Palladium(II) Complexes derived from the Potentially Chelating Ligands 2,2,*NN*-Tetramethylpent-4-enylamine and 2,2-Dimethylpent-4-enyl Methyl Sulphide. Crystal Structures of Dichloro[2,2-dimethylpent-(*E*)-3-enyl methyl sulphide]palladium(II) and Chloro[1—3-η-*syn*-1-(1,1′-dimethyl-2′-methylthioethyl)allyl]palladium(II)

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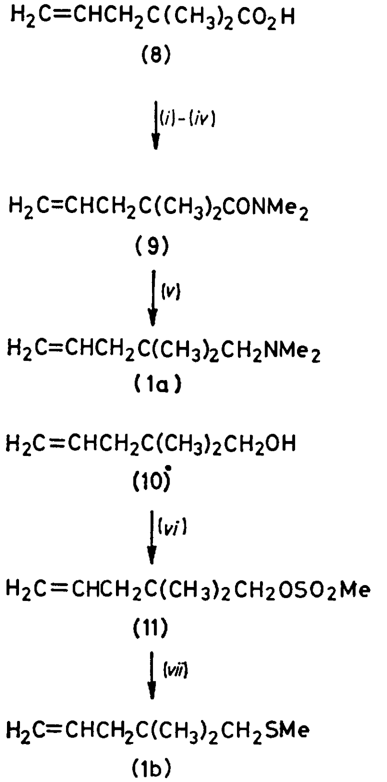
Reaction of $PdX_2{\cdot}2PhCN$ (X = Cl or Br) with 2,2,*NN*-tetramethylpent-4-enylamine (1a) gives complexes (2) of stoicheiometry $PdX_2{\cdot}$(1a) in which Pd–X has added to the olefinic bond to generate a seven-membered chelate ring. In contrast, 2,2-dimethylpent-4-enyl methyl sulphide (1b) initially gives labile olefinic complexes, which readily rearrange to the derivatives (5a) and (5b) of 2,2-dimethylpent-(*E*)-3-enyl methyl sulphide (13). Variable-temperature ^1H n.m.r. studies show that at low temperatures (5a) and (5b) exist in solution as pairs of epimers at sulphur, while heating leads first to equilibration of the epimers and then to labilisation of the metal–olefin bond. The π-allyl species (6a) and (6b) have been prepared from (5a) and (5b). *X*-Ray structures of (5a) and (6a) are reported. Crystals of (5a) are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 8.365(2)$, $b = 15.068(2)$, $c = 9.595(1)$ Å, and $\beta = 94.00(1)°$. Crystals of (6a) are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 6.583$, $b = 12.462$, $c = 12.859(6)$ Å, and $\beta = 96.20(5)°$. Both structures have been solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R = 0.023$ for 2 414 reflections for (5a) and to $R = 0.046$ for 2 515 reflections for (6a). The five-membered chelate rings in (5a) and (6a) have C(2)-envelope conformations. In (5a) principal dimensions are Pd–Cl 2.313 and 2.320(1), Pd–S 2.269(1), and Pd–C 2.195 and 2.231(3) Å, and the interplanar angle between the $PdCl_2S$ plane and the Pd–ethylenic carbon plane is 96.0°. In (6a) dimensions are Pd–Cl 2.381(1), Pd–S 2.364(1), Pd–C 2.089, 2.120, and 2.173(5) Å; the plane of the allyl moiety forms a dihedral angle of 116.4° with the PdSClC(5) plane.

CONTINUING our studies[1] of the complexes of aliphatic polydentate ligands which have quaternary carbon atoms in the backbone, we have prepared the potentially chelating olefinic ligands 2,2-*NN*-tetramethylpent-4-enylamine (1a) and 2,2-dimethylpent-4-enyl methyl sulphide (1b) and examined their reactions with the bis(benzonitrile) complexes of palladium(II) chloride and bromide. Reports of complexes of palladium(II) with potentially chelating ligands containing the pent-4-en-1-yl moiety are sparse[2,3] and in these complexes the double bond is free. However, chelated complexes are formed with *o*-allylphenyl arsines and phosphines[4] and with *O*-methyl *N*-allylthiocarbamate.[5] In these cases, ring formation presumably involves a smaller loss of rotational entropy and, in addition, some of the bonds between the ligating moieties are shorter than in simple pentenyl systems. The present study was undertaken to determine if the '*gem*-dialkyl effect'[1,6] would be of sufficient magnitude to force chelation.

RESULTS AND DISCUSSION

The ligands, (1a) and (1b), were prepared as outlined in the Scheme.[7,8] The sulphide ligand (1b) contained a significant amount of a by-product which gave 2 : 1 complexes with $PdCl_2$ and $PdBr_2$ (see Experimental section); this by-product has been identified as 2,4,4-trimethyltetrahydrothiophen presumably formed (*cf.* ref. 9) from the mesylate precursor and sodium sulphide which, in turn, would result from the presence of higher sulphides in the dimethyl disulphide. A purer sample of (1b) was obtained, although in poorer yield, by using the tosylate rather than the mesylate, a change which apparently reduces the tendency for formation of this by-product.

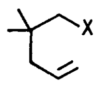
Addition of (1a) to solutions of $PdCl_2{\cdot}2PhCN$ in a variety of solvents (benzene, dichloromethane, acetone, nitromethane, and benzonitrile) resulted in the precipitation of a product which is practically insoluble in non-co-ordinating solvents and which analysed for $PdCl_2{\cdot}$(1a). Its ^1H n.m.r. spectrum in $(CD_3)_2SO$ {see [4a; L = dmso (dimethyl sulphoxide)] in Table 1} suggests a structure (2a) in which Pd–Cl has added across the olefinic bond. The presence of a single highly coupled proton at δ 3.99 allows assignment of structure (2a) rather than the alternative (3). Proton n.m.r. spectra of the solutions remaining after precipitation of (2a) from dichloromethane, nitromethane, and benzonitrile showed essentially the same peak pattern as solutions of (2a) in dimethyl sulphoxide. The formation of an analogous seven-membered ring in the case of platinum(II) has been reported.[10] The absence of i.r. absorptions between 1 500 and 1 650 cm^{-1} confirms that (2a) contains neither a free, nor a co-ordinated, double bond while a moderately strong band at 770 cm^{-1} may be assigned to ν(C–Cl). The insolubility of this complex in non-co-ordinating solvents precluded a determination of the relative molecular mass, although it is likely that it has the dimeric structure shown. Its ready solubility in dimethyl sulphoxide is presumably due to cleavage to monomeric species in this solvent. As anticipated, addition of 1 mol equivalent (per palladium atom) of pyridine, triphenylphosphine, or methyldiphenylphosphine to a suspension of (2a) in dichloromethane resulted in dissolution of the complex. Proton n.m.r. spectra of the material precipitated from these solutions by dilution with n-hexane indicated that cleaved products (4a) were formed {see for example ^{1}H n.m.r. of [4a; L = py (py = pyridine)] in Table 1}. However, the spectra also showed resonances arising from free ligand (1a), and attempts to recrystallise the precipitates led to decomposition and release of (1a).



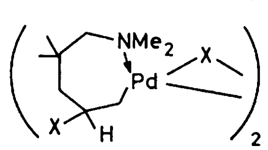
SCHEME Preparation of the ligands (1a) and (1b): (*i*) Na[HCO_3]; (*ii*) dry; (*iii*) ClCOCOCl–C_6H_6; (*iv*) $HNMe_2$; (*v*) Li[AlH_4]; (*vi*) $MeSO_2Cl$–C_6H_5CN; (*vii*) Na–MeSSMe–P(NMe_2)$_3$O.

Similar treatment of (2a) with 1 mol equivalent of 2,2'-bipyridyl (bipy) resulted in clean regeneration of (1a) with formation of $PdCl_2$·bipy. Treatment of (2a) in dichloromethane–dimethyl sulphoxide with acetylacetone in the presence of anhydrous potassium carbonate also led to displacement of the olefinic ligand.

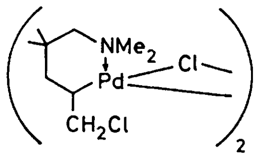
Addition of (1a) to a solution prepared by heating palladium(II) bromide in benzonitrile resulted in the precipitation of a product, (2b), the ^{1}H n.m.r. [(4b), Table 1] and i.r. spectra of which confirm that it is analogous to the chloride discussed above. Addition of benzene to a solution of the complex in dimethyl sulphoxide gave a crystalline precipitate which analysed for (4b; L = dmso). The co-ordination of the dimethyl sulphoxide through sulphur is shown[11] by the presence of a very strong band in its i.r. spectrum at 1 091 cm^{-1} while a strong band at 220 cm^{-1} may be assigned to terminal Pd–Br *trans* to N rather than C.



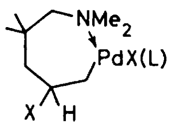
(1a) X = NMe_2
(1b) X = SMe



(2a) X = Cl
(2b) X = Br



(3)



(4a) X = Cl
(4b) X = Br

Reaction of (1b) with PdX_2·2PhCN (X = Cl or Br) gave labile olefinic complexes rather than insoluble products of Pd–X addition analogous to those discussed above. Thus, $PdCl_2$·2PhCN dissolved readily in $CDCl_3$ containing 1 mol equivalent of (1b). The ^{1}H n.m.r.

TABLE 1

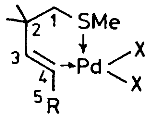
Hydrogen-1 n.m.r. data (p.p.m., Hz observed) for ligands and complexes at ambient temperature

Compound	Solvent	C–Me	N(S)–Me	N(S)–CH_2	C(3)–H	C(4)–H	C(5)–H
(1a)[a]	$CDCl_3$	0.87	2.28	2.08	2.03 (2 H,d,br[b])	5.80 (m)	5.04 (2 H, m)
(4a; L = dmso)[c]	$(CD_3)_2SO$	1.15, 1.19	2.85, 3.06	3.37	1.66 (m), 1.95 (m)	3.99 (m)	1.95 (m), 2.36 (dd[d])
(4a; L = py)[a]	$CDCl_3$	1.18, 1.20	2.97, 3.53	3.27 (m)	*e* *e*	4.27 (m)	*e* 2.58 (dd[f])
(4b; L = dmso)[c]	$(CD_3)_2SO$	1.15, 1.18	2.79, 3.02	3.35	*g* *g*	4.06 (m)	*g* 2.35 (dd[d])
(1b)[a]	$CDCl_3$	0.95	2.05	2.38	2.03 (2 H, d,br[h])	5.67 (m)	4.98 (2 H, m)
$PdCl_2$·(1b)[a]	$CDCl_3$	1.26	2.38	2.78 (vbr)	2.30 (2 H, d,br[h])	5.85 (m)	5.08 (d,br[i]), 5.28 (d,br[j])
(5a)[c] (i)[k]	$CDCl_3$	1.30, 1.64	2.74	2.71 (d[l]), 2.81 (d[l])	5.70 (d[i])	5.61 (m)	2.09 (3 H, d[m])
(ii)		1.29, 2.00	2.59	2.35 (d[i]), 3.11 (d[i])	5.80 (d[i])	5.61 (m)	2.00 (3 H, d[m])
$PdBr_2$·2 PhCN + (1b)[a]	$CDCl_3$	1.17	2.52	3.00 (br)	2.19 (2 H, d,br[h])	5.80 (m)	5.17 (2 H, m)
(5b)[c,n] (i)[k]	$CDCl_3$	1.30, 1.59	2.63	2.75 (d[l]), 2.81 (d[l])	5.81 (d[i])	5.64 (m)	2.18 (3 H, d[o])
(ii)		1.27, 1.93	2.86	2.32 (d[i]), 3.15 (d[i])	5.91 (d[i])	5.64 (m)	2.06 (3 H, d[o])
(13)[a]	$CDCl_3$	1.07	2.08	2.48	*p* *p*	*p*	1.66 (3 H, m)
(6a)[a]	$CDCl_3$	1.29, 1.33	2.57	3.50	4.27 (d[q])	5.68 (m)	3.03 (dd[r]), 4.00 (dd[s])
(6b)[b]	$CDCl_3$	1.32, 1.36	2.60	3.42	4.33 (d[q])	5.64 (m)	3.03 (dd[r]), 4.00 (dd[t])
(12a)[a]	$CDCl_3$	1.15, 1.33		2.70 (d[u]), 3.27 (dd[v])	*w* 1.93 (m[x])	4.05 (m)	1.48 (2 H, d[y])
(12b)[a]	$CDCl_3$	1.18, 1.31		3.05 (d[z]), 3.48 (d,br[z])	*w* 1.93 (m *)	4.36 (m)	1.51 (2 H, d[y])

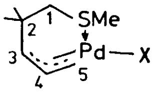
[a] 60 MHz. [b] J = 7.5 Hz. [c] 220 MHz. [d] J = 14.6 Hz. [e] Overlapping multiplet 1.68—2.33. [f] J = 14.0, 5.8 Hz. [g] Overlapping multiplet 1.86—2.11. [h] J = 7 Hz. [i] J = 15 Hz. [j] J = 8 Hz. [k] (i) Major isomer, (ii) minor isomer in mixture. [l] J = 12 Hz. [m] J = 5 Hz. [n] At −40 °C. [o] J = 6 Hz. [p] Overlapping narrow multiplet 5.38—5.53. [q] J = 10.8 Hz. [r] *anti*-H, J = 11.0, 1.0 Hz. [s] *syn*-H, J = 6.8, 0.9 Hz. [t] *syn*-H, J = 6.5, 1.0 Hz. [u] J = 11.3 Hz. [v] J = 11.3, 1.4 Hz. [w] Partially obscured multiplet at *ca.* 1.5. [x] J = 12.0, 6.0, 1.4 Hz. [y] J = 6.3 Hz. [z] J = 11.7 Hz. * J = 12.8, 6.6, 1.6 Hz.

spectrum of the resulting solution shows downfield shifts, relative to free-ligand values, of all resonances. Addition of hexane to this solution gave a pale yellow precipitate free of benzonitrile. The ^{1}H n.m.r. spectrum of this material at ambient temperature (Table 1) shows additional downfield shifts of all resonances, except those attributed to *S*-methyl and *S*-methylene protons although the overall change in shift for each resonance is still significantly smaller than those observed for authentic chelating olefin complexes of palladium(II) (see for example ref. 1). Upon cooling, all the resonances broaden and split and as temperatures approach —40 °C the lines resharpen. The resulting spectrum is very complicated but particularly noteworthy are the olefinic resonances which cover a wider range of chemical shifts (δ 4.5—6.8) than in a spectrum run at ambient temperature (δ 4.85—6.5). The changes in the spectrum upon cooling cannot be explained as arising solely from the freezing out of sulphur inversion [1] but may also involve a reduction in the rate of equilibration of complexes containing free and co-ordinated olefin. Evidence for the presence of such species was provided by the i.r. spectrum of a solution † of this material in dichloromethane which showed absorptions at 1 643 and 1 552 cm^{-1}, the latter being the more intense. Attempts to purify this material either by crystallisation, or chromatography, converted it into a product whose ^{1}H n.m.r. (Table 1) and i.r. spectra (see Experimental section) establish its structure as (5a). Indeed the growth of resonances due to this isomerised product was observed when spectra of the precursor were run at temperatures above ambient. The *trans* configuration of the olefinic bond in (5a) is also established by the *X*-ray analysis discussed below and by the absence of detectable amounts of *cis* isomer in the ligand displaced from (5a) with 2,2′-bipyridyl. Double bond isomerisation in a potentially chelating olefinic ligand has apparently not been reported for palladium.

The ^{1}H n.m.r. spectrum of (5a) at ambient temperatures shows resonances attributable to two isomers differing only in their configuration at sulphur. Upon heating, this spectrum shows changes due first (>50 °C) to the onset of rapid (on the n.m.r. time scale) inversion at sulphur and then (>90 °C) labilisation of the palladium–olefin bond. This situation is analogous to that described earlier [1] for the complex (5c; X = Cl). However, two interesting observations can be made when the spectra of (5c; X = Cl) and of (5a) are compared. First, palladium–olefin bond labilisation becomes rapid at a lower temperature for the latter, presumably reflecting a weaker interaction. Second, the proportion of the minor sulphur epimer is significantly greater in (5a) [minor : major, 5 : 9 as compared with 2 : 7 [1] in (5c; X = Cl)]. The second observation can be rationalised in terms of chelate-ring geometries related to those proposed [1] for (5c), the S–CH_2 proton resonance pattern for (5a) showing that the latter adopts similar conformations about the S–CH_2 bond to those of the former. In our earlier paper [1] we suggested, on the basis of ^{1}H n.m.r. evidence, that the complexes (5c) adopt an envelope conformation in which the double bond is not perpendicular to the metal co-ordination plane, while the terminal olefinic carbon atom may lie closer to palladium than does the other one. If (5a) were to adopt a similar conformation, the vinylic methyl group would experience a substantial interaction with the *cis*-chlorine. This interaction could be relieved by rotation of the double bond back towards the perpendicular orientation and/or by bringing Pd closer to C(3) and away from C(4). Our *X*-ray study of (5a) shows that the chelate ring does adopt an envelope conformation and that C(3) is closer to Pd than C(4) by 0.036 Å.



(5a) R = Me, X = Cl
(5b) R = Me, X = Br
(5c) R = H, X = Cl, Br, or I



(6a) X = Cl
(6b) X = Br

The crystal structure (Figure 1) contains discrete monomeric molecules (Figure 2) separated by normal van der Waals distances. The palladium atom is four-co-ordinate [Pd–Cl 2.313 and 2.320(1), Pd–S 2.269(1), and Pd–C 2.195 and 2.231(3) Å] but is distorted from square-planar geometry. Thus, if one chooses the Pd–Cl(1)–Cl(2) moiety as a reference plane then S lies 0.254 Å below this plane and olefinic carbon atoms C(3) and C(4) are respectively 0.606 Å below and 0.772 Å above the plane. These distortions presumably help to minimise intramolecular repulsions between (*i*) the ethylenic proton H(4) and both axial proton H(1a) [H(4) · · · H(1a) 2.21 Å] and the pseudo-equatorial *S*-methyl group [H(4) · · · H(61) 2.45 Å], and (*ii*) terminal methyl group C(5) and Cl(1) [C(5) · · · Cl(1) 3.237 Å].

The interplanar angle between the best Pd–Cl_2–S plane and the Pd–C(3)–C(4) plane is 96.0° and the S–Pd–C(3)–C(4) torsion angle is 98.5°. The five-membered chelate ring Pd–S–C(1)–C(2)–C(3) is close to a C(2)-envelope conformation with C(2) 0.663 Å below the plane through Pd, S, C(1), and C(3) and the C(3)–Pd–S–C(1) torsion angle is —4.1°. This conformation is remarkably similar to that found [12] in di-μ-chloro-bis[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*CN*]dipalladium. The remaining molecular dimensions (Table 2) are not significantly different from expected values.

These *X*-ray results appear to lend credibility to our earlier conclusions concerning the conformations of the (5a) epimeric pair, the major epimer corresponding to the solid-state structure. The greater proportion of minor epimer found for (5a) as compared with (5c; X = Cl) may

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† A Nujol-mull spectrum of the solid showed bands at 1 642 and 1 522br cm^{-1}. The latter band is probably due to (5a) (see below) formed *during the mulling procedure* since a ^{1}H n.m.r. spectrum of the material recovered from the Nujol mull showed resonances ascribable to both the starting complex and the rearranged product (5a).

be rationalised as follows. Rotation of the double bond closer to the normal with respect to the average co-ordination plane in order to reduce the compression between C(5) and Cl(1) is accompanied in the major isomer of (5a) by the development of interactions between H(4) and both the *S*-methyl group and H(1a). Similar rotation in the minor isomer of (5a) leads to the development of only the H(4), H(1a) interaction and to some relief of the interaction between the pseudo-axial *C*-methyl and *S*-methyl groups.

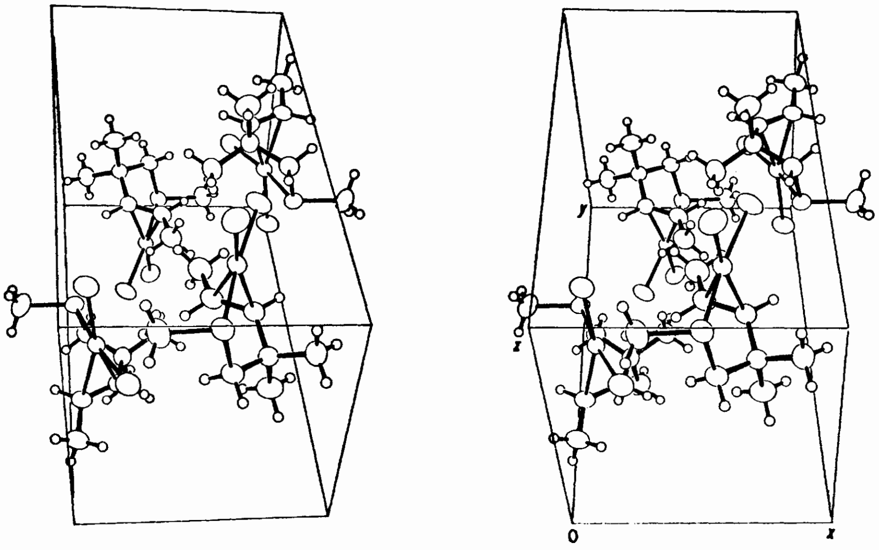


FIGURE 1 Stereoview of the crystal structure of (5a)

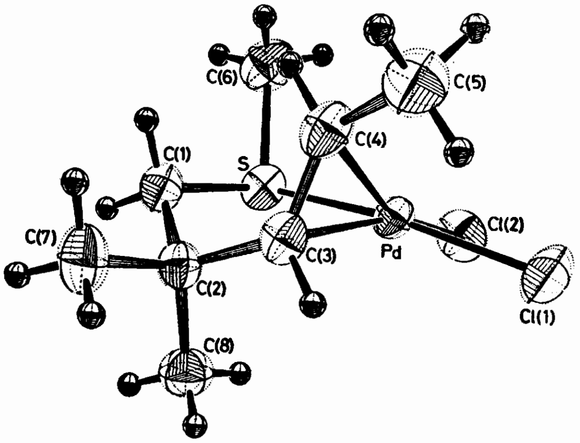


FIGURE 2 The molecule (5a) with the numbering scheme

Reaction of $PdBr_2{\cdot}2PhCN$ with (1b) in $CDCl_3$ afforded a solution, the ^1H n.m.r. spectrum of which is analogous to that obtained for the chloride under the same conditions. The solvent was evaporated and attempts were made to purify the residue by crystallisation. These led only to recovery of the complex (5b), which contains isomerised ligand. Chromatography of the initial residue also failed to yield pure $PdBr_2{\cdot}(1b)$ giving instead (5b) and additionally, on occasions when (5b) was left for long periods on the plates before recovery, the π-allyl complex (6b). Infrared and ^1H n.m.r. data for these complexes are recorded (Experimental section and Table 1 respectively).

At ambient temperature the ^1H n.m.r. spectrum of (5b) is broadened due to relatively slow inversion at sulphur and upon cooling resonances due to the two possible sulphur epimers are resolved. The *S*-methylene resonance pattern again suggests pseudo-equatorial and pseudo-axial *S*-methyl orientations in the major and minor isomers respectively. Integration gives an isomer ratio of 5 : 2, a value which accords with earlier indications that in this type of complex the contribution of the minor isomer to the equilibrium is enhanced on going from iodide to bromide to chloride [1] and from complexes

TABLE 2

Interatomic distances (Å) and angles (°) for (5a)

(*a*) Bond lengths			
Pd–Cl(1)	2.313(1)	C(1)–C(2)	1.529(5)
Pd–Cl(2)	2.320(1)	C(2)–C(3)	1.532(4)
Pd–S	2.269(1)	C(2)–C(7)	1.546(5)
Pd–C(3)	2.195(3)	C(2)–C(8)	1.530(5)
Pd–C(4)	2.231(3)	C(3)–C(4)	1.380(5)
S–C(1)	1.814(3)	C(4)–C(5)	1.495(5)
S–C(6)	1.805(4)		
(*b*) Angles			
Cl(1)–Pd–Cl(2)	91.3(1)	S–C(1)–C(2)	108.9(2)
Cl(1)–Pd–S	173.0(1)	C(1)–C(2)–C(3)	109.8(3)
Cl(1)–Pd–C(3)	85.9(1)	C(1)–C(2)–C(7)	108.8(3)
Cl(1)–Pd–C(4)	93.5(1)	C(1)–C(2)–C(8)	112.5(3)
Cl(2)–Pd–S	85.9(1)	C(3)–C(2)–C(7)	106.3(3)
Cl(2)–Pd–C(3)	162.5(1)	C(3)–C(2)–C(8)	110.0(3)
Cl(2)–Pd–C(4)	159.2(1)	C(7)–C(2)–C(8)	109.2(3)
S–Pd–C(3)	85.5(1)	Pd–C(3)–C(2)	108.2(2)
S–Pd–C(4)	91.4(1)	Pd–C(3)–C(4)	73.3(2)
C(3)–Pd–C(4)	36.3(1)	C(2)–C(3)–C(4)	125.1(3)
Pd–S–C(1)	101.8(1)	Pd–C(4)–C(3)	70.4(2)
Pd–S–C(6)	108.3(1)	Pd–C(4)–C(5)	114.8(2)
C(1)–S–C(6)	102.3(2)	C(3)–C(4)–C(5)	123.8(3)
(*c*) Non-bonded distances			
Pd · · · C(5)	3.164	H(4) · · · H(11)	2.21
Cl(1) · · · C(5)	3.237	H(4) · · · H(61)	2.45
C(1) · · · C(4)	2.940		

of 2,2-dimethylbut-3-enyl methyl sulphide to complexes of 2,2-dimethylpent-(*E*)-3-enyl methyl sulphide (see above). As found for the complexes of the former, (5c), both inversion at sulphur and labilisation of the Pd–olefin bond become rapid on the n.m.r. time scale at lower temperatures for the bromide than the chloride. Thus, for (5b), broadening and collapse due to acceleration of these two processes occurs in the ranges 10—40 and 60—90 °C respectively.

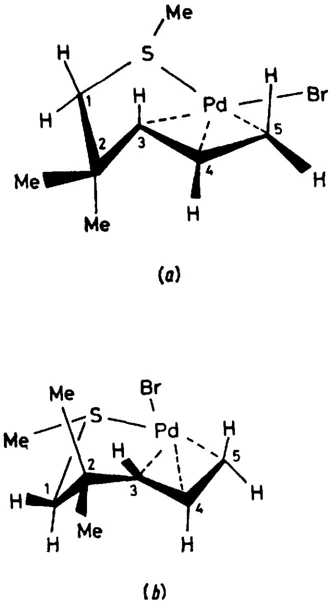
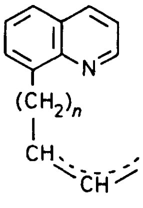


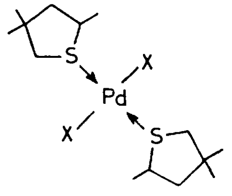
FIGURE 3 Possible solution conformations of (6b)

The resonance pattern of the vinylic protons in the ^{1}H n.m.r. spectrum of (6b) indicates that the $-C(CH_3)_2CH_2-SCH_3$ fragment adopts the *syn* configuration, as is found for (6a) in the solid state (see below). In $CDCl_3$ two resonances are observed for the *C*-methyl groups as expected. However, both the *S*-methylene and the *S*-methyl resonances are sharp singlets at ambient temperature although their shift positions indicate that the sulphur atom is co-ordinated to palladium. When a CD_2Cl_2 solution of (6b) was cooled to −90 °C the *S*-methylene resonance split into an AB quartet (*J ca.* 11.5 Hz) but no other significant change occurred in the spectrum. Unless the chemical shifts of these methylene protons have different temperature dependencies then a single species has been frozen out. In either case the conformation about the *S*-methylene carbon atom is probably similar to that ascribed to the major isomers of (5c; X = Cl), (5a), and (5b), namely with the *S*-methyl bond intersecting the neighbouring methylene H–C–H bond angle. The solid-state conformations of this moiety in (5a) and (6a) are compared below. A study of molecular models indicates that if (6b) is monomeric [see discussion of (6a) below] two possible solution conformations [Figures 3(*a*) and 3(*b*)] may be drawn which fulfil this requirement. Of these, the one shown in Figure 3(a) should be preferred since it lacks the eclipsing interaction between Pd–Br and the *S*-methyl group present in the other one. The lack of an observable long-range coupling[1] between the C(3)–H and the pseudo-equatorial *S*-methylene proton even in the low-temperature spectrum supports this conclusion.

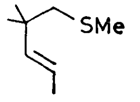
No π-allyl product was obtained during the purification of (5a) by chromatography. However, addition of 1 equivalent of triethylamine to $PdCl_2 \cdot 2PhCN$ and (1b) in acetone afforded (6a) in good yield. Its ^{1}H n.m.r. spectrum (Table 1) shows a similar temperature dependence to that described for (6b). A strong band in the i.r. spectrum at 277 cm^{-1} indicates the presence of terminal Pd–Cl while the mass spectrum contains a group of strong peaks corresponding to the various isotopic compositions expected for the monomeric species (6a). However, in the latter spectrum a group of very weak peaks at *m*/*e* values corresponding to dimeric species could be discerned.[13] This, along with the ^{1}H n.m.r. and i.r. evidence that sulphur is co-ordinated and chlorine terminal, led us to consider a ligand-bridged dimeric structure rather than the monomeric chelate (6a). Indeed, a dimeric structure appeared reasonable in the light of the suggestion[14] that relatively strain-free chelating π-allylic complexes are to be expected from ligands of the type (7) only when *n* = 2 or 3. The temperature dependence of the ^{1}H n.m.r. spectrum might then have been explained as resulting from dimer–monomer or perhaps ligand-bridged dimer–halogen-bridged dimer equilibria. However, our *X*-ray analysis shows unequivocally that the crystal structure (Figure 4) contains discrete monomeric species (Figure 5) separated by normal van der Waals distances; molecular dimensions are in Table 3. In addition to the allyl–metal interactions the complex (6a) contains a simple five-membered chelate ring which adopts a C(2)-envelope conformation [torsion angle C(1)–S–Pd–C(3) 8.7°, C(2) 0.653 Å from the plane of C(1)–S–Pd–C(3)]. Further, C(2) is displaced 0.306 Å from the allyl plane towards the Pd atom. Such a displacement is a feature common[14] to alkyl allyl complexes and in the case of (6a) doubtless favours the formation of the chelated π-allyl system. The conformations of the chelate rings in (5a) and (6a) are similar, the major differences being in the Pd–C(3)–C(2) angle [increased by 7.5° in 6(a)] and the Pd–S (increased by 0.095 Å) and S–C(1) (increased by 0.030 Å) bond lengths. The orientations of the pseudo-equatorial *S*-methyl group in (5a) and (6a) are also very similar and the *S*-methyl bond intersects the neighbouring methylene



(7)



(12a) X = Cl
(12b) X = Br



(13)

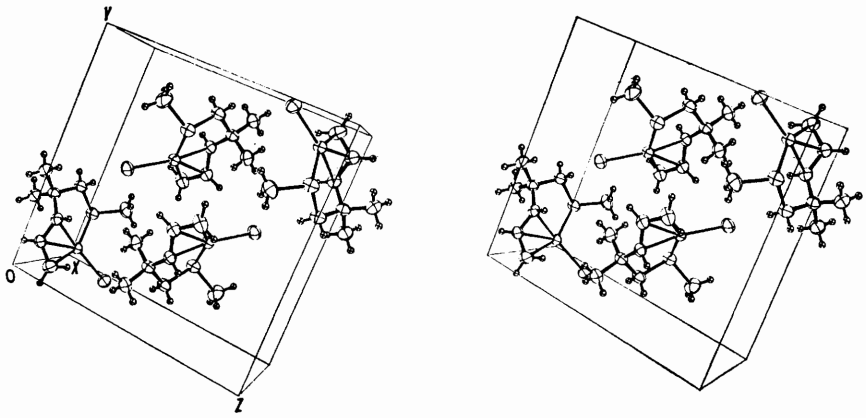


FIGURE 4 Stereoview of the crystal structure of (6a)

TABLE 3

Interatomic distances (Å) and angles (°) for (6a)

(*a*) Bond lengths

Pd–Cl	2.381(1)	C(1)–C(2)	1.530(8)
Pd–S	2.364(1)	C(2)–C(3)	1.530(7)
Pd–C(3)	2.089(5)	C(2)–C(7)	1.517(8)
Pd–C(4)	2.120(6)	C(2)–C(8)	1.515(8)
Pd–C(5)	2.173(5)	C(3)–C(4)	1.407(7)
S–C(1)	1.845(6)	C(4)–C(5)	1.430(8)
S–C(6)	1.797(6)		

(*b*) Angles

Cl–Pd–S	100.5(1)	C(1)–C(2)–C(3)	106.2(4)
Cl–Pd–C(3)	167.0(2)	C(1)–C(2)–C(7)	107.6(5)
Cl–Pd–C(4)	142.9(2)	C(1)–C(2)–C(8)	111.0(5)
Cl–Pd–C(5)	107.2(2)	C(3)–C(2)–C(7)	109.4(5)
S–Pd–C(3)	84.1(1)	C(3)–C(2)–C(8)	112.4(5)
S–Pd–C(4)	114.3(2)	C(7)–C(2)–C(8)	110.0(5)
S–Pd–C(5)	152.3(2)	Pd–C(3)–C(2)	115.8(3)
C(3)–Pd–C(4)	39.0(2)	Pd–C(3)–C(4)	71.7(3)
C(3)–Pd–C(5)	68.8(2)	C(2)–C(3)–C(4)	125.6(5)
C(4)–Pd–C(5)	38.9(2)	Pd–C(4)–C(3)	69.3(2)
Pd–S–C(1)	98.3(2)	Pd–C(4)–C(5)	72.6(3)
Pd–S–C(6)	110.4(2)	C(3)–C(4)–C(5)	116.4(5)
C(1)–S–C(6)	101.2(3)	Pd–C(5)–C(4)	68.5(3)
S–C(1)–C(2)	109.9(4)		

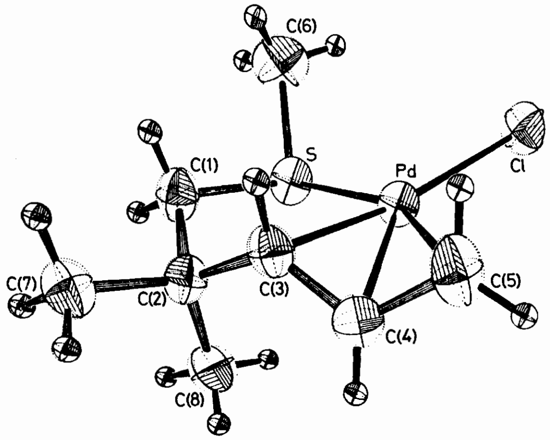


FIGURE 5 The molecule (6a) with the numbering scheme

H-C-H bond angle [Me-S-C(1)-H torsion angles in (5a) are 22 and $-96°$; in (6a) the corresponding values are 29 and $-90°$].

The co-ordination about palladium [with Pd-C(3) 2.089(5), Pd-C(4) 2.120(6), and Pd-C(5) 2.173(5) Å; Table 3] is similar to that reported[15] for other π-allyl systems. Thus the Pd, S, Cl, and C(5) atoms form a planar system (maximum deviation 0.003 Å) with C(3) 0.447 Å above and C(4) 0.426 Å below this plane while the plane of the allyl moiety forms a dihedral angle of 116.4° with the Pd-S-Cl-C(5) plane. The rotation of the allyl system to bring C(5) into the co-ordination plane might suggest a significant contribution of a localised σ-π form [C(5) σ-bonded] to the ground-state structure. Similar distortions in unsymmetrical π-allyl complexes have been taken[16] to suggest contributions from localised σ-π structures. In (6a), such a situation would call for C(3)-C(4) [1.407(7) Å] having more double bond character than C(4)-C(5) [1.430(8) Å] and indeed the difference in the bond lengths lies in this direction. Unfortunately, it is not possible to evaluate this suggestion further on the basis of the Pd-C distances because of *trans* influences and the unsymmetrical substitution of the allyl system. It should be noted that in (6a) the Pd-C bond with greater σ character lies *trans* to the ligand atom of higher *trans* influence. This contrasts with the situation for previously reported unsymmetrical π-allyl complexes of Pd.

The ^{1}H n.m.r. data discussed above are compatible with (6a) [and (6b)] having similar structures in both solution and solid states. The observation of geminal coupling (Table 1) for the C(5) protons is consistent with the conclusion that the Pd-C(5) bond has some σ character.

EXPERIMENTAL

General details have been reported.[1] Proton n.m.r. data for ligands and complexes are collected in Table 1 and physical and analytical data for complexes in Table 4.

Ligands.—Ligands were prepared by the routes outlined in the Scheme. Amide (9) [36.0 g, b.p. 98—102 °C (water pump)] was prepared from 2,2-dimethylpent-4-enoic acid[7] (8) (39.4 g) and reduced with lithium aluminium hydride (8.8 g) to (1a) [19.5 g, b.p. 145 °C (760 mmHg)].* The mesylate (11) [19.2 g, b.p. 98—99 °C (0.003 mmHg)] of the alcohol[8] (10) (16.8 g) was added to the mixture obtained by reaction of sodium (2.4 g) with dimethyl disulphide (4.95 g)

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

in hexamethylphosphoramide (70 cm^3). After heating at 100 °C for 16 h the mixture was distilled to minimum volume at the water pump. The distillate was poured into water (700 cm^3) and the resulting mixture extracted with pentane. Distillation of the pentane extract afforded impure (1b) [7.0 g, b.p. 68—69 °C (water pump)]. This contained (^{1}H n.m.r.) a small amount of (10) and 2,4,4-trimethyltetrahydrothiophen. The former was removed by heating over sodium and redistilling.

Complexes of (1a).—Addition of a solution of (1a) (283 mg, 2 mmol) in dichloromethane (10 cm^3) to a solution of bis(benzonitrile)dichloropalladium(II) (767 mg, 2 mmol) in the same solvent (50 cm^3) gave an orange solution from which a dark brown gum (169 mg) soon precipitated. The supernatant solution was decanted and upon standing a yellow solid (2a) (426 mg) gradually separated. A ^{1}H n.m.r. spectrum of the gum in $(CD_3)_2SO$ was very similar to that of the yellow solid. Addition of (1a) to $PdCl_2{\cdot}2PhCN$ in any one of benzene, benzonitrile, acetone, or nitromethane gave similar results.

A solution of dibromopalladium(II) in benzonitrile was prepared by heating $PdBr_2$ (266 mg) with the solvent (7 cm^3) at 100 °C for 3 h and then filtering the mixture. When the ligand (141 mg) was added to this solution an orange-yellow solid (2b) (361 mg) was deposited during 16 h. Addition of benzene to a concentrated solution of this compound in dimethyl sulphoxide resulted in the precipitation of yellow crystalline (4b; L = dmso).

Complexes of (1b).—A solution of (1b) (148 mg, 1.03 mmol) and $PdCl_2{\cdot}2PhCN$ (383 mg, 1.0 mmol) in dichloromethane (5 cm^3) was chromatographed on a silica gel column (10 g). Elution with dichloromethane afforded fractions containing benzonitrile, dichlorobis(2,4,4-trimethyltetrahydrothiophen)palladium(II) (12a) (47 mg), and a small amount (9 mg) of (5a), which were separated by preparative t.l.c. Elution of the column with dichloromethane–acetone (19 : 1) afforded essentially pure (5a) (251 mg); $\nu_{max.}$ at 1 535m (co-ordinated C=C), 318s ν(Pd–Cl), 301m cm^{-1} ν(Pd–Cl). Treatment of a solution of (5a) (80 mg) in dichloromethane (10 cm^3) with 2,2′-bipyridyl (40 mg) resulted in the deposition of $PdCl_2{\cdot}$bipy and the liberation of 2,2-dimethylpent-3-enyl methyl sulphide (13) which was identified by ^{1}H n.m.r. (see Table 1).

A solution of $PdCl_2{\cdot}2PhCN$ (384 mg, 1.00 mmol), (1b) (144 mg, 1.00 mmol), and triethylamine (101 mg, 1.00 mmol) in acetone (8 cm^3) was stirred at ambient temperature for 1 h during which time a black precipitate [Pd^0] separated. Evaporation of the solvent and preparative t.l.c. (dichloromethane–acetone, 97 : 3) of the residue afforded the π-allyl complex, (6a) (194 mg).

A solution of lithium bromide (191 mg, 2.20 mmol) in acetone (10 cm^3) was added to a solution of $PdCl_2{\cdot}2PhCN$ (384 mg, 1.00 mmol) and (1b) (144 mg, 1.00 mmol) in the same solvent (10 cm^3). Evaporation of the acetone gave the crude palladium complex, $PdBr_2{\cdot}$(1b), which dissolved readily in $CDCl_3$ (see ^{1}H n.m.r. in Table 1). [A solution giving an identical ^{1}H n.m.r. spectrum was obtained by dissolving $PdBr_2{\cdot}2PhCN$ (1 mmol) in $CDCl_3$ (2 cm^3) containing (1b) (1 mmol).] Chromatography of the crude $PdBr_2{\cdot}$(1b) complex over silica gel (10 g) and successive elution with dichloromethane containing acetone (0,2,5, and 10%) gave first benzonitrile and dibromobis(2,4,4-trimethyltetrahydrothiophen)palladium(II) (12b) (51 mg after preparative t.l.c.) followed by mixtures containing the relatively insoluble (5b) (247 mg); $\nu_{max.}$ at 1 535s cm^{-1} (co-ordinated C=C).

TABLE 4

Analytical and physical data for the complexes

Compound	Colour	M.p.*	Analysis (%) Found C	H	N	Calc. C	H	N
(2a)	Yellow	153—155	33.7	6.25	4.35	33.95	6.0	4.4
(4b; L = dmso)	Yellow	118—120	27.45	5.35	2.85	27.2	5.2	2.9
(5a)	Yellow	200—202	29.95	5.25		29.9	5.0	
(12a)	Orange	104—105	38.0	6.15		38.4	6.45	
(6a)	Yellow	160—162	33.65	5.4		33.7	5.3	
(5b)	Orange-red	187—188	23.1	4.1		23.4	3.95	
(12b)	Orange-red	146—147	31.8	5.7		31.9	5.35	
(6b)	Yellow	168—171	29.15	4.85		29.15	4.6	

* Uncorrected, °C, with decomposition.

Treatment of a solution of (5b) (151 mg) in acetone (50 cm^3) with triethylamine (100 mg) for 4 h at ambient temperature gave (6b) (96 mg after preparative t.l.c.).

Structure Analyses of (5a) *and* (6a).—*Crystal Data.* (i) (5a), $C_8H_{16}Cl_2PdS$, M = 321.6, Monoclinic, a = 8.365(2), b = 15.068(2), c = 9.595(1) Å, β = 94.00(1)°, U = 1 206.4 Å^3, Z = 4, D_c = 1.77 g cm^{-3}, $F(000)$ = 640, space group $P2_1/n$ (C_{2h}^5, no. 14) uniquely from systematic absences $h0l$ if $h + l = 2n + 1$, $0k0$ if $k = 2n + 1$, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 19.4 cm^{-1}.

(ii) (6a), $C_8H_{15}ClPdS$, M = 285.1, Monoclinic a = 6.583(5), b = 12.462(9), c = 12.859(6) Å, β = 96.20(5)°, U = 1 048.8 Å^3, Z = 4, D_c = 1.81 g cm^{-3}, $F(000)$ = 568, space group $P2_1/c$ (C_{2h}^5, no. 14) uniquely from systematic absences $h0l$ if $l = 2n + 1$, $0k0$ if $k = 2n + 1$, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 19.9 cm^{-1}.

For both structures, accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflections (with θ in the range 10—20°) measured on a Hilger and Watts Y290 four-circle diffractometer. Intensity data were collected in our usual way[12] to a maximum θ of 25°; 2 414 unique data were collected for (5a) and 2 515 for (6a). After corrections for Lorentz, polarization, and absorption effects, the data with $I > 2\sigma(I)$ [1 650 for (5a), 1 672 for (6a)] were labelled observed and used in structure solution and refinement.

Both structures were solved by the heavy-atom method and Fourier maps based on palladium phases revealed the complete structures. Initial refinement by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms lowered R to 0.084 for (5a) and 0.056 for (6a). Difference maps then revealed all hydrogen atoms; these were allowed for (in geometrically idealized positions with C–H 0.95 and $U_{\text{iso.}}$ 0.10 Å^2) in subsequent calculations. For (5a), refinement converged at $R = 0.023$ and $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.029$; for (6a), the final R and R' values were 0.046 and 0.050 respectively. In the least-squares calculations, scattering factors for Pd, Cl, S, and C were taken from ref. 17; those for hydrogen were from ref. 18 and allowance was made for anomalous dispersion.[19] Weights in the refinement were based on counting statistics and final difference syntheses were devoid of any significant features.

For (5a), final fractional co-ordinates are in Table 5 and molecular dimensions are in Table 2; the crystal structure is shown in Figure 1 and the molecule and numbering scheme are in Figure 2. For (6a), final co-ordinates are in Table 6 and molecular dimensions are in Table 3; Figures 4 and 5 show the crystal structure and molecular structure respectively.

For both (5a) and (6a) lists of observed and calculated structure factors, anisotropic thermal parameters, and mean plane data have been deposited as Supplementary Publication No. SUP 22653 (29 pp.).*

TABLE 5

Final positional parameters ($\times 10^4$) for (5a) with standard deviations in parentheses

Atom	x/a	y/b	z/c
Pd	3 805(1)	2 158(1)	1 045(1)
Cl(1)	2 715(1)	3 531(1)	467(1)
Cl(2)	4 084(1)	1 831(1)	−1 288(1)
S	4 600(1)	738(1)	1 476(1)
C(1)	4 174(4)	605(2)	3 292(3)
C(2)	2 713(4)	1 170(2)	3 577(3)
C(3)	3 010(4)	2 137(2)	3 177(3)
C(4)	4 487(4)	2 548(3)	3 249(3)
C(5)	4 721(5)	3 523(3)	3 477(4)
C(6)	6 762(5)	708(3)	1 570(4)
C(7)	2 502(5)	1 167(3)	5 164(4)
C(8)	1 173(5)	830(3)	2 801(4)
H(11)	5 078	773	3 895
H(12)	3 951	−15	3 479
H(3)	1 973	2 498	3 131
H(4)	5 540	2 183	3 425
H(51)	5 549	3 745	2 913
H(52)	3 756	3 833	3 209
H(53)	5 032	3 653	4 428
H(61)	7 162	904	719
H(62)	7 199	1 085	2 312
H(63)	7 146	117	1 759
H(71)	3 441	1 400	5 668
H(72)	1 608	1 526	5 373
H(73)	2 328	578	5 490
H(81)	281	1 174	3 029
H(82)	1 265	864	1 806
H(83)	990	223	3 032

The hydrogen atoms are numbered to correspond with the carbon atoms to which they are bonded, *e.g.* H(3) is bonded to C(3), methyl H(51) is bonded to C(5), *etc.*

TABLE 6

Final positional parameters ($\times 10^4$) for (6a) with standard deviations in parentheses

Atom	x/a	y/b	z/c
Pd	4 925(1)	1 162(1)	1 292(1)
Cl	7 058(2)	181(1)	2 570(1)
S	7 225(2)	2 504(1)	856(1)
C(1)	5 333(9)	3 499(5)	299(5)
C(2)	3 516(8)	2 926(4)	−303(4)
C(3)	2 720(7)	2 130(4)	463(4)
C(4)	2 215(9)	1 050(4)	246(5)
C(5)	1 952(9)	384(5)	1 127(5)
C(6)	8 313(10)	3 190(6)	2 014(6)
C(7)	1 887(12)	3 762(5)	−610(6)
C(8)	4 140(11)	2 380(5)	−1 273(4)
H(11)	5 951	3 967	−161
H(12)	4 868	3 916	851
H(3)	2 153	2 442	1 069
H(4)	2 038	782	−451
H(51)	2 074	695	1 810
H(52)	1 684	−353	1 035
H(61)	7 251	3 523	2 356
H(62)	9 026	2 699	2 487
H(63)	9 233	3 735	1 836
H(71)	696	3 423	−956
H(72)	1 553	4 142	−25
H(73)	2 393	4 256	−1 102
H(81)	5 189	1 856	−1 075
H(82)	2 990	2 023	−1 624
H(83)	4 620	2 906	−1 719

The hydrogen atoms are numbered to correspond with the carbon atoms to which they are bonded, *e.g.* H(3) is bonded to C(3), methyl H(51) is bonded to C(5), *etc.*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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