Complexes of Potentially Chelating Vinylsilanes and their Carbon Analogues with Palladium(II) Halides

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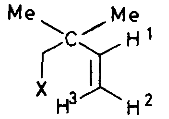
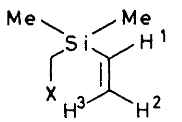
Eight members of the series of 1 : 1 complexes of palladium(II) halides (chloride, bromide, and iodide) with the ligands 2,2,*NN*-tetramethylbut-3-enylamine (1a), 2,2-dimethylbut-3-enyl methyl sulphide (1b), and 2,2-dimethyl-2-silabut-3-enyl methyl sulphide (2b) have been isolated. The remaining complex, PdI_2·(2b), is unstable, disproportionating to give PdI_2·2(2b). Infrared and ^1H n.m.r. data are reported. In solution all the 1 : 1 complexes, even the iodides, are chelated and the ring apparently adopts similar conformations. Variable-temperature ^1H n.m.r. studies of two exchange processes, labilisation of the metal–olefin bond and, for the sulphur chelates, inversion at sulphur, are discussed.

In the course of a study of the complexes of aliphatic polydentate ligands having quaternary carbon atoms in the backbone, and their silicon-containing analogues, we have prepared a series of palladium(II) halide complexes of the potentially chelating olefinic amines (1a) and (2a) * and sulphides (1b) and (2b). Ligands of this type have several advantages over but-3-enylamines[1] and but-3-enyl sulphides,[2] *viz.* the neopentyl type unit would be expected to (*i*) enhance any tendency for chelation (*gem*-dialkyl effect[3]), (*ii*) increase the solubility of complexes in organic solvents, (*iii*) provide a sensitive n.m.r. probe for co-ordination of the double bond which should give rise to magnetic non-equivalence of the methyl groups, and (*iv*) markedly reduce the complexity of the ^1H n.m.r. spectra of the ligands and complexes.



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



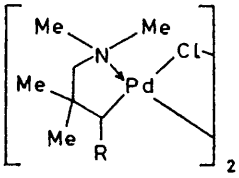
(2a) X = NMe_2
(2b) X = SMe

We wished to examine the influence of variation of the ligand atom and the halogen, and in particular of replacement of the allylic carbon atom with silicon, on the strength of the palladium–olefin co-ordination. In contrast to the extensive coverage of transition-metal complexes of chelating olefinic phosphines and arsines, there have been relatively few reports dealing with the analogous complexes of olefinic amines[1,4-7] and sulphides.[2,8] Indeed, there is a dearth of information on all of these classes of complexes in the case of palladium.[1,2,4,5,9-12]

RESULTS

The palladium(II) chloride complexes were prepared by displacement of benzonitrile from $PdCl_2$·2PhCN with the appropriate ligand. Bromo- and iodo-complexes were prepared from the chlorides by metathesis. All the complexes are non-conducting in nitromethane. Relative molecular masses (see Experimental section, Table 3) in 1,2-dichloroethane show the chlorides and bromides to be monomers while PdI_2·2(2b) gives values which suggest dissociation [*cf.* PdI_2·2(1b) discussed below]. In this solvent the 1 : 1 iodides, particularly PdI_2·(1b), are not stable (see below) but these complexes give relative molecular-mass values consistent with their being monomeric in acetone, a solvent in which they decompose less readily.

Complexes of 2,2,NN-*Tetramethylbut*-3-*enylamine* (1a).—The pure chloro-complex was obtained by preparative t.l.c. of the reaction mixture followed by crystallisation. The t.l.c. plates showed the presence of two minor by-products, the more polar aldehyde (3a) and a less-polar complex [probably (3b)] which decomposed readily on the plates. These minor products presumably arise[13] by attack of trace amounts of water on $PdCl_2$·(1a), with free ligand acting as base. The bromo-complex can also be purified by t.l.c., but the iodide only partially survives this treatment.



(3a) R = CHO
(3b) R = Me

Infrared spectra indicate that in all three complexes the olefinic function is bonded to palladium (see Table 1). Their ^1H n.m.r. spectra, in which all protons are resolved (see Figure 1 and Table 2), clearly demonstrate that both nitrogen and the olefin are co-ordinated. There is only one report[14] of a complex of PdI_2 with a potentially bidentate chelating olefinic ligand, but apparently the olefin is complexed only in the solid state. On heating the $PdCl_2$·(1a) complex to >100 °C the ^1H n.m.r. spectra showed evidence of the onset of an exchange process, but concomitant palladium deposition prevented studies at higher temperatures. In the case of PdI_2·(1a), broadening and collapse of the separate *N*-methylene and the *N*- and *C*-methyl resonances and additionally the appearance of new signals were observed on heating to 60 °C.

Complexes of 2,2-*Dimethylbut*-3-*enyl Methyl Sulphide*

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* No chelating olefin complex of palladium(II) halides has been obtained with the ligand (2a). Apparently, in the 1 : 1 chloro- and bromo-complexes, Pd–X (X = Cl or Br) adds across the olefinic bond.

(1b).—Formation of the chloro-complex does not appear to yield by-products analogous to those mentioned above for PdCl$_2$·(1a) and all three halogeno-complexes are more stable thermally (in nitrobenzene, see below) than their (1a) counterparts.

TABLE 1

I.r. data for ligands [a] and complexes [b]

Compound	1 650—1 500 cm^{-1}	$\Delta\nu$ [e]	1 030—900 cm^{-1}	ν(Pd–X)
(1a)	1643ms, 1 595vw		1 015wm, 1 000m, 969w, 936w(sh), 908vs	
PdCl$_2$·(1a)	1 544vw, *1 530*vw, 1 509vw	113	1.027wm, 1 001ms, 985m, 972m, 968w, 940w, 923w	331ms, 323m, 304m
PdCl$_2$·(1a) [c]	1 545vvw, *1 526*w	117	1 021wm, 1 000m, 984ms, 977m, 968w, 940w, 921vvw, 900wm	
PdBr$_2$·(1a)	1 540w, *1 526*vw, 1 501w	117	1 023wm, 998s, 984m, 972wm, 968w, 940w, 921w	199m, 191s
PdBr$_2$·(1a) [c]	1 540vw, *1 524*w	119	1 020wm, 1 000m, 983s, 975m, 968w, 940w, 920vw	
PdI$_2$·(1a)	*1 535*w, 1 521vvw(sh)	108	1 021wm, 999m, 980s, 971wm, 968w(sh), 938w, 920w	164m
(1b)	1 641ms, 1 582vw		1 020w(sh), 999ms, 978wm, 957wm, 910vs	
PdCl$_2$·(1b)	1 545vvw, *1 513*w, 1 500vvw(sh)	128	987m, 981ms, 972m, 967ms, 952w, 939w, 916w	334s, 312s, 294s [d]
PdCl$_2$·(1b) [c]	1 541vvw, *1 514*w	127	1 019vvw, 983ms, 972ms, 963m, 950w, 939vvw	
PdBr$_2$·(1b)	1 540w, *1 514*w	127	990m, 983ms, 977m(sh), 972ms, 958w, 942w, 920w	190s, 185(sh)
PdBr$_2$·(1b) [c]	1 540w, *1 515*w	126	1 018vw, 982ms, 980(sh), 971s, 965ms, 951w, 940vw	
PdI$_2$·(1b)	1 534w	107	1 020vvw, 980(sh), 974ms, 970ms, 954w, 940vw, 918vvw	166m, 152m
(2b)	1 595w		1 010s, 957s	
PdCl$_2$·(2b)	1 512vw	83	1 020w, 1 004wm, 994m, 972(sh), 967ms	334s, 328s, 303s
PdCl$_2$·(2b) [c]	1 509vw	86	1 015w, 1 003wm, 992wm, 965ms	
PdBr$_2$·(2b)	1 503vw	92	1 009ms, 1 000m, 974ms, 967s, 963(sh)	206s, 191m
PdBr$_2$·(2b) [c]	1 504vw	91	1 015w, 999 wm, 980m, 964s	
PdI$_2$·2(2b)	1 597w		1 006m, 965(sh), 958s	206m, br

[a] Liquid film. [b] Nujol mull. [c] Methylene chloride solution. [d] One of these bands may not be due to Pd–Cl stretching since the corresponding bromide and iodide show strong bands at 320 and 308 cm^{-1} respectively. [e] Calculated from the italicised values where more than one band is present.

TABLE 2

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

		CMe		N(S)–Me		N(S)–CH$_2$						J	J	J
Compound	Solvent	(a)	(e)	(a)	(e)	(a)	(e)	J_{gem} [a]	H^1 [a]	H^2 [a]	H^3 [a]	(H^1–H^2)[a]	(H^1–H^3)[a]	(H^2–H^3)[a]
(1a)	CDCl$_3$	1.01		2.26		2.17			5.86 *	4.93 *	4.96 *	10.8 *	18.0 *	1.3 *
PdCl$_2$·(1a)	CDCl$_3$	1.86	1.15	2.93	2.82	3.05	2.35	14	6.01	5.47	5.08	8.1	15.0	0
	C$_6$D$_5$NO$_2$	1.81	1.17	2.97	3.06	3.33	2.50	14	6.12	5.57	5.40	7.9	15.3	0
PdBr$_2$·(1a)	C$_6$D$_5$NO$_2$	1.79	1.16	3.15	2.99	3.35	2.42	14	6.15	5.71	5.43	8.2	15.0	0
PdI$_2$·(1a)	CDCl$_3$	1.80	1.11	3.12	2.87	3.12	2.16	14	6.05	5.79	5.08	8.7	15.5	0
(1b)	C$_6$D$_5$NO$_2$	1.05		2.22		2.44			5.83 *	4.93 *	4.97 *	10.8 *	18.0 *	1.3 *
PdCl$_2$·(1b) (*i*) [b]	C$_6$D$_5$NO$_2$	1.56	1.38		2.84	3.17	3.03 [c]	12.5	6.23	5.73	5.24	8.4	15.3	0
(*ii*)		1.90	1.34	2.90		3.45	2.74	14	6.33	5.30	5.06	*d*	15.0	0
PdBr$_2$·(1b)(*i*) [b]	C$_6$D$_5$NO$_2$	1.52	1.38		2.81	3.23	2.99 [c]	12	6.29	5.90	5.27	8.5	15.3	0
(*ii*)		1.85	1.34	3.02		3.50	2.75	*d*	*d*	5.45	5.13	8.3	15.1	0
PdI$_2$·(1b) (*i*) [b]	(CD$_3$)$_2$CO [e]	1.43	1.36		2.74	3.37	2.98 [c]	12	6.24	5.83	5.46	8.3	15.5	0
(*ii*)		1.75	1.31	3.04		3.69	*d*	14	6.35	5.50	5.42	*d*	15.8	
PdI$_2$·(1b) (*i*) [b,f]	CDCl$_3$ [e]	1.52	1.38		2.73	2.89	2.82 [c]	12	6.23	6.05	4.99	8.8	15.0	0
PdI$_2$·(1b) + (1b) [g]	CDCl$_3$ [h,i]	1.20		2.67		2.78 and 3.67		13	5.89 *	5.14 *	5.13 *	10.7 *	16.7 *	1.3*
(2b)	CDCl$_3$ [i]	0.10		2.14		1.83			6.17 *	6.01 *	5.76 *	14.8 *	20.4*	3.3 *
PdCl$_2$·(2b) (*i*) [b]	CD$_2$Cl$_2$ [e]	0.38 and 0.57			2.64	2.01	1.88 [c]	12	5.62	6.02	5.24	11.7	17.6	2.7
		0.36 and 0.78		2.67		2.20	1.59	15	*d*	*d*	*d*	*d*	*d*	*d*
PdBr$_2$·(2b)(*i*) [b]	CD$_2$Cl$_2$ [e]	0.39 and 0.54			2.68	1.94 [j]			5.79	6.18	5.30	12.0	17.9	2.8
		0.36 and 0.75		2.80		2.27	1.51	15	*d*	*d*	*d*	*d*	*d*	*d*
PdI$_2$·(2b)	CDCl$_3$	0.36		2.69		2.69 [k]			6.25 *	6.09 *	5.81 *	14.8 *	20.4 *	3.3 *

[a] Observed at 220 MHz; values distinguished by an asterisk have been optimised by computer matching; J(H^2–H^3) couplings of <0.5 Hz would probably be difficult to detect. [b] (*i*) Major isomer, (*ii*) minor isomer in mixture. [c] Assignment uncertain. [d] Obscured. [e] At −40 °C. [f] Resonances of minor isomer not observable due to substantial disproportionation to PdI$_2$·2(1b) in this solvent. [g] Slightly more than 1 equivalent of (1b) added. [h] At −50 °C. [i] At 60 MHz. [j] Singlet. [k] Broad.

Co-ordination of the olefin is shown by the i.r. absorptions in the 1 500—1 550 and 900—1 030 cm^{-1} regions and the ^{1}H n.m.r. spectra (see Tables 1 and 2 respectively). The latter are complicated in all cases by the presence of two isomers, corresponding to two possible configurations at sulphur. At higher temperatures spectral changes are observed which result (see Discussion section) from sulphur inversion and labilisation of the metal–olefin bond. This is illustrated in the case of PdCl$_2$·(1b) in Figure 2. A further complication arises in the case of the iodo-complex. In (CD$_3$)$_2$CO and C$_6$D$_5$NO$_2$ its spectra are analogous to those of PdX$_2$·(1b) (X = Cl or Br). However, attempts to dissolve the complex in CDCl$_3$ leave residues (probably PdI$_2$) and the resulting solutions show peaks due to both PdI$_2$·(1b) and PdI$_2$·2(1b). In the presence of an excess of ligand, dissolution is complete and there is a distinct colour change from purple-brown to red-brown. Solutions prepared using >1 equivalent of excess of ligand showed peaks due to both PdI$_2$·2(1b) (see Table 2) and free ligand at low temperatures.* In contrast, the nitrogen analogue PdI_2·(1a) appears to be more stable to disproportionation in $CDCl_3$.

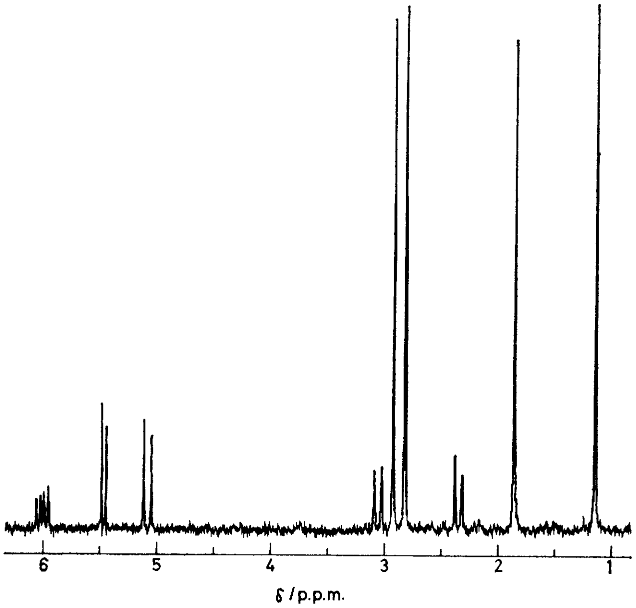

FIGURE 1 220-MHz ^1H n.m.r. spectrum of $PdCl_2$·(1a) in $CDCl_3$ at ambient temperature

Indeed, on addition of an excess of ligand to the purple-brown solution no noticeable colour change is observed and the only change in the ^1H n.m.r. spectrum is the appearance of peaks due to free ligand.

TABLE 3

Analytical and physical data for the complexes

			Relative molecular mass		Analysis (%)					
					Found			Calc.		
Complex	Colour	M.p. (θ_c/°C)	Found	Calc.	C	H	N	C	H	N
$PdCl_2$·(1a)	Yellow	153—154	313 [a]	305	31.55	5.65	4.55	31.55	5.65	4.6
$PdBr_2$·(1a)	Orange-red	132—133	385 [a]	393	24.65	4.3	3.35	24.4	4.35	3.55
PdI_2·(1a)	Dark crimson	112—113	484 [b]	487	20.0	3.6	2.5	19.7	3.5	2.85
$PdCl_2$·(1b)	Orange-yellow	208—210	309 [a]	308	27.4	4.6		27.35	4.6	
$PdBr_2$·(1b)	Orange-red	198—199	412 [a]	396	21.4	3.75		21.2	3.55	
PdI_2·(1b)	Dark crimson	135—138	491 [b]	490	17.35	3.0		17.15	2.9	
$PdCl_2$·(2b)	Yellow	115—116	320 [a]	324	22.15	4.55		22.25	4.35	
$PdBr_2$·(2b)	Orange-red	126—127	329 [a]	413	17.4	3.75		17.45	3.45	
PdI_2·2(2b)	Brown	57—58	468 [a]	653	21.1	4.35		22.1	4.35	

[a] In 1,2-dichloroethane. [b] In acetone.

Complexes of 2,2-*Dimethyl*-2-*silabut*-3-*enyl Methyl Sulphide* (2b).—In contrast to the complexes of (2a) (see above), $PdCl_2$·(2b) and $PdBr_2$·(2b) are reasonably stable chelated olefin complexes, although they did not survive attempted purification by t.l.c. However, in the course of attempts to prepare PdI_2·(2b) only the 1 : 2 complex, PdI_2·(2b), could be isolated, presumably arising by disproportionation [14] of the 1 : 1 complex. Infrared spectral studies show that the olefin is co-ordinated in the chloro- and bromo- but free in the iodo-complex (see Table 1). Variable-temperature ^1H n.m.r. studies show that, for the chloro- and bromo-complexes, exchange processes involving both sulphur inversion and metal–olefin bond rupture and reformation take place.

DISCUSSION

Infrared Studies.—In the few publications [1,2,4,5,9-12] concerning chelating olefinic complexes of Pd^{II} the authors have in general noted loss of the C=C stretching vibration due to free olefin upon complexation and the appearance of a much weaker band in the range 1 520—1 550 cm^{-1}. The majority of the chelated olefin complexes reported here show ***more than one band*** in the 1 500—1 550 cm^{-1} region as Nujol mulls, although in spectra run in solution the relative intensity of one band is noticeably enhanced (see Table 1 and Figure 3). Assuming that the strongest solution band is comparable with that observed by previous workers, the frequency differences between this band and the free ligand C=C stretch ($\Delta\nu$, Table 1) may indicate [15] that the metal–olefin interaction is weaker for the vinylsilane than for its carbon analogues. It is also noteworthy that $\Delta\nu$ for PdX_2·(1b) (X = Cl or Br) is *ca.* 20 cm^{-1} greater than for the analogous complexes [2] of but-3-enyl butyl sulphide, perhaps reflecting the contribution of the *gem*-dialkyl effect in the former. Further, the larger values of $\Delta\nu$ found for the complexes of (1b) when compared with those of (1a) may suggest that the metal–olefin interaction is weaker in the latter.

Significant differences between the spectra of the free and complexed olefin are also found in the region associated with terminal-olefin deformations (900—1 050 cm^{-1}). The two prominent bands in this region in the free ligands (see Table 1) appear to split and move towards each other on complexation, the lower-frequency band suffering a larger displacement in all cases (see Figure 3). The shifts are smaller for the silabutenyl complexes, consistent with the suggestion that the olefin is more weakly complexed.

The metal–halogen stretching frequencies (Table 1) are consistent with *cis* halogens in monomeric species. Although there are few published data on palladium–iodine stretching frequencies, the values listed here are very similar to those reported [16] for PdI_2·$RSCH_2CH_2SR$.

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* When a sample of this solution was applied to a t.l.c. plate the initially orange spot, on development with dichloromethane, gradually changed to the purple colour characteristic of PdI_2·(1b), indicating that dissociation [PdI_2·2(1b) $\longrightarrow$ PdI_2·(1b) + (1b)] was occurring.

The complex $PdI_2 \cdot 2(2b)$ shows a strong band at 206 cm^{-1}, consistent [17-19] with its formulation as a *trans* monomer.

Hydrogen-1 *N.M.R. Investigations.—Structures of the complexes.* The three complexes $PdX_2 \cdot (1a)$ ($X = Cl$, Br, or I) show very similar spectra at ambient temperature (see Table 2). In each, complexation of the olefin leads not only to marked magnetic non-equivalence between the CMe groups, the NMe groups, and the NCH_2 protons, but also to a general downfield displacement of the olefinic proton resonances. The greatest shift is suffered by H^2, which resonates at higher field than H^3 in the ligand but at lower field in the complexes. Coordination of the olefin also results in a reduction in the magnitude of the spin–spin coupling constants of the olefinic protons including $J(H^2–H^3)$.

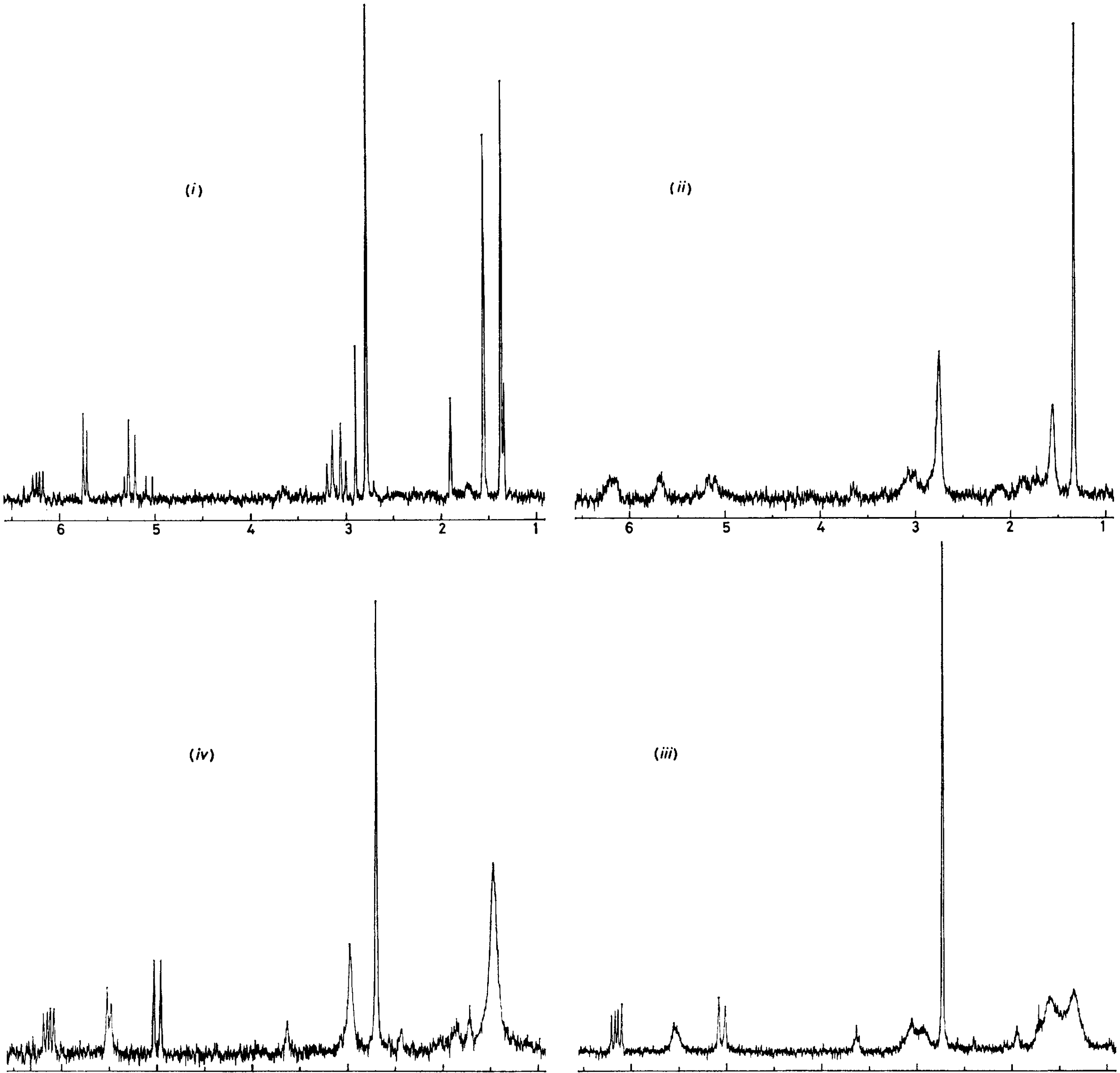


FIGURE 2 220-MHz ^1H n.m.r. spectra of $PdCl_2 \cdot (1b)$ in $C_6D_5NO_2$ at (*i*) ambient temperature, (*ii*) 70, (*iii*) 110, and (*iv*) 150 °C

The signals arising from H^1, NCH(axial), NCH(equatorial), and both axial methyl groups are all broadened at ambient temperature. Decoupling experiments show that H^1 is coupled (J 1.2 Hz) to N-CH(e) ('W' conformation) [20] while NCH(a) is probably coupled to the axial methyl groups. These observations are consistent with the complexes having the envelope conformation shown in Figure 4(*a*), in which the Pd, N, methylene C, and midpoint of the C=C bond define a plane, while the quaternary carbon atom constitutes the apex of the flap. Pseudo-axial and -equatorial methyl groups and protons are designated as (a) and (e) in the Figure. A similar conformation has been found in the solid state for chelated butenylphosphine complexes[21,22] of Rh^{I} and for complex (4).[23] The broadening of the resonance of the axial *N*-methyl group becomes progressively more marked in the spectra of $PdBr_2$·(1a) and PdI_2·(1a) while no comparable change is observed in the relative heights of the *C*-methyl signals. This is taken to suggest that the NMe_2 group has some conformational mobility and that increasing non-bonded interaction of the neighbouring halogen atom with NMe(a) opposes the expected tendency of the latter to relax away from a 1,3-diaxial interaction with CMe(a). On moving from $CDCl_3$ to $C_6D_5NO_2$ as solvent all the resonances of $PdCl_2$·(1a) move downfield but the shifts of H^3, NCH(a), and NMe(e) are particularly marked. This is in accord with prepreferential solvation of the complex *in the assigned conformation* on the less-hindered side.

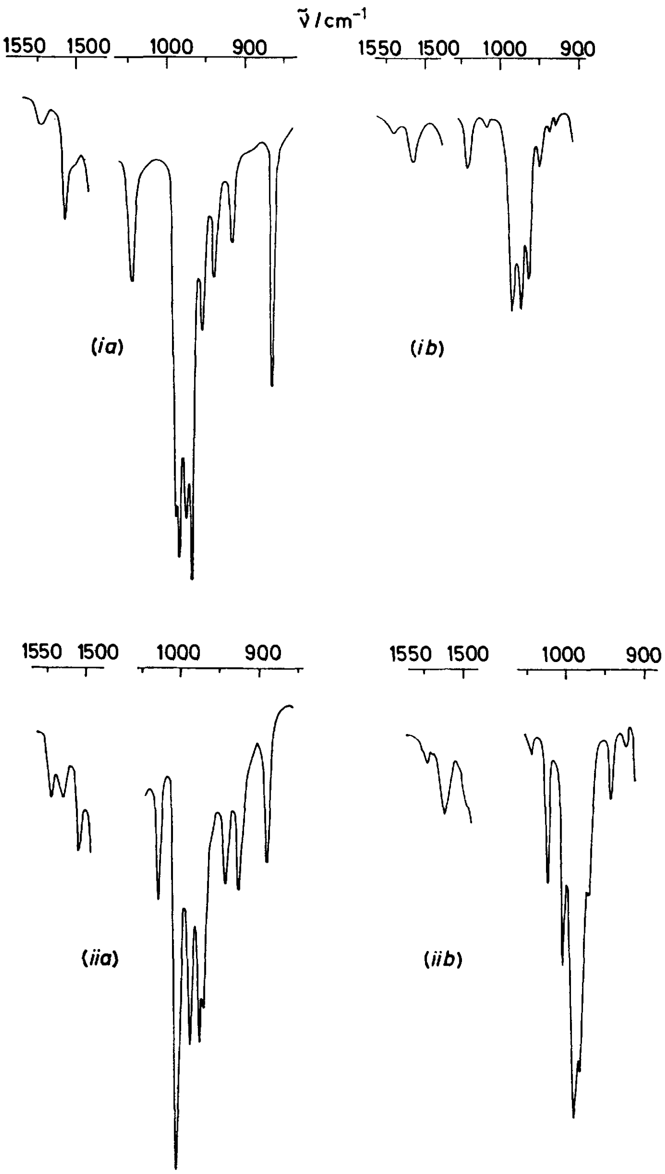
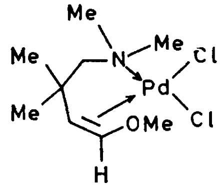


FIGURE 3 Infrared spectra of (*i*) $PdCl_2$·(1b) and (*ii*) $PdCl_2$·(1a) as (*a*) Nujol mulls, (*b*) solutions in dichloromethane



(4)

In the complexes PdX_2·(1b) (X = Cl, Br, or I) there are two possible configurations for the sulphur atom. At temperatures at which exchange between these two configurations is slow on the n.m.r. time scale, resonances arising from the individual isomers may be assigned (see Table 2 and Figure 2). Integration of these spectra allows an estimate of the ratios of the two epimers at sulphur as 3.5 : 1 for $PdCl_2$·(1b) (in $C_6D_5NO_2$), 6 : 1 for $PdBr_2$·(1b) (in $C_6D_5NO_2$), and 12 : 1 for PdI_2·(1b) [in $(CD_3)_2CO$]. For the major isomers the H^1, SCH_2, and CMe(a) signals are broadened, an observation that

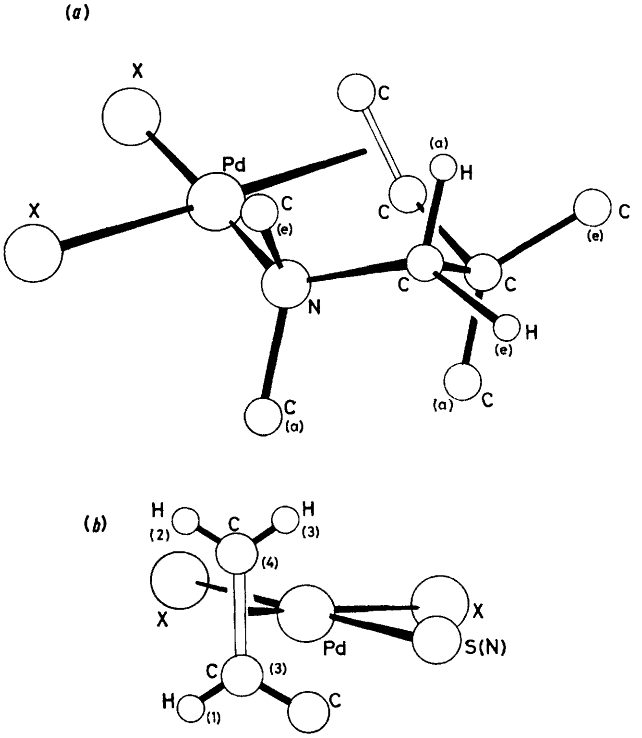
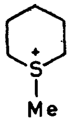


FIGURE 4 (*a*) Idealised geometry of PdX_2·(1a) complexes in solution. (*b*) Orientation of the olefinic moiety with respect to the co-ordination plane for the complexes PdX_2·L [L = (1a), (1b), or (2b)] is only explicable if these complexes adopt similar conformations to their (1a) analogues. In a study of the *S*-methylthianium cation (5) and alkylated derivatives thereof it has been observed[24] that the magnitude of J_{gem} for the C^2 and C^6 methylene protons is greater when the Me is axial than when it is equatorial. As listed in Table 2, J_{gem} for SCH_2 in the major isomers of PdX_2·(1b) is consistently smaller (*ca.* 12 Hz) than in the corresponding minor isomers (*ca.* 15 Hz). This is consistent with the major and minor isomers having a similar chelate-ring conformation, with the *S*-methyl group equatorial in the former and axial in the latter where it experiences a destabilising 1,3-diaxial interaction with a *C*-methyl group. Indeed, some distortion of the chelate ring from the idealised geometry depicted in Figure 4(*a*) to relieve this interaction is probably reflected in the differences observed in the chemical shifts of the olefinic protons when comparing the major and minor isomers. Before discussing these differences it is necessary to define a probable orientation of the olefinic moiety with respect to the co-ordination plane for the PdX_2·(1a) complexes and the major PdX_2·(1b) isomers. These show very similar resonance patterns for the olefinic protons in the ^1H n.m.r. spectra. The observations (*i*) that of the olefinic resonances H^2 suffers the most marked downfield shift on complexation and (*ii*) that this is accentuated on going from the chloro- to bromo- to iodo-complex are taken to indicate that this proton lies nearer the *cis* halogen than H^1 and H^3. This can be achieved by rotation of the double bond away from perpendicular about the palladium–olefin axis [see Figure 4(*b*)]. The $H^2 \cdots X$ distance would be decreased even further if the palladium atom lies closer to C^4 than to C^3. In the minor PdX_2·(1b) isomers, a study of molecular models indicates that rotation of the axial SMe to relieve the 1,3-diaxial interaction is accompanied by movement of the double bond towards the perpendicular orientation. The consequent increase in the $H^2 \cdots X$ distance and decrease in the $H^1 \cdots X$ distance lead to upfield and downfield shifts respectively. A similar rotation is hindered in the PdX_2·(1a) complexes by interaction of the NMe(e) with H^3. However, it seems likely that some rotation of this type is possible since the signal arising from NMe(a) in $PdCl_2$·(1a) is broader in $C_6D_5NO_2$ than in $CDCl_3$. Preferential solvation by the former on the less-hindered side of the co-ordination plane (see above) should oppose relief of the 1,3-diaxial interaction and produce a more ideal 'W' geometry for CH(a)–NMe(a). As mentioned above, in the ^1H n.m.r. spectra of the PdX_2·(1a) complexes, the breadth of the NMe(a) resonance increases on going from X = Cl to Br to I, the bulkier halogens also opposing relief of this 1,3-diaxial interaction. It is therefore not surprising that the proportions of the minor PdX_2·(1b) isomers decrease in the same sequence.



(5)

In the ^1H n.m.r. spectra of the complexes $PdCl_2$·(2b) and $PdBr_2$·(2b) at temperatures at which inversion at sulphur is slow, signals due to two isomers are observed (see Table 2) although the olefinic resonances for the minor isomers could not be distinguished. All the observable olefinic proton spin–spin coupling constants were again found to be smaller than in the free olefin. In contrast to the downfield shifts observed for the olefinic protons of (1a) and (1b), the resonances due to H^1 and H^3 of (2b) suffer significant *upfield* shifts while H^2 undergoes a small downfield shift on complexation. The most plausible explanation for this would appear to be that metal-to-olefin back bonding is significantly more important for the vinylsilane than for its carbon analogue (the downfield shift of H^2 being due to its proximity to the *cis* halogen). This accords with the proposal[25,26] that, in vinylsilanes, overlap of silicon *d* orbitals with the olefinic π^* orbital provides a more favourable orbital for backbonding. It should be noted that, if the $\Delta\nu$ values in Table 1 may be taken as a guide to the relative strengths of metal–olefin interactions, then the increase in backbonding in the vinylsilane complexes over their carbon analogues must be more than offset by a decrease in the magnitude of the σ (olefin $\longrightarrow$ Pd) component. The greater length of C–Si compared with C–C bonds should also play a role in decreasing the strength of the metal–olefin bond in these silanes with respect to their carbon analogues both by making the chelate-ring size less favourable (*cf.* pentenyl *vs.* butenyl ligands) and by reducing the strength of the *gem*-dialkyl effect. The chelate rings in PdX_2·(2b) (X = Cl or Br) seem to adopt very similar conformations to those described above for their (1b) analogues. The most striking evidence for this is the close similarity of the signal patterns for the *S*-methylene protons in both series of complexes (*cf.* Figures 2 and 5) including the J_{gem} values for the major and minor isomers. Somewhat larger proportions of the minor isomers [major : minor, 2 : 1 for $PdCl_2$·(2b) and 3.5 : 1 for $PdBr_2$·(2b)] are present in the (2b) complexes, consistent with the expectation of reduced 1,3-diaxial interaction between SMe(a) and SiMe(a). The ^1H n.m.r. spectrum of PdI_2·2(2b) suggests that the ligand is complexed through sulphur only (see Table 2), although at the temperature (21 °C) at which this spectrum was run broadening of the SCH_2 resonance is observed. This may be due to slow inversion at sulphur or reversible dissociation of ligand (see above).

Variable temperature. The labilities of the metal–olefin bonds in these complexes were investigated by observing ^1H n.m.r. spectral changes on heating in $C_6D_5NO_2$. The most convenient probe for detecting the labilisation of these bonds is the *C*-methyl resonance pattern. The groups become equivalent only if the metal–olefin bond is cleaved and the resulting species has a lifetime long enough to allow reorganisation of the ligand framework into a conformation suitable for complexation of the other face of the double bond. This process also leads to equivalence of the NMe groups and *N*-methylene protons in $PdX_2\cdot$(1a), while for equivalence of the *S*-methylene protons (and strictly speaking the C*Me* groups) in $PdX_2\cdot$(1b) fast inversion at sulphur (see below) is required in addition.

In the case of the (1a) complexes, only the chloride and iodide have been examined. The spectrum of the former shows marked broadening of the non-olefinic resonances only at >100 °C where, however, the onset of palladium deposition is observed. For the iodo-complex, collapse of the individual resonances occurs at *ca.* 60 °C. Again, decomposition takes place as evidenced by the growth of new resonances during heating and the finding that less than half the original material remained on cooling a sample from 60 °C to ambient. It should be noted that the relative labilities of the metal–olefin bonds in these complexes may not necessarily reflect the relative strengths of these bonds since the mechanisms of cleavage may differ. For example, halide bridging may play a role particularly in the case of iodides.*

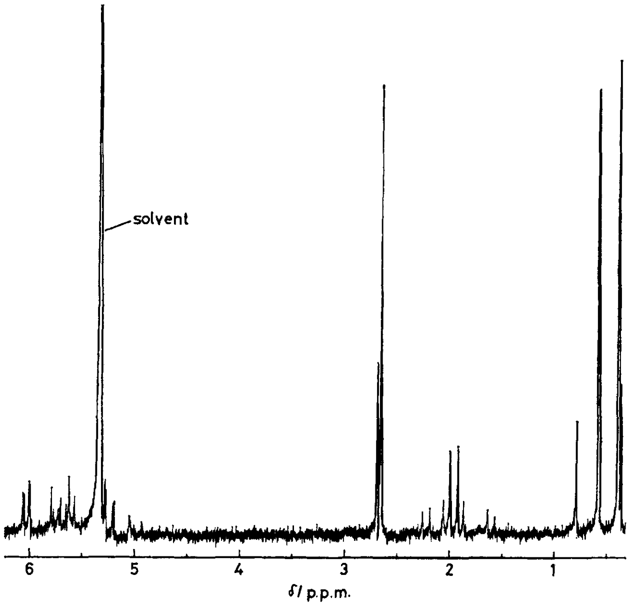


FIGURE 5 220-MHz ^{1}H n.m.r. spectrum of $PdCl_2\cdot$(2b) in CD_2Cl_2 at −40 °C

The (1b) complexes can be heated to higher temperatures than their (1a) analogues without suffering decomposition. Interpretation of spectral changes with temperature is complicated by the intervention of sulphur inversion. However, in all three cases sulphur inversion appears to be more ready than metal–olefin bond labilisation [see, for example, Figure 2 in the case of $PdCl_2\cdot$(1b)]. Signal coalescence due to fast inversion at sulphur [27–29] (or indeed labilisation of the metal–sulphur bond) is complete at >70, >60, and *ca.* 0 °C for $PdCl_2\cdot$(1b), $PdBr_2\cdot$(1b), and $PdI_2\cdot$(1b) [in $(CD_3)_2CO$] respectively. This dependence on halogen parallels earlier observations.[27] Additional severe broadening and collapse occurs in the CMe region due to metal–olefin bond labilisation in the ranges 110—150, 60—90, and 20—40 °C [the last in either $(CD_3)_2CO$ or $C_6D_5NO_2$] in the spectra of these three complexes.

In the ^{1}H n.m.r. spectra of $PdBr_2\cdot$(2b) the onset of broadening due to SMe inversion is evident at −20 °C (in CD_2Cl_2) with collapse by *ca.* 20 °C, while similar changes occur for the corresponding chloride at *ca.* 0 and >20 °C. It is noteworthy that these coalescence temperatures are *ca.* 50 °C below those for their (1b) analogues, although previous reports [27,29] have included the suggestion that changing the ligand atom *cis* to sulphur has little effect on the ease of its inversion. In the present case, reduction of the electron density at palladium by backbonding to the vinylsilane moiety might lead to an enhancement in the ability of the former to interact with the second lone pair on the sulphur atom in the transition state, whether this is envisaged as involving tetrahedral [30] or trigonal [27,28] sulphur. Metal–olefin bond labilisation in both $PdCl_2\cdot$(2b) and $PdBr_2\cdot$(2b) becomes rapid on the ^{1}H n.m.r. time scale at temperatures in the range 60—90 °C, although broadening is more apparent for the bromide than the chloride at 60 °C.

EXPERIMENTAL

Melting points were determined in capillary tubes. Infrared spectra were recorded on Beckman IR-12 and Perkin-Elmer model 180 spectrophotometers. Hydrogen-1 n.m.r. spectra were obtained on a Bruker WP-60 spectrometer and from the Canadian 220-MHz NMR Centre, University of Toronto, with tetramethylsilane as an internal standard. Microanalyses were performed by Mr. S. H. McKinnon and molecular weights were determined on a Hitachi–Perkin-Elmer 115 osmometer or by Galbraith Laboratories Inc., Knoxville, Tennessee. T.l.c. plates were spread with Kieselgel G (Merck) and developed with dichloromethane–acetone (97 : 3).

Ligands.—2,2,*NN*-Tetramethylbut-3-enylamine [31] (1a) and 2,2-dimethylbut-3-enyl methyl sulphide [32] (1b) have been reported earlier, although the mode of preparation of the former has apparently not been revealed. For the present work, (1a) was prepared (50% yield, b.p. 123—125 °C) by Wittig reaction of 2,2,*NN*-tetramethyl-3-aminopropanal (Eastman).

2,2-Dimethyl-2-silabut-3-enyl methyl sulphide (2b) was obtained (67% yield) by addition of dimethyl disulphide (9.42 g) to the Grignard reagent prepared from chloromethyldimethylvinylsilane (14.14 g; PCR Inc., Gainesville, Florida) and magnesium (2.67 g) in diethyl ether (100 cm^3). Rapid precipitation of magnesium salts occurred and the resulting mixture was stirred overnight at room temperature. Pentane (100 cm^3) was added and (2b) (9.85 g, b.p. 154 °C) recovered by filtration and distillation.

Complexes of (1a).—Addition of (1a) (127.3 mg) in dichloromethane (2 cm^3) to a solution of bis(benzonitrile)-dichloropalladium(II) (383.6 mg) in the same solvent (8 cm^3)

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* Indeed, the greater stability of $PdI_2\cdot$(1a) and $PdI_2\cdot$(1b) to disproportionation in acetone than in halogenated alkanes may be explained by stronger solvation of monomer in the former solvent and thus protection from halide bridging.

gave a dark cloudy solution from which a discoloured product crystallised. Preparative t.l.c. of the total reaction mixture gave $\mathrm{PdCl_2}$·(1a) (260 mg) and the aldehyde complex (3a) (20 mg). A third, less polar, component [probably (3b)] decomposed rapidly on the plate. The main product was crystallised from dichloromethane–hexane. Reaction of this material in acetone for 5 min at ambient temperature with lithium bromide (4 equivalents) or sodium iodide (2.1 equivalents) gave solutions of $\mathrm{PdBr_2}$·(1a) and $\mathrm{PdI_2}$·(1a) respectively. The former was purified by preparative t.l.c. followed by crystallisation. The latter was obtained as dark crimson prisms after filtration to remove precipitated sodium chloride, evaporation of the acetone at ambient temperature (rotary evaporator), and crystallisation of the residue from dichloromethane–heptane. In the course of crystallisation a thin film of dichloromethane-insoluble material ($\mathrm{PdI_2}$) was always deposited on the walls of the flask.

Complexes of (1b).—The complexes $\mathrm{PdX_2}$·(1b) (X = Cl, Br, and I) were prepared and purified in a similar fashion to that outlined above, the only major difference being that reaction of (1b) with $\mathrm{PdCl_2}$·2PhCN gave clear orange solutions.

Complexes of (2b).—The complexes $\mathrm{PdX_2}$·(2b) (X = Cl or Br) were prepared as described above and purified by crystallisation from dichloromethane. These complexes decomposed on attempted t.l.c. Treatment of $\mathrm{PdCl_2}$·(2b) with NaI in acetone gave a dark purple-brown solution similar in colour to those obtained from (1a) and (1b). When the NaCl and acetone were removed, attempts to crystallise the residue from dichloromethane–heptane led to gradual deposition of $\mathrm{PdI_2}$. The supernatant red-brown solution was evaporated to dryness and the residue extracted with hexane. This extract, on evaporation to small bulk at ambient temperature, afforded crystalline $\mathrm{PdI_2}$·2(2b) [19% yield based on $\mathrm{PdCl_2}$·(2b)].

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