relevant details are given in the Experimental section.

Crystal and Molecular Structure of cis-*Dibromo*(2-*thia*-6-*heptene*)*platinum*(II).—The molecular structure of $[PtBr_2\{MeS(CH_2)_3CH{=}CH_2\}]$ is illustrated in the Figure and selected intramolecular bond lengths and angles are given in Table 3. The fractional atomic co-ordinates are in Table 4.

The molecular structure is not dissimilar to that reported for *cis*-dichloro[2,2-dimethylpent-(*E*)-3-enyl methyl sulphide]-palladium(II); the palladium atom is situated at the centre of a square plane and the exocyclic methyl moiety is oriented pseudoequatorially at the sulphur atom. In the present case, the platinum atom is at the centre of the square plane described by the two bromine atoms, the sulphur atom, and the alkene double bond. In fact the centroid of the double bond is displaced by 0.294 Å out of the square-planar co-ordination sphere of the metal and the C–C vector of the double bond is tilted slightly away from the perpendicular to the $PtBr_2S$ plane. This is, perhaps, a result of the relatively large seven-membered ring, the steric strain within which results in a torsion about the metal–alkene axis.

The platinum–sulphur bond length in this complex [2.286(7) Å] is typical of that observed with other chelating sulphur ligands, *e.g.* *cis*-dichloro(L-methionine)platinum(II) (2.26 Å).[8]

As a consequence of the pyramidal geometry at the sulphur atom there are two possible orientations for the sulphur methyl group relative to the ring: it may be either pseudoaxial or pseudoequatorial. The *X*-ray diffraction study shows the solid-state configuration at sulphur to be pseudoequatorial. This places the methyl group as far from the rest of the complex as possible in the least sterically hindered position, as is the case in *cis*-dichloro[2,2-dimethylpent-(*E*)-3-enyl methyl sulphide]-palladium(II).[2]

N.M.R. Studies.—Proton n.m.r. data for the complexes are reported in Table 5. The solid-state structure of each of the compounds is assumed to be analogous to that observed for *cis*-dibromo(2-thia-6-heptene)platinum(II) (see above). In each case the n.m.r. results show that the complex exists as two conformers in solution, one with the S/Se-methyl group pseudoequatorial and the other with the S/Se-methyl group pseudoaxial. Although it cannot be unambiguously determined on the basis of the n.m.r. measurements which of these conformers predominates in solution, it is reasonable to assume that the favoured conformer in solution is that with the S/Se-methyl group pseudoequatorial, since that is the geometry observed in the solid state.

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for $[PtBr_2\{MeS(CH_2)_3CH=CH_2\}]$

Atom	*x*	*y*	*z*
Pt	691.8(4)	975.1(5)	1 381.1(6)
Br(1)	1 253(2)	−355(1)	2 812(2)
Br(2)	−812(1)	517(2)	1 999(2)
S	251(3)	2 123(3)	−146(4)
C(1)	−899(11)	2 344(16)	−145(23)
C(2)	626(11)	3 342(12)	391(17)
C(3)	1 598(13)	3 406(15)	581(17)
C(4)	1 940(12)	2 783(15)	1 757(17)
C(5)	1 988(12)	1 699(15)	1 649(16)
C(6)	1 965(12)	1 117(14)	494(18)

Above a certain temperature (the coalescence temperature, T_c) these two conformers will interconvert rapidly on the n.m.r. time-scale by sulphur inversion. For the sulphide complexes, at temperatures below about −30 °C, inversion of configuration at the sulphur atom is slow on the n.m.r. time-scale and two easily distinguishable SMe proton peaks in the ^1H n.m.r. spectrum for the different epimers are observed, at shifts of about 2.6 p.p.m., each with satellites due to $^3J(^1H-^{195}Pt)$ coupling (45—50 Hz) of the S-methyl protons with ^{195}Pt (33.9%, $I = \frac{1}{2}$). The n.m.r. spectra also show two sets of resonances at δ 4.0 to 6.0 for each olefinic proton, both of which are coupled to the platinum nucleus with $^2J(^1H-^{195}Pt) \approx 70$ (H_b) and 55—65 Hz (H_c). Protons H_b and H_c are coupled to H_a with $^3J(^1H_a-^1H_b) \approx 8$ and $^3J(^1H_a-^1H_c) \approx 14$ Hz. The pairs of resonances for each olefinic proton arise from the two isomers and show that the steric difference between the two configurations at the sulphur atom is sufficient for the olefinic protons to distinguish between them. Warming above −30 °C results in the gradual coalescence of the peaks as exchange between the two states commences. Above the coalescence temperature, the averaged signal of the two original (static state) peaks sharpens. The n.m.r. characteristics of the selenide complexes are similar to those of the analogous sulphide complexes, but the coalescence temperature is observed to be higher. The quantitative analysis of the pyramidal inversion process may be carried out by complete bandshape analysis to produce the activation free energy $\Delta G^\ddagger$ at any temperature by evaluating both $\Delta H^\ddagger$ and $\Delta S^\ddagger$. Alternatively, a less rigorous, but still useful, method to find $\Delta G^\ddagger$ at the coalescence temperature only may be employed. By such use of the Eyring equation $\Delta G^\ddagger_{T_c}$ for the complex *cis*-dichloro(2-thia-6-heptene)platinum(II) was found to be 67.3 ± 0.1 kJ mol^{-1} at the coalescence temperature (308 K).

It was apparent that the olefin was fairly strongly co-ordinated, as attempts to labilise it at higher temperatures failed, and the complex decomposed at 120 °C. The olefin moiety was, nevertheless, displaced by monodentate ligands such as triphenylphosphine and 2,6-dimethylphenyl isocyanide.

Table 5. N.m.r. data[a]

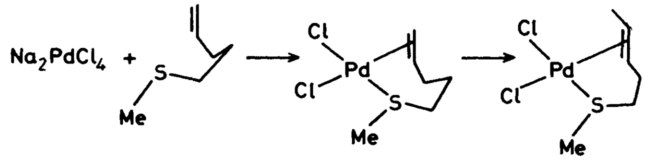
Sample	δ(SMe)	^3J[Pt–H(Me)]	δ(H_a)	δ(H_b)	δ(H_c)	$^3J(H_a-H_b)$	$^3J(H_a-H_c)$	$^3J(Pt-H_b)$	$^3J(Pt-H_c)$
$MeS(CH_2)_2CH=CH_2$	1.96		5.70	4.90	4.90				
$MeS(CH_2)_3CH=CH_2$	2.09		5.80	5.00	5.00				
$MeSe(CH_2)_2CH=CH_2$[b]	1.99		5.83	5.05	5.05				
$[PtCl_2\{MeS(CH_2)_2CH=CH_2\}]$	2.67	41.75	4.92[c]	4.52	4.02	8.5	14.4	68.0	64.0
$[PtBr_2\{MeS(CH_2)_2CH=CH_2\}]$	2.70	44.0	5.05	4.75[c]	4.13	8.0	13.7	70.0	65.0
$[PtI_2\{MeS(CH_2)_2CH=CH_2\}]$	2.73[d]	45.0	5.35[d]	5.16[d]	4.22[d]	7.6	13.8	71.0	66.5
$[PtCl_2\{MeS(CH_2)_3CH=CH_2\}]$	2.50	47.3	5.75	4.57	4.22	8.5	14.0	71.7	55.0
$[PtBr_2\{MeS(CH_2)_3CH=CH_2\}]$	2.65	50.0	6.00	4.71	4.32	8.9	15.0	73.5	56.6
$[PtI_2\{MeS(CH_2)_3CH=CH_2\}]$	2.63[d]	46.05	6.28[d]	5.00[d]	4.61[d]	8.61	14.35	74.61	52.80
$[PdCl_2\{MeS(CH_2)_2CH=CH_2\}]$	2.64		6.32	5.37	4.90	9.0	15.5		
$[PdCl_2\{MeS(CH_2)_3CH=CH_2\}]$[e]	3.68[c]		5.90		5.78				
$[PtCl_2\{MeSe(CH_2)_2CH=CH_2\}]$[c]	2.53	36.0	5.00	4.46	3.87	8.0	13.8	68.6	62.6
$[PtBr_2\{MeSe(CH_2)_2CH=CH_2\}]$	2.57	37.0	5.09	4.67	3.96	8.0	14.0	69.4	63.2
$[PtI_2\{MeSe(CH_2)_2CH=CH_2\}]$[b]	2.64[c]	36.5	5.25	5.00	4.12	8.5	13.8	70.4	64.0

[a] Shifts (δ) measured in p.p.m.; coupling constants (*J*) in Hz and are temperature-dependent. [b] Selenium-77 satellites observed. [c] Values for major isomer. [d] Average of epimer values. [e] Ligand isomerises upon co-ordination.

Table 6. Coalescence data from variable-temperature ^{1}H n.m.r. studies

Complex	Isomer ratio	Protons coalescing at T_c	T_c S-inv./K	ΔG_{T_c} S-inv./ kJ mol^{-1} ± 0.1
$[PtCl_2\{MeS(CH_2)_2CH=CH_2\}]$	2.8:1	H_b	383	79.5
$[PtBr_2\{MeS(CH_2)_2CH=CH_2\}]$	*a*	SMe	358	78.1
$[PtI_2\{MeS(CH_2)_2CH=CH_2\}]$	1.3:1	SMe	348	74.3
$[PtCl_2\{MeS(CH_2)_3CH=CH_2\}]$	3.8:1	SMe	308	67.3
$[PtBr_2\{MeS(CH_2)_3CH=CH_2\}]$	2.7:1	H_b	325	67.1
$[PtI_2\{MeS(CH_2)_3CH=CH_2\}]$	1.3:1	H_a	308	62.8
$[PdCl_2\{MeS(CH_2)_2CH=CH_2\}]$	2.9:1	H_b	353	72.3
$[PdCl_2\{MeS(CH_2)_3CH=CH_2\}]^b$	5.0:1	Me(ol)^c	313	66.9
$[PtCl_2\{MeSe(CH_2)_2CH=CH_2\}]$	5.7:1	SMe	325	85.0
$[PtBr_2\{MeSe(CH_2)_2CH=CH_2\}]$	3.0:1		*d*	
$[PtI_2\{MeSe(CH_2)_2CH=CH_2\}]$	3.2:1		*d*	

[a] Obscure. [b] Ligand isomerises upon co-ordination; becomes 2-thia-*trans*-5-heptene. [c] Refers to methyl group on olefinic moiety. [d] Out of temperature range.



Scheme.

Within any set of halide complexes of the ligands, n.m.r. spectroscopy, at temperatures well below those at which coalescence due to chalcogen inversion would occur, indicated a trend towards greater equivalence in the populations of the two epimers on replacing chloride with bromide and then with iodide (see Table 6). This is presumably due to the steric difference experienced by the S/Se*Me* group between the pseudoaxial and pseudoequatorial positions: as the size of the halogen increases (Cl < Br < I), so the halogen provides more effective steric hindrance to the methyl group when it is pseudoequatorially oriented, as in this configuration the methyl group extends more towards the van der Waals sphere of the closest halogen.

For the *cis*-dihalogeno(alkenyl methyl sulphide)metal(II) complexes, the reduction in ring size from a seven-membered ring, as in $[MX_2\{MeS(CH_2)_3CH=CH_2\}]$, to a six-membered ring, as in $[MX_2\{MeS(CH_2)_2CH=CH_2\}]$, causes an increase in the energy barrier to sulphur inversion of about 12 kJ mol^{-1}, due presumably to the increased angle constraint for access to the planar transition state in the inversion process. For complexes containing platinum(II) the energy barriers are about 7 kJ mol^{-1} greater than those in the palladium(II) analogues. This is probably due to the palladium(II) centre accepting more *s*-electron density from the sulphur atom than the platinum(II) centre, thus allowing easier access to the transition state in which the inverting lone pair of electrons is regarded as having pure *p* character. Another factor is the more effective 3*p*(S)–4*d*(Pd) overlap compared with the 3*p*(S)–5*d*(Pt) overlap. The inversion barrier, $\Delta G^{\ddagger}$, also decreases with halogen in the order Cl > Br > I. This reflects the differing *trans* influences of the halogens which increase in the same order. Calculations of $\Delta G^{\ddagger}_{T_c}$ for the alkenyl methyl selenide complexes show that the energy barrier to chalcogen inversion is about 6 kJ mol^{-1} greater than that in the sulphide complexes.

The ^{1}H n.m.r. spectrum of the product of the reaction between sodium tetrachloropalladate(II) and 2-thia-6-heptene shows a pattern very different to the expected spectrum and the spectra of the platinum complexes: a doublet integrating to three protons is observed at 1.95 p.p.m. and the olefinic region is markedly different with an integration of only two protons. This is consistent with the isomerisation of the ligand from 2-thia-6-heptene to 2-thia-*trans*-5-heptene, as shown in the Scheme. This phenomenon has been observed in the case of the potentially chelating alkene–thioether ligand 2,2-dimethylpent-4-enyl methyl sulphide,[2] where the resulting ligand has a terminal methyl group in the *trans* position.

Table 7. Crystal data, details of intensity measurements, and structure refinements for $[PtBr_2\{MeS(CH_2)_3CH=CH_2\}]$

Formula	$C_6H_{12}Br_2PtS$
M	471.119
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	15.098(9)
b/Å	13.245(3)
c/Å	10.299(2)
U/Å^3	2 060(1)
Z	8
D_c/g cm^{-3}	3.039
F(000)	1 696
Crystal size (mm)	0.45 × 0.25 × 0.23
μ(Mo-*K*)/cm^{-1}	215.9

The effect of this isomerisation is to reduce the size of the ring from seven to six atoms, which is presumably favoured on steric grounds for palladium. The seven-membered ring in $[PtCl_2\{MeS(CH_2)_3CH=CH_2\}]$ shows no tendency to rearrange however. A similar observation has been made[9a,b] for the platinum complex of the alkenyl ketonic ligand 5-hexen-2-one, $[PtCl_2\{OC(Me)CH_2CH_2CH=CH_2\}]$, which does not rearrange although the seven-membered ring in $[PtBr_2(Me_2AsC_6H_4-CH_2CH=CHOMe)]$ does isomerise[9c] to a six-membered ring and forms $[PtBr_2(Me_2AsC_6H_4CH=CHCH_2OMe)]$. In the latter case conjugation of the double bond with the aromatic ring provides an additional driving force for rearrangement.

Although the ligand 5-hexen-2-one does not isomerise on co-ordination to platinum, its reaction with $PdCl_4^{2-}$ gives a dimeric η-allyl complex $[Pd_2Cl_2\{MeCH\text{-}CH\text{-}CHC(O)Me\}_2]$,[9b] presumably produced by reaction of the initially formed $[PdCl_2\{OC(Me)CH_2CH_2CH=CH_2\}]$. An analogous rearrangement of $[PdCl_2\{MeS(CH_2)_3CH=CH_2\}]$ is not favourable however since the sulphur atom in the ligand is bonded much more strongly to palladium than is the oxygen atom in the alkenyl ketonic ligand, and the isomerisation shown in the Scheme, in which co-ordination of sulphur is maintained, is observed instead. The analytical and spectroscopic data for $[PdCl_2\{MeS(CH_2)_3CH=CH_2\}]$ are consistent with its formulation given in the Scheme and are inconsistent with those expected for an allyl complex.

In addition to the two major isomers due to the two possible configurations at the sulphur atom in $[\mathrm{PdCl_2\{MeS(CH_2)_3CH=CH_2\}}]$, a further set of minor isomers is observed, representing 18% of the total. These presumably arise from the possibility of geometric isomerism at the alkene double bond.

Experimental

General.—Reactions were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen, and solvents were dried and distilled under nitrogen before use (although the products are not noticeably sensitive to either air or water). The ligands were prepared from the alkenyl bromide and potassium methyl sulphide in ethanol by analogy to a literature method,[1] and distilled. The selenide ligand, $\mathrm{MeSe(CH_2)_2CH=CH_2}$ was prepared from dimethyl diselenide: solid sodium tetrahydroborate (3.75 g, 0.1 mol) was added in 0.5-g quantities to a stirred solution of dimethyl diselenide (9.39 g, 0.05 mol) in tetrahydrofuran (100 cm^3) and methanol (100 cm^3) at room temperature in a flask (250 cm^3) fitted with a reflux condenser (**CAUTION**: hydrogen evolved). When addition of the $\mathrm{NaBH_4}$ was complete and the orange colour of the dimethyl diselenide had disappeared, the solution was brought to reflux and a solution of 4-bromo-1-butene (0.1 mol, 13.50 g) in methanol (75 cm^3) was added over a period of 15 min. The solution was stirred under reflux for a further 2 h. The ligand was obtained as a clear, yellow, evil-smelling liquid after chromatography (using Kieselgel 60-H silica) and distillation [b.p. 30 °C, 2 mmHg (*ca.* 266 Pa)].

All ligands were characterised by their i.r., ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra.

Preparations of the complexes *cis*-$[\mathrm{MCl_2(L)}]$ (M = Pd or Pt, L = alkenyl methyl selenide or sulphide) are exemplified below by that of $[\mathrm{PtCl_2\{MeS(CH_2)_3CH=CH_2\}}]$.

Preparation of cis-*Dichloro*(2-*thia*-6-*heptene*)*platinum*(II).—To a stirring solution of potassium tetrachloroplatinate(II) (1.00 g, 2.41 mmol) in water (10 cm^3), ethanol (3 cm^3), and 1 mol dm^{-3} hydrochloric acid (0.5 cm^3) was added 1 equivalent of the alkenyl methyl sulphide ligand, $\mathrm{MeS(CH_2)_3CH=CH_2}$ (0.280 g, 2.41 mmol). The initially red solution was left to stir at room temperature overnight. The precipitate was filtered off and washed with water, ethanol, and diethyl ether. After drying *in vacuo*, the complex was obtained in high yield as a pale yellow powder (0.76 g, 82%) which may be recrystallised from warm chloroform (Table 2).

Preparation of Bromo- and Iodo-derivatives.—These were prepared by metathesis of the chloro-derivative in warm acetone solution using the appropriate lithium halide in excess. In a typical preparation, for example that of *cis*-di-iodo(2-thia-6-heptene)platinum(II), a solution of lithium iodide (0.536 g, 4.0 mmol) in acetone was added to a warm (50 °C) stirring solution of *cis*-dichloro(2-thia-6-heptene)platinum(II) (0.5 g, 1.309 mmol) in acetone (15 cm^3). The colour darkens as the new halide complex forms. The acetone was removed under reduced pressure and the residue dissolved in chloroform from which the complex may be recrystallised after removal of the salt, lithium chloride, by filtration.

Reaction of $[\mathrm{PtCl_2\{MeS(CH_2)_3CH=CH_2\}}]$ *with* 2,6-*Dimethylphenyl Isocyanide.*—To a stirred solution of *cis*-dichloro(2-thia-6-heptene)platinum(II) (0.10 g, 0.262 mmol) in chloroform (5 cm^3) was added a solution of 2,6-dimethylphenyl isocyanide (0.034 g, 0.262 mmol) in chloroform (2 cm^3). After stirring at room temperature for 1 h, the solvent was removed under reduced pressure to yield the off-white product.

N.M.R. Studies.—Proton and ^{13}C-{^{1}H} experiments were performed on a Bruker AM250 instrument at 250 MHz. Unless solubility factors dictated otherwise, spectra between −30 and +55 °C were taken using $\mathrm{CDCl_3}$ as solvent, with $\mathrm{CDCl_2CDCl_2}$ being employed at high temperatures and $\mathrm{CD_2Cl_2}$ at low temperatures.

Crystal Structure Determination of $[\mathrm{PtBr_2\{MeS(CH_2)_3CH=CH_2\}}]$.—Crystals were grown from a two-layer liquid system of hexane over a chloroform solution of the complex. Crystal data and details of the structure refinement are summarised in Table 7.

Data collection. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[10] using a CAD4 diffractometer operating in the ω—2θ scan mode, with graphite-monochromated Mo-K_α radiation. A total of 1 805 unique reflections were collected ($3 \leqslant 2\theta \leqslant 50°$). The segment of reciprocal space scanned was h 0—17, k 0—15, l 0—12. The reflection intensities were corrected for absorption, using the azimuthal-scan method;[11] maximum transmission factor 1.00, minimum value 0.61.

Structure solution and refinement. The structure was solved by the application of routine heavy-atom methods (SHELX 86),[12] and refined by full-matrix least squares (SHELX 76).[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but in constrained positions (C–H 0.96 Å, U = 0.10 Å^2). The final residuals R and R' were 0.050 and 0.044 respectively for the 103 variables and 1 184 data for which $F_o > 3\sigma(F_o)$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, w, being defined as $1/[\sigma^2(F_o) + 0.0004F_o^2]$.

Atomic scattering factors and anomalous scattering parameters were taken from refs. 14 and 15 respectively. All computations were made on a DEC VAX-11/750 computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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