Platinum and Rhodium Complexes of Dialkenyl Telluroether Ligands: Synthesis, Dynamic Nuclear Magnetic Resonance and Crystal Structure of *cis*-Dibromo(3,3,7,7-tetramethyl-5-tellura-3,7-disilanona-1,8-diene)platinum(II)[‡]

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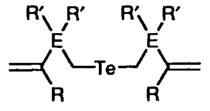
A number of dialkenyl telluroether ligands have been synthesised. Reaction with platinum(II) and rhodium(I) metal centres at low temperature in non-aqueous media yielded complexes in which the ligands are bidentate (binding through the tellurium atom and one alkene function) and tridentate, respectively. The bidentate platinum complexes are fluxional, exhibiting exchange of the alkene moieties, the energy barriers for which have been evaluated. Tellurium-125 NMR data have been obtained and are discussed with reference to the chelate ring effect. The crystal structure of $[PtBr_2\{Te(CH_2SiMe_2CH{=}CH_2)_2\}]$ has been determined: crystals are triclinic of space group $P\bar{1}$ with $a = 6.5837(9)$, $b = 8.8594(8)$, $c = 17.860(2)$ Å, $\alpha = 98.65(2)$, $\beta = 97.73(1)$, $\gamma = 111.26(1)°$ and $Z = 2$. The structure is monomeric with the platinum atom exhibiting square-planar geometry. The two bromine atoms are mutually *cis* and the di(silaalkenyl) telluroether ligand chelates to the metal *via* the tellurium atom and one alkene moiety.

Organotellurium chemistry (recently reviewed in an excellent article[1]), relative to that of its lighter chalcogen congeners, selenium[2] and sulfur,[3] has received considerably less investigative attention[4] due to the lower stability of many compounds. Recently, however, interest in tellurium chemistry has increased in a range of areas: organic,[5] inorganic[6] and co-ordination chemistry,[7] and has resulted in an expanding body of knowledge in terms of synthetic and analytical (NMR) procedures.[8–11]

Few telluroether metal complexes have been analysed crystallographically[1,10] and only two contain platinum: one is a double salt[12] and the other contains two methyl phenyl telluride ligands.[13] Hitherto, there have been no reported crystallographic studies of organometallic telluroether complexes of platinum.

As part of our continuing research[14–19] into dialkenyl chalcogenoether complexes of the platinum metals, we describe herein the synthesis and analysis of a range of telluroether ligands and complexes in order to effect a comparative study of structure and dynamic stereochemistry between sulfur-, selenium- and tellurium-containing species. In addition to ^1H and ^{13}C NMR, ^{125}Te NMR spectroscopy was undertaken. The latter nucleus is highly sensitive to its molecular environment, temperature, solvent and viscosity, and the shifts in resonance frequency upon co-ordination can aid in the understanding of structure and stereochemistry. The effect of ring size in chelate complexes upon ^{125}Te chemical shifts has been documented for a series of ditelluroether chelate complexes[1,11] and is discussed in the present work.



L^1 R = R′ = H, E = C
L^2 R = Me, R′ = H, E = C
L^3 R = R′ = H, E = Si

Results and Discussion

Preparation and Properties of the Complexes.—The dialkenyl telluroether ligands L^1–L^3 were prepared analogously to the selenoether ligands reported previously,[15,19] *i.e.* by reaction of an alkenyl halide with an aqueous solution of Na_2Te generated *in situ* by reduction of elemental tellurium using Rongalite $[Na(O_2SCH_2OH)]$ in aqueous sodium hydroxide. Since the ligands oxidise in air, forming intractable white solids (telluroxides[20]), manipulations were carried out under a reducing atmosphere of CO or an inert atmosphere of N_2. In marked contrast to the preparation of analogous dialkenylthioether and -selenoether complexes, it was necessary to synthesise the telluroether complexes in a non-aqueous medium at low temperature by displacement of the more labile monodentate ligand, dimethyl sulfide, from the dihalogenobis(dimethyl sulfide)platinum(II) complex. Initial attempts in both aqueous and non-aqueous media at room temperature resulted in decomposition to unidentifiable black materials. Preparation of the bromo- and iodo-derivatives by metathesis of the dichloro(dialkenyl telluride)platinum(II) complexes was also precluded by decomposition and required metathesis of the precursor dimethyl sulfide complex. The products were isolated as crystalline solids, somewhat less soluble and less stable in common solvents than their thio- and seleno-ether counterparts, and fully characterised on the basis of analytical and spectroscopic data. Infrared and analytical data for all the new complexes are reported in Table 1.

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[‡] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Characterisation of compounds

			Analysis^a (%)				Alkene stretch^b/cm^{-1}	
Sample	Nature	M.p./°C	C		H		Co-ordinated	Unco-ordinated
L^1	Orange malodorous oil		40.65	(40.40)	5.70	(5.95)	—	1639
L^2	Orange malodorous oil		45.20	(45.20)	6.85	(6.80)	—	1646
L^3	Orange malodorous oil						—	1594
$[PtCl_2L^1]$	Pale yellow crystals	156^c	18.80	(19.05)	2.80	(2.65)	1499	1637
$[PtBr_2L^1]$	Yellow crystals	134	16.20	(16.20)	2.40	(2.40)	1494	1631
$[PtCl_2L^2]$	Pale yellow crystals	161^c	22.50	(22.60)	3.30	(3.40)	1500	1641
$[PtBr_2L^2]$	Yellow needles	138^c	19.20	(19.35)	2.85	(2.90)	1504	1643
$[PtI_2L^2]$	Olive needles	129^c	16.80	(16.80)	2.35	(2.55)	1505	1645
$[PtCl_2L^3]$	Pale yellow crystals	143^c	19.90	(20.30)	3.60	(3.75)	1483	1594
$[PtBr_2L^3]$	Yellow crystals	139^c	17.65	(17.65)	3.05	(3.25)	1482	1594
$[PtI_2L^3]$	Dark yellow crystals	135^d	15.35	(15.50)	2.70	(2.85)	1484	1594
$[PtCl_2L^3(PPh_3)]^e$	Yellow crystals	160^d	38.50	(39.35)	4.20	(4.35)	—	1594
$[(RhClL^3)_2]$	Red crystals	135^d	25.95	(25.85)	4.70	(4.80)	1476	—

^{a} Calculated values in parentheses. ^{b} Ligand samples as liquid films; complexes as KBr discs. ^{c} Melts and decomposes. ^{d} Decomposes. ^{e} Far IR: 310.3s, 287.5s cm^{-1}.

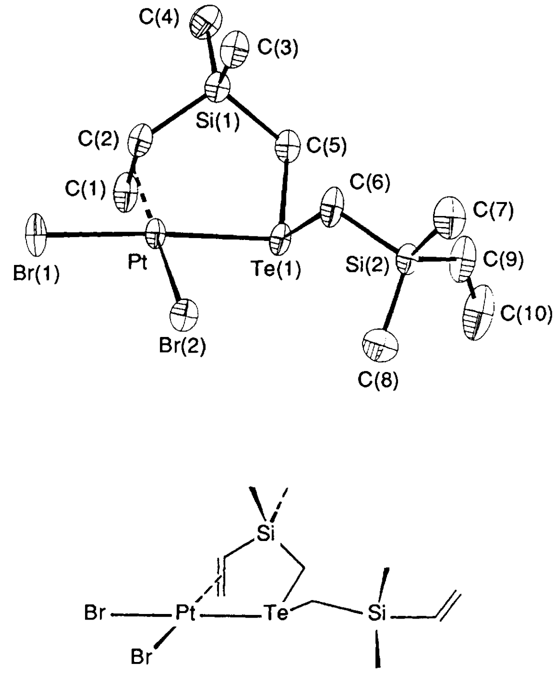


Fig. 1 Crystal structure of *cis*-dibromo(3,3,7,7-tetramethyl-5-tellura-3,7-disilanona-1,8-diene)platinum(II), $[PtBr_2L^3]$

Table 2 Selected bond lengths (Å) and angles (°) for $[PtBr_2L^3]$

Pt–Te(1)	2.544(1)	Pt–Br(1)	2.472(1)
Pt–Br(2)	2.444(1)	Pt–C(1)	2.157(5)
Pt–C(2)	2.156(5)	Te(1)–C(5)	2.142(9)
Te(1)–C(6)	2.152(7)	Si(1)–C(4)	1.852(11)
Si(1)–C(3)	1.863(9)	Si(1)–C(2)	1.865(9)
Si(1)–C(5)	1.881(9)	Si(2)–C(8)	1.852(11)
Si(2)–C(7)	1.849(9)	Si(2)–C(9)	1.866(10)
Si(2)–C(6)	1.878(9)	C(1)–C(2)	1.358(13)
C(9)–C(10)	1.279(16)	Pt–C(01)*	2.047(5)
Br(2)–Pt–Br(1)	91.43(4)	Br(2)–Pt–Te(1)	85.99(3)
Br(1)–Pt–Te(1)	176.66(3)	Te(1)–Pt–C(1)	92.7(1)
Br(1)–Pt–C(1)	89.1(1)	Br(2)–Pt–C(1)	160.0(1)
Te(1)–Pt–C(2)	92.1(1)	Br(1)–Pt–C(2)	90.9(1)
Br(2)–Pt–C(2)	163.1(1)	Te(1)–Pt–C(01)*	92.5(1)
Br(1)–Pt–C(01)*	90.0(1)	Br(2)–Pt–C(01)*	177.8(1)
C(5)–Te(1)–C(6)	96.3(4)	C(5)–Te(1)–Pt	99.1(2)
C(6)–Te(1)–Pt	102.9(2)	C(4)–Si(1)–C(3)	111.1(5)
C(4)–Si(1)–C(2)	109.4(5)	C(3)–Si(1)–C(2)	110.0(4)
C(4)–Si(1)–C(5)	108.4(5)	C(3)–Si(1)–C(5)	113.1(4)
C(2)–Si(1)–C(5)	104.7(4)	C(8)–Si(2)–C(7)	110.9(5)
C(8)–Si(2)–C(9)	111.8(6)	C(7)–Si(2)–C(9)	110.4(5)
C(8)–Si(2)–C(6)	109.2(5)	C(7)–Si(2)–C(6)	106.6(5)
C(9)–Si(2)–C(6)	107.6(5)	Pt–C(1)–C(2)	71.6(4)
C(1)–C(2)–Si(1)	125.9(7)	Pt–C(2)–C(1)	71.7(4)
Pt–C(2)–Si(1)	113.4(4)	Si(1)–C(5)–Te(1)	109.8(4)
Si(2)–C(6)–Te(1)	112.8(4)	C(10)–C(9)–Si(2)	124.2(11)

* C(01) denotes the centre of the co-ordinated C(1)=C(2) double bond.

Considering the rarity of crystallographic structural analyses of platinum telluroether complexes, and in order to make a detailed comparison of these complexes with their seleno- and thio-ether analogues, single-crystal X-ray diffraction was used to determine the solid-state structure of *cis*-dibromo(3,3,7,7-tetramethyl-5-tellura-3,7-disilanona-1,8-diene)platinum(II).

Crystal Structure of cis-*Dibromo*(3,3,7,7-*tetramethyl*-5-*tellura*-3,7-*disilanona*-1,8-*diene)platinum*(II), $[PtBr_2L^3]$.—The molecular structure of $[PtBr_2L^3]$ is shown in Fig. 1 and selected intramolecular bond lengths and angles are given in Table 2. The fractional atomic coordinates are given in Table 3

The complex is a square-planar monomer, the di(silaalkenyl) telluroether ligand chelating *via* the tellurium atom and an alkene moiety to adjacent co-ordination sites, while the two bromine atoms occupy the two remaining *cis* sites. The other alkene moiety is not co-ordinated to the metal and the alkenyl chain is positioned so as to minimise steric interaction with the bulk of the complex. In this respect, the structure is similar to that of *cis*-diiodo(3,3,7,7-tetramethyl-5-thia-3,7-disilanona-1,8-diene)platinum(II)[19] and *cis*-diiodo(5-thianona-1,8-diene)platinum(II),[15] although the configuration at the chalcogen atoms differs: in the present complex the pendant alkenyl chain is pseudoequatorially oriented, whereas in the latter two, it is pseudoaxial. This difference appears to be governed by the fact that the larger tellurium atom, smaller halogen and longer bonds to platinum (Pt–Te 2.544 Å) and carbon [Te–C(6) 2.152(7) Å] permit this pseudoequatorial geometry which is disfavoured in the sulfur complexes by the smaller chalcogen, larger halogen and shorter bond lengths (for $[PtI_2\{S(CH_2SiMe_2CH{=}CH_2)_2\}]$[19], Pt–S 2.287(3) and S–C(6) = 1.788(12) Å), resulting in the pseudoaxial arrangement at sulfur.

The Pt–Te bond distance [2.544(1) Å] is similar to that observed[12] in the double salt $[Pt\{PhTe(C_6H_4PPh_2\text{-}o)\}_2][Pt(SCN)_4]$ (2.575 Å); these are comparable with Pd–Te bond distances (*e.g.* for the co-ordinatively bound Te in $[\{Pd[o\text{-}C_6H_4(TeMe)Te]I\}_4]$, the Pd–Te bond length[21] is 2.540 Å) due to the similarity of the covalent radii[22] of platinum and palladium (1.31 Å). The co-ordinated alkene centroid–platinum bond length [2.047(5) Å] is shorter than that in the analogous iodo thioether complex [19] [2.052(14) Å]. This difference mirrors that between the bromo alkenyl thioether complex $[PtBr_2\{MeS(CH_2)_3CH{=}CH_2\}]$[14] (2.047 Å) and the iodo dialkenyl thioether complex $[PtI_2\{S(CH_2CH_2CH{=}CH_2)_2\}]$[15] (2.086 Å) and appears to be due to the greater *trans* influence of iodine compared to bromine. The co-ordinated and unco-ordinated C=C bond lengths are 1.358(13) and 1.279(16) Å, the lengthening upon co-ordination, Δ*d*, thus being 0.08 Å. This is considerably less than Δ*d* for $[PtI_2\{S(CH_2SiMe_2CH{=}CH_2)_2\}]$[19] (0.13 Å) and $[PtI_2\{S(CH_2CH_2CH{=}CH_2)_2\}]$[15] (0.19 Å) and may be taken as an indication of a weaker metal–alkene interaction.[19] This is consistent with an earlier comparison[23] between co-ordinated vinylsilanes and their carbon analogues based on ^1H NMR data.

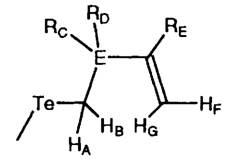
NMR Studies.—Variable-temperature ^1H NMR data are given in Table 4; ^{13}C, ^{29}Si and ^{125}Te data are in Table 5. It is reasonable to assume that each of the platinum complexes has a structure similar to that of $[PtBr_2L^3]$ discussed above and that the rhodium complex has a structure similar to that observed for the sulfur analogue.[19]

Considering first the platinum complexes: at low temperature (173 K), the ^1H NMR spectrum of the representative complex $[PtBr_2L^3]$ indicates the presence of two alkene moieties in different environments, one co-ordinated (^1H resonances at about δ 4.3 and 4.6) and the other unco-ordinated (resonances at δ 5.8 and 6.1). Conclusive proof for this would be the

Table 3 Atomic coordinates (× 10^4) for $[PtBr_2L^3]$

Atom	*x*	*y*	*z*
Pt	1059.1(5)	1204.6(3)	2212.6(2)
Te(1)	−1432.8(9)	−678.2(6)	2950.8(3)
Br(1)	3617(2)	3135(1)	1569(1)
Br(2)	4168(2)	1382(1)	3187(1)
Si(1)	−3592(4)	−1789(3)	1082(2)
Si(2)	−70(4)	−3384(3)	3825(1)
C(1)	−1630(15)	1751(11)	1656(6)
C(2)	−1580(15)	393(11)	1203(5)
C(3)	−2271(17)	−3252(12)	773(6)
C(4)	−6129(18)	−2170(15)	365(6)
C(5)	−4361(14)	−1910(11)	2054(5)
C(6)	−367(16)	−2713(10)	2881(6)
C(7)	522(19)	−5276(12)	3627(7)
C(8)	2250(18)	−1705(14)	4539(7)
C(9)	−2775(19)	−3859(14)	4146(7)
C(10)	−3011(25)	−3091(19)	4773(9)

Table 4 Proton NMR data for ligands and complexes[a]



L^1 R = H, E = C
L^2 $R_C = R_D = H, R_E = Me, E = C$
L^3 $R_C = R_D = Me, R_E = H, E = Si$

(*i*) Value at fast-alkene exchange

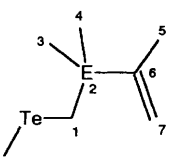
Sample	A	B	C	D	E	F	G
L^1	2.54	2.54	2.68	2.68	5.80	5.10	5.10
L^2	3.43	3.43	3.57	3.57	3.07[b]	4.56	4.56
L^3	1.78	1.78	0.17[c]	0.17[c]	6.17	5.97	5.72
$[PtCl_2L^1]$[d,e]	2.78	2.78	2.78	2.78	5.40	4.80	4.54
$[PtBr_2L^1]$[d,e]	2.75	2.75	2.75	2.75	5.45	4.89	4.53
$[PtCl_2L^2]$[d,f]	2.81	2.81	2.81	2.81	1.96[b]	4.71	4.42
$[PtBr_2L^2]$[d]	2.82	2.82	2.82	2.82	1.96[b]	4.84	4.42
$[PtI_2L^2]$[d]	2.64	2.64	2.82	2.82	1.97[b]	5.10	4.49
$[PtCl_2L^3]$[d,g]	1.84	1.84	0.32[c]	0.39[c]	4.50	5.37	5.37
$[PtBr_2L^3]$[d]	1.83	1.83	0.33[c]	0.39[c]	4.95	5.43	5.43
$[PtI_2L^3]$	1.78	1.91	0.32[c]	0.38[c]	5.08	5.57	5.57
$[PtCl_2L^3(PPh_3)]$	1.73	2.82	0.12[c]	0.12[c]	6.04	5.84	5.60
$[(RhClL^3)_2]$	1.42	1.82[h]	0.29[c]	0.48[c]	4.26	4.26	3.22

(*ii*) Values at static state

	Co-ordinated			Unco-ordinated		
Sample	E	F	G	E	F	G
$[PtBr_2L^1]$	5.7	4.4	4.0	5.5	5.1	5.1
$[PtCl_2L^2]$	2.0	4.3	4.1	1.7	4.8	4.7
$[PtBr_2L^2]$	2.0	4.8	4.2	1.7	4.8	4.6
$[PtI_2L^2]$	2.1	4.8	4.3	1.7	5.1	4.7
$[PtCl_2L^3]$	4.4	4.3	4.3	6.0	5.7	5.7
$[PtBr_2L^3]$	4.6	4.3	4.3	6.1	5.8	5.8
$[PtI_2L^3]$	4.9	4.3	4.3	6.0	5.7	5.7

[a] In $CDCl_3$ at 303 K unless indicated otherwise; shifts (δ) relative to $SiMe_4$ in ppm. [b] Refers to methyl protons. [c] C and D refer to silyl methyl protons. [d] Overlapping alkyl signals. [e] In $CDCl_2CDCl_2$. [f] At 333 K. [g] At 313 K. [h] Broad.

Table 5 Carbon-13 ^{29}Si and ^{125}Te NMR data[a]



L^1 3,4,5 = H, E = C
L^2 3,4 = H, 5 = C, E = C
L^3 3,4 = C, 5 = H, E = Si

	^{13}C[b]								
Sample	1	2	3	4	5	6	7	^{29}Si[b]	^{125}Te[c]
L^1	1.18	36.37	—	—	—	139.05	115.15	—	275.41
L^2	−0.03	21.92	—	—	40.58	146.17	110.47	—	289.36
L^3	−2.21	—	−14.49	−14.49	—	138.58	132.18	−4.61	53.87
$[PtCl_2L^3]$	—	—		—	—	—	—	—	463[d]
$[PtBr_2L^3]$[e]	−2.26	—	−0.98	−1.38	—	103.9	110.9	—	—
$[PtI_2L^3]$[e]	−1.07	—	−1.79	−1.49	—	103.8	111.6	—	—
$[PtCl_2L^3(PPh_3)]$[f]	2.17	—	−1.57	−1.67	—	137.36	133.62	−5.38	388.3, 389.3

[a] At 303 K in $CDCl_3$; non-silyl-substituted complexes too insoluble. [b] Shifts (δ) relative to $SiMe_4$. [c] Shifts (δ) relative to $TeMe_2$. [d] Broad. [e] At 310 K. [f] Phenyl resonances: δ *o*, 128.3; *m*, 134.85; *p*, 131.3; *i*, 129.8.

observation of $^2J(^{195}\text{Pt}-^1\text{H})$ coupling between the co-ordinated alkene protons and the platinum nucleus. This was precluded, however, by the broadness of the spectrum at low temperatures and also due to the temperature dependence of the chemical shift anisotropy term in the relaxation expression for the platinum nucleus which results in short T_1 values.[15,24] The alkene proton resonances for the free ligand L^3 (δ 5.72, 5.97 and 6.17) correlate well with the peaks at δ 5.8 and 6.1 for $[PtBr_2L^3]$, multiplicity being determined by integration. This is less direct, but still valid, evidence for the assignments given above.

The infrared spectra of the complexes in the solid state are consistent with the low-temperature NMR data in that each shows two bands: for $[PtBr_2L^3]$ these occur at 1482 and 1594 cm^{-1} (see Table 1). These are characteristic of co-ordinated and unco-ordinated vinylsilane, respectively.[19] The far IR spectrum of the (phosphine)chloro complex, $[PtCl_2L^3(PPh_3)]$, shows two bands at 287.5 and 310.3 cm^{-1}, consistent with the retention of a *cis* structure.

Whereas for certain of the thioether complexes [15] two sets of co-ordinated alkenyl chain resonances are observed at low temperature, due to the two epimers arising from the two possible configurations at the pyramidal sulfur atom, only one set is observed for the telluroether complexes. This does not necessarily indicate, however, the existence of only one epimer, rather that they are indistinguishable, resulting from the fact that the minor isomer peaks are likely to be very small (because the larger tellurium atom sterically favours one configuration—presumably pseudoequatorial, as observed in the solid state) and are overlapped by major isomer peaks.

As the temperature is raised, the signals in the ^1H NMR spectra undergo broadening and gradual coalescence as the unco-ordinated alkene begins to exchange with the co-ordinated alkene. Coalescence occurs at about −50 °C, at which temperature the lines are very broad. Above −50 °C, the spectra sharpen yielding peaks with chemical shifts at the average of the static-state values. This is entirely analogous to the observations made for other dialkenyl chalcogenoether complexes.[15,18,19]. The Gibbs free energies of the exchange transition state, $\Delta G^‡$, have been calculated, based on the coalescence temperature for the alkene exchange process and the data are given in Table 6.

In contrast to the thioether and some selenoether complexes,[15,18,19] where at higher temperature further signal broadening and coalescence due to pyramidal atomic inversion[25,26] of the chalcogen atom was observed, no further broadening was evident for the telluroether complexes up to temperatures at which decomposition occurred (110 °C). This is indicative of a higher inversion energy barrier for tellurium, and is consistent with the established barrier trend of S < Se < Te.[27,28]

Tellurium-125 *NMR*. Tellurium has a total of 39 isotopes[29] (including nuclear isomers), although the vast majority of these are unstable or of negligible abundance. Of the key isotopes, two have nuclear spin of $I = \frac{1}{2}$ and are thus potential candidates for use as NMR probes: ^{123}Te and ^{125}Te. The former occurs in 0.89% abundance, rather low for easy observation, but the latter, occurring in 7.10% natural abundance, is much more suitable. With a receptivity[30] relative to ^1H of 2.21×10^{-3} (12.5 relative to ^{13}C) observation of the ^{125}Te signal might initially appear a routine matter. However, the absence of a positive nuclear Overhauser effect (NOE) whilst decoupling the protons and sensitivity to the factors outlined earlier, *vis.* molecular environment, solvent, temperature and viscosity, render observation a little less trivial.

Table 6 Coalescence and energy barrier data for alkene exchange from variable-temperature ^1H NMR studies

Complex	T_c/K	$\Delta G_{T_c}^‡$/kJ mol^{-1}
$[PtCl_2L^1]$*	—	—
$[PtBr_2L^1]$	193	37
$[PtCl_2L^2]$	246	49.3
$[PtBr_2L^2]$	238	47.6
$[PtI_2L^2]$	243	49
$[PtCl_2L^3]$	253	47.4
$[PtBr_2L^3]$	240	45.0
$[PtI_2L^3]$	223	41

* Too insoluble at low temperature.

Spectra of the ligands were relatively easily recorded, since the concentration of the solution could be made quite high (≈30% m/v). The peaks occurred at around δ 200 relative to $TeMe_2$ with the exception of L^3, the peak for which appears at about δ 55, probably due to the proximity of the silicon atom. These values are within the range expected[1] for dialkyl telluroethers (δ 150–300). For the complex $[PtCl_2L^3]$, chosen because of its considerably greater solubility due to the presence of the silyl moieties, a broad ($\nu_{\frac{1}{2}}$ *ca.* 780 Hz, *cf. ca.* 10 Hz for L^3), weak signal was detected with difficulty at δ 463. (The broadness of this signal is possibly due to the existence of two epimeric forms of the complex, differing in chirality at tellurium, the ^{125}Te NMR signals of which partially overlap.) This downfield shift relative to the free ligand is indicative of a co-ordinated tellurium atom and is considered also to be influenced by the chelation of the ligand. Garrou,[31] discussing phosphorus NMR spectroscopy, initially correlated the variation of ^{31}P chemical shift upon co-ordination of diphosphine ligands to a metal with metallacycle size in terms of a 'chelate ring parameter'. Subsequently, a similar correlation was noted for both ^{77}Se[32,33] and ^{125}Te.[11] The chemical shift depends upon co-ordination to a metal (the difference from the free ligand signal to which is termed the 'co-ordination shift', Δ), and for chelating ligands, the size of the metallacycle (the value due to which is the chelate ring parameter, ΔR).

In the complex $[PtCl_2L^3]$, the 3,3,7,7-tetramethyl-5-tellura-3,7-disilanona-1,8-diene ligand forms a five and a half-membered ring upon chelation in the solid state, but in solution at 303 K the alkenyl chains are exchanging, resulting in a considerably more flexible ensemble. When one equivalent of triphenylphosphine is added to a solution of $[PtCl_2L^3]$, the broad weak signal at δ 463 is replaced by two much stronger, sharper ($\Delta\nu_{\frac{1}{2}}$ *ca.* 10 Hz) resonances of equal intensity (centred at δ 388.8) separated by a, presumably *cis*-^2J(P–Te), coupling of 79 Hz and coupled to platinum [with $^1J(^{125}\text{Te}-^{195}\text{Pt})$ 571.5 Hz]. This indicates displacement of the co-ordinated alkene moiety by the phosphorus atom.

The various chemical shift parameters due to co-ordination and chelation (Δ and ΔR, respectively), above, may thus be quantified [equations (1) and (2)]. Thus from equation (1)

$$\Delta_{\text{complex}} = \delta_{\text{complex}} - \delta_{\text{free ligand}} \quad (1)$$

$\Delta_{[PtCl_2L^3]} = 409.1$ ppm and $\Delta_{[PtCl_2L^3(PPh_3)]} = 334.1$ ppm, and using these values in equation (2), the chelate ring parameter

$$\Delta R = \Delta_{\text{chelate complex}} - \Delta_{\text{equivalent monodentate complex}} \quad (2)$$

ΔR for $[PtCl_2L^3]$ may be evaluated as 75.0 ppm.

Literature data on the chelate ring parameter for ^{125}Te[1,11] are rather sparse, but show clearly that ΔR is large and positive (⩾200 ppm) for five-membered rings and small (⩽50 ppm, positive or negative) for six-membered rings. The value of ΔR derived above for $[PtCl_2L^3]$ which contains a five and a half-membered ring is thus consistent with the published data since it is between the values for the five- and six-membered rings. The fact that it lies closer to the six-membered ring values is arguably a result of the alkene exchange process which effectively enlarges and renders more flexible the time-averaged structure of the $[PtCl_2L^3]$ metallacycle. The complex $[PtCl_2L^3]$ appears to be the first example of a hetero-donor ligand complex for which the ^{125}Te chelate ring parameter has been evaluated, and the first for which the evaluations of $\Delta_{\text{chelate complex}}$ and $\Delta_{\text{equivalent monodentate complex}}$ have been made using complexes containing identical ligands, L^3 in each case (previous evaluations of $\Delta_{\text{equivalent monodentate complex}}$ were based upon complexes containing the nearest structurally equivalent monodentate ligand, rather than the identical ligand).

Considering now the rhodium complex $[(RhClL^3)_2]$: the NMR spectrum at room temperature is broad, suggesting the occurrence of a fluxional process. However, the infrared spectrum shows only one absorption at 1476 cm^{-1}, characteristic of a co-ordinated alkene and no absorption due to un-co-ordinated alkene. A possible explanation may be that, in the solid state, both alkene functions co-ordinate in a dimeric, chloride-bridged structure containing two trigonal-bipyramidal rhodium atoms, as was observed in the case of the sulfur analogue of this ligand, $[\{RhCl[S(CH_2SiMe_2CH{=}CH_2)_2]\}_2]$,[19] but that in solution, metallacycle ring-twisting, or, despite the absence of a pendant alkene, some alkene labilisation and reco-ordination, may occur, although at a rate sufficiently slow as to be comparable with, and hence broad on, the NMR time-scale. It is not possible to identify absolutely this process yet. At lower temperatures (273 K and below), however, in contrast to the platinum complexes, the ^1H NMR spectra, although sharpening, become extremely complicated, showing eight major resonances in the $SiMe_2$ region. Such complexity in the low-temperature spectra is consistent with the freezing out of the fluxional process into three chemically distinct molecular geometries, which, for the alkene-labilisation scenario, would correspond to the following (referring to just one half of the dimer): first, a species in which the two alkene ends point towards each other; secondly, one in which they point away from each other; and thirdly, one in which they both point in the same direction. Whilst the elemental analysis data corroborate the assigned stoichiometry, obtaining other NMR spectroscopic data (^{13}C, ^{29}Si and ^{125}Te) was precluded by the fluxional process.

Experimental

General.—Reactions were carried out using standard Schlenk techniques under a reducing atmosphere of carbon monoxide during preparation and purification of the ligands, and under dry nitrogen during synthesis of the complexes. Solvents were dried and distilled under nitrogen before use.

The ligands were prepared from the alkenyl chloride (L^3) or bromide (L^1 and L^2) and sodium telluride (formed *in situ*) as exemplified in the synthesis of L^3. Under an atmosphere of CO, tellurium powder (3.424 g, 26.83 mmol) and Rongalite $[Na(O_2SCH_2OH)]$ (7.691 g, 49.90 mmol) were combined in a warm (50 °C) solution of sodium hydroxide (5.989 g, 149.71 mmol) in water (35 cm^3) and stirred for 1 h to generate Na_2Te. The mixture was then heated to reflux and (chloromethyl)-dimethyl(vinyl)silane (7.000 g, 51.97 mmol) was added dropwise. The mixture was refluxed for a further 5 h. After diethyl ether extraction of the cool mixture, drying over magnesium sulfate and molecular distillation [115 °C, 8 mmHg (*ca.* 10.6 × 10^2 Pa)], the ligand was obtained as an orange liquid (0.922 g, 11%).

Preparations of the complexes are exemplified by those of $[PtCl_2L^3]$ and $[(RhClL^3)_2]$.

Preparation of cis-*Dichloro*(3,3,7,7-*tetramethyl*-5-*tellura*-3,7-*disilanona*-1,8-*diene*)*platinum*(II), $[PtCl_2L^3]$.—To a cold (−80 °C) stirring solution of dichlorobis(dimethyl sulfide)-platinum(II) (0.493 g, 1.059 mmol) in dichloromethane (75 cm^3) was added dropwise a solution of 1 equivalent of L^3 (0.413 g, 1.267 mmol) in dichloromethane (2 cm^3). The solution was allowed to warm to room temperature over 18 h, and stirring continued after that for a further 6 h. The solvent was then removed under reduced pressure, the yellow product washed with hexane and recrystallised from a cold (−25 °C) dichloromethane–hexane two-layer liquid system.

Table 7 Crystal data and structure refinement for $[PtBr_2L^3]$

Empirical formula	$C_{10}H_{22}Br_2PtSi_2Te$
M	680.97
Crystal system	Triclinic
a/Å	6.5837(9)
b/Å	8.8594(8)
c/Å	17.860(2)
α/°	98.65(2)
β/°	97.73(1)
γ/°	111.26(1)
U/Å^3	939.4(2)
Space group	$P\bar{1}$
Z	2
D_c/g cm^{-3}	2.408
$F(000)$	620
μ/cm^{-1}	133.51
Crystal size/mm	0.36 × 0.28 × 0.20
θ range for data/°	3.36–29.99
h_{min}, h_{max}	−5, 8
k_{min}, k_{max}	−12, 12
l_{min}, l_{max}	−17, 24
Total data measured	5024
Total unique (R_{int})	4350 (0.0574)
No. of parameters/data	149/4350
Absorption correction factors, min/max.	0.846/1.451
Goodness-of-fit on F_o^2	0.490
ρ_{min}, ρ_{max}/e Å^{-3}	−1.635, 1.702
R_1*	0.057 (0.047)
wR_2*	0.127 (0.115)

* $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o)^2]$; R_1 and wR_2 values for 2800 data with $I > 2\sigma(I)$ are given in parentheses.

The bromo- and iodo-derivatives were similarly prepared from the appropriate dihalogenobis(dimethyl sulfide)platinum(II) complex [obtained by metathesis of dichlorobis-(dimethyl sulfide)platinum(II) using 3.5 equivalents of the appropriate lithium halide in hot acetone].

*Preparation of Di-*μ*-chlorobis*[(3,3,7,7-*tetramethyl*-5-*tellura*-3,7-*disilanona*-1,8-*diene*)*rhodium*(I)], $[(RhClL^3)_2]$.—To a cold (−80 °C) stirring suspension of $[\{Rh(CH_2CH_2)_2Cl\}_2]$ (0.300 g, 0.771 mmol) in dichloromethane (30 cm^3) was added dropwise a solution of L^3 (0.503 g, 1.543 mmol) in dichloromethane (2 cm^3). The mixture was stirred for 28 h and then allowed to warm to room temperature and stirred for a further 5 h. The solvent was then removed under reduced pressure and the red-brown product washed with hexane and recrystallised from cold (−25 °C) dichloromethane–hexane.

NMR Studies.—The NMR experiments were performed on a Brüker AM250 instrument operating at: ^1H, 250.130; ^{13}C, 62.896; ^{29}Si, 49.690 and ^{125}Te, 78.950 MHz, the former three relative to $SiMe_4$, and the latter relative to $TeMe_2$. Low-temperature spectra were recorded in CD_2Cl_2; otherwise, $CDCl_3$ was used.

Crystal Structure Determination of $[PtBr_2L_3]$.—Crystals suitable for X-ray analysis were grown from a cold, concentrated methylene chloride solution. The crystal data, details of intensity measurements and structure refinement are summarised in Table 7.

The unit-cell parameters and intensity data were obtained at 293 K using a Delft Instruments FAST TV area detector diffractometer and Mo-Kα radiation (λ = 0.710 69 Å) by following previously described procedures.[34] The structure was solved by Patterson methods (SHELX-S)[35] and refined by full-matrix least squares (SHELXL-93)[36] using all unique F_o^2 data corrected for absorption (DIFABS).[37] All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in idealised positions with U_{iso} parameters tied to the U_{eq}

parameters of the parent carbons. Sources of scattering factors are as in ref. 36.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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