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_o·2PhCN (X = Cl or Br) with 2,2,NN-tetramethylpent-4-enylamine (1a) gives complexes (2) of stoicheiometry PdX_v·(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). Variabletemperature 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 β = 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 $\beta = 96.20(5)^{\circ}$. 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 PdCl₃S plane and the Pdethylenic 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 PdSCIC(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-4envlamine (1a) and 2,2-dimethylpent-4-envl 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-4en-l-vl 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 2:1complexes with PdCl₂ and PdBr₂ (see Experimental section); this by-product has been identified as 2,4,4trimethyltetrahydrothiophen 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 PdCl₂·2PhCN in a variety of solvents (benzene, dichloromethane, acetone, nitromethane, and benzonitrile) resulted in the precipitation of a product which is practically insoluble in nonco-ordinating solvents and which analysed for PdCl₂. (1a). Its ¹H n.m.r. spectrum in $(CD_3)_2SO$ {see [4a; L = dmso (dimethyl sulphoxide) in Table 1 suggests astructure (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 v(C-Cl). The insolubility of this complex in nonco-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 ¹H n.m.r. of [4a; L = py (py = pyridine)] in Table 1}. However, the spectra also

$H_2C = CHCH_2C(CH_3)_2CO_2H$
(8)
(i)-(iv)
H ₂ C=CHCH ₂ C(CH ₃) ₂ CONMe ₂
(9)
(v)
$H_2C=CHCH_2C(CH_3)_2CH_2NMe_2$
(1a)
H ₂ C=CHCH ₂ C(CH ₃) ₂ CH ₂ OH (10)
(<i>vi</i>)
$H_2C = CHCH_2C(CH_3)_2CH_2OSO_2Me$
(11)
(vii)
$H_2C=CHCH_2C(CH_3)_2CH_2SMe$
(1b)
Preparation of the ligands $(1a)$ and $(1b)$: (i)

showed resonances arising from free ligand (la), and attempts to recrystallise the precipitates led to decomposition and release of (la).

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 ¹H 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 shown¹¹ 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.

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

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

• •			•	, 0			•
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; $L = dmso)^{\circ}$	$(CD_3)_2SO$	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)	$e 2.58 (\mathrm{dd}^{f})$
(4b; $L = dmso)^{o}$	$(CD_3)_2SO$	1.15, 1.18	2.79, 3.02	3.35	g g	4.06 (m)	$g = 2.35 (\mathrm{d}\mathrm{d}^d)$
(1b) ^a	CDCl ₃	0.95	2.05	2.38	2.03 (2 H, d,br [*])	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)° (i)*	CDCl ₃	1.30, 1.64	2.74	$2.71 (d^{l}), 2.81 (d^{l})$	5.70 (d ⁴)	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)
$PdBr_2 \cdot 2 PhCN + (1b)^a$	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°)
(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, dº)
(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)	$3.03 (\mathrm{dd}^r), 4.00 (\mathrm{dd}^s)$
(6b) ^ø	CDCl ₃	1.32, 1.36	2.60	3.42	4.33 (d ^q)	5. 64 (m)	3.03 (dd ^r), 4.00 (dd ⁴)
(12a) ^a	CDCl ₃	1.15, 1.33		$2.70 (d^u), 3.27 (dd^v)$	$w 1.93 ({ m m}^{x})$	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 ^v)

^a 60 MHz. ^b J = 7.5 Hz. ^c 220 MHz. ^d J = 14.6 Hz. ^c Overlapping multiplet 1.68—2.33. ^f J = 14.0, 5.8 Hz. ^g Overlapping multiplet 1.86—2.11. ^b 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. ^e syn-H, J = 6.8, 0.9 Hz. ⁱ syn-H, J = 6.3 Hz. ^{*} J = 11.7 Hz. ^{*} J = 11.3 Hz. ^{*} J = 11.3, 1.4 Hz. ^w Partially obscured multiplet at ca. 1.5. ^{*} J = 12.0, 6.0, 1.4 Hz. ^{*} J = 6.3 Hz. ^{*} 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 ¹H 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 $(\delta 4.5-6.8)$ 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 inversion¹ 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 ¹H 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 isometrisation in a potentially chelating olefinic ligand has apparently not been reported for palladium.

The ¹H 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 palladiumolefin 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-CH₂ bond to those of the former. In our earlier paper ¹ we suggested, on the basis of ¹H 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.



The crystal structure (Figure 1) contains discrete monomeric molecules (Figure 2) separated by normal van der Waals distances. The palladium atom is fourco-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) \cdots H(1a) 2.21 Å] and the pseudo-equatorial Smethyl group [H(4) \cdots H(61) 2.45 Å], and (*ii*) terminal methyl group C(5) and Cl(1) [C(5) \cdots 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 fivemembered 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 -chlorobis[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

[†] 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 ¹H 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 coordination plane in order to reduce the compression between C(5) and Cl(1) is accompanied in the major 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



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

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



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

some relief of the interaction between the pseudo-axial C-methyl and S-methyl groups.

Reaction of PdBr₂•2PhCN with (1b) in CDCl₃ 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 PdBr₂•(1b) giving instead (5b) and additionally, on occasions when (5b) was left for long periods on the plates before recovery, the π -allyl (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

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-C1(2)	2.320(1)	$C(2) \rightarrow C(3)$	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)PdS	173.0(1)	C(1) - C(2) - C(3)	109.8(3)
Cl(1)PdC(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)
$Cl(2) \rightarrow Pd \rightarrow C(4)$	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 d	listances		
$Pd \cdot \cdot \cdot C(5)$	3.164	$H(4) \cdot \cdot \cdot H(11)$	2.21
$Cl(1) \cdot \cdot \cdot C(5)$	3.237	$H(4) \cdots H(61)$	2.45
$C(1)' \cdots C(4)'$	2.940		

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 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



FIGURE 3 Possible solution conformations of (6b)

these two processes occurs in the ranges 10-40 and 60-90 °C respectively.

The resonance pattern of the vinylic protons in the ¹H n.m.r. spectrum of (6b) indicates that the $-C(CH_{2})_{2}CH_{2}$ - SCH_3 fragment adopts the syn configuration, as is found for (6a) in the solid state (see below). In CDCl_a 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 Smethylene 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 coupling¹ between the C(3)-H and the pseudo-equatorial S-methylene proton even in the lowtemperature 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, 2PhCN and (1b) in acetone afforded (6a) in good yield. Its ¹H 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 ¹H 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 suggestion¹⁴ 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 ¹H n.m.r. spectrum might then have been explained as resulting from dimermonomer or perhaps ligand-bridged dimer-halogenbridged 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 fivemembered 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 Smethyl group in (5a) and (6a) are also very similar and the S-methyl bond intersects the neighbouring methylene

J.C.S. Dalton



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

TABLE 3

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

(a) Bond le	engths		
Pd-Cl	2.381(1)	C(1) - C(2)	1.530(8)
Pd-S	2.364(1)	C(2) - C(3)	1.530(7)
PdC(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 $\sigma - \pi$ 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 $\sigma - \pi$ 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 ¹H 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)

* Throughout this paper: $1 \text{ mmHg} \approx 13.6 \times 9.8 \text{ Pa.}$

methane-acetone, 97:3) of the residue afforded the π -allyl

in hexamethylphosphoramide (70 cm³). 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 cm³) 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 (¹H 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 cm³) to a solution of bis-(benzonitrile)dichloropalladium(11) (767 mg, 2 mmol) in the same solvent (50 cm³) gave an orange solution from which a

complex, (6a) (194 mg). A solution of lithium bromide (191 mg, 2.20 mmol) in acetone (10 cm³) 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 cm³). Evaporation of the acetone gave the crude palladium complex, $PdBr_2 \cdot (1b)$, which dissolved readily in CDCl₃ (see ¹H n.m.r. in Table 1). [A solution giving an identical ¹H n.m.r. spectrum was obtained by dissolving $PdBr_2 \cdot 2PhCN$ (1 mmol) in CDCl₃ (2 cm³) 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

TABLE 4

Analytical and physical data for the complexes

			Analysis $(\%)$					
				Found		·	Calc.	
Compound	Colour	M.p.*	C	Н	N	C C	Н	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.

dark brown gum (169 mg) soon precipitated. The supernatant solution was decanted and upon standing a yellow solid (2a) (426 mg) gradually separated. A ¹H n.m.r. spectrum of the gum in $(CD_3)_2SO$ was very similar to that of the yellow solid. Addition of (1a) to $PdCl_2$ ·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 cm³) at 100 °C for 3 h and then filtering the mixture. When the ligand (141 mg) was added to this solution an orangeyellow 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 PdCl₂·2PhCN (383 mg, 1.0 mmol) in dichloromethane (5 cm³) was chromatographed on a silica gel column (10 g). Elution with dichloromethane afforded fractions containing benzonitrile, dichlorobis(2,4,4-trimethyltetrahydrothiophen)palladium(11) (12a) (47 mg), and a small amount (9 mg) of (5a), which were separated by preparative t.l.c. Elution of the column with dichloromethaneacetone (19:1) afforded essentially pure (5a) (251 mg); v_{max} at 1 535m (co-ordinated C=C), 318s v(Pd-Cl), 301m cm⁻¹ v(Pd-Cl). Treatment of a solution of (5a) (80 mg) in dichloromethane (10 cm³) with 2,2'-bipyridyl (40 mg) resulted in the deposition of PdCl₂·bipy and the liberation of 2,2-dimethylpent-3-enyl methyl sulphide (13) which was identified by ¹H 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 cm³) was stirred at ambient temperature for 1 h during which time a black precipitate [Pd⁰] separated. Evaporation of the solvent and preparative t.l.c. (dichloro-

10%) gave first benzonitrile and dibromobis (2,4,4-trimethyl-tetrahydrothiophen)palladium(II) (12b) (51 mg after preparative t.l.c.) followed by mixtures containing the relatively insoluble (5b) (247 mg); $\nu_{\rm max.}$ at 1 535s cm⁻¹ (coordinated C=C).

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, $\beta = 94.00(1)^\circ$, U = 1.206.4Å³, Z = 4, $D_c = 1.77$ g cm⁻³, F(000) = 640, space group $P2_1/n$ ($C_2^{5}h$, no. 14) uniquely from systematic absences h0lif h + l = 2n + 1, 0k0 if k = 2n + 1, Mo^-K_{α} radiation, $\lambda = 0.710$ 69 Å, $\mu(Mo^-K_{\alpha}) = 19.4$ 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, $\beta = 96.20(5)^{\circ}$, U = 1.048.8 Å³, 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, $\lambda = 0.710$ 69 Å, $\mu(Mo^-K_{\alpha}) = 19.9$ 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 way¹² to a maximum θ of 25°; 2414 unique data were collected for (5a) and 2515 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 para-

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

		reason reasons	
Atom	x a	y/b	z/c
Pd	3 805(1)	$2\ 158(1)$	1045(1)
Cl(1)	2715(1)	$3\ 531(1)$	467(1)
Cl(2)	4 084(1)	1831(1)	-1288(1)
S	4 600(1)	738(1)	1 476(1)
C(1)	4 174(4)	605(2)	$3\ 292(3)$
C(2)	2713(4)	$1 \ 170(2)$	3 577(3)
C(3)	$3\ 010(4)$	2 137(2)	3 177(3)
C(4)	4 487(4)	2548(3)	3 249(3)
C(5)	4 721(5)	3523(3)	3 477(4)
C(6)	6 762(5)	708(3)	1570(4)
C(7)	2 502(5)	1 167(3)	5 164(4)
C(8)	1 173(5)	830(3)	2801(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	3745	2 913
H(52)	3756	3 833	$3\ 209$
H(53)	$5\ 032$	3653	$4\ 428$
H(61)	$7\ 162$	904	719
H(62)	7 199	1.085	$2 \ 312$
H(63)	7 146	117	1 759
H(71)	3 4 4 1	1 400	5668
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
\mathbf{Pd}	4925(1)	1162(1)	$1\ 292(1)$
Cl	7 058(2)	181(1)	2 570(1)
S	7 225(2)	2 504(1)	856(1)
ĈΩ	5 333(9)	3 499(5)	299 (5)
Č(ž)	3 516(8)	2 926(4)	-303(4)
$\widetilde{C}(\overline{3})$	2 720(7)	2130(4)	463 (4)
$\tilde{C}(4)$	2215(9)	1.050(4)	246(5)
$\tilde{C}(\bar{5})$	1 952(9)	384(5)	1 127(5)
$\tilde{C}(\tilde{6})$	8 313(10)	3 190(6)	2 014(6)
$\tilde{C}(\tilde{7})$	1887(12)	3 762(5)	-610(6)
Č(8)	4 140(11)	2 380(5)	-1273(4)
HAN	5 951	3 967`´	161
H(12)	4 868	3916	851
H(3)	$2\ 153$	2 442	1 069
H(4)	2038	782	-451
H(51)	2074	695	1 810
H(52)	1 684	-353	$1\ 035$
H(61)	7 251	3 523	$2 \ 356$
H(62)	9 0 2 6	2699	2 487
H(63)	9 233	3735	1836
H(71)	696	3 423	-956
H(72)	1553	4 142	-25
H(73)	2 393	4256	-1.102
H(81)	5 189	1856	-1075
H(82)	2 990	2 023	-1624
H(83)	4 620	2 906	-1719

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.

meters 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 $U_{\rm iso.}$ 0.10 Å²) in subsequent calculations. For (5a), refinement converged at R = 0.023 and $R' = (\Sigma w \Delta^2 / \Sigma w F_0^2)^{\frac{1}{2}} = 0.029$; 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.).*

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

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