Synthesis of Sulphimide Complexes of Palladium and Platinum. Crystal and Molecular Structure of *cis*-Dichloro[*S*,*S*-dimethyl-*N*-(2-pyrimidinyl)-sulphimide](triphenylphosphine)palladium(II) †

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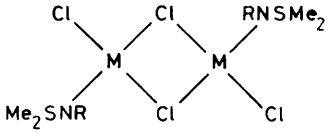
Reactions of $[MCl_2(PhCN)_2]$ (M = Pd or Pt) and $K_2[PtCl_4]$ with *S*,*S*-dimethyl-*N*-heteroaromatic sulphimides Me_2SNR (R = 2-pyridyl, 4-methyl-2-pyridyl, 2-pyrimidinyl, 4-methyl-2-pyrimidinyl, or 2-pyrazinyl) give 1:1 adducts *trans*-$[M_2Cl_2(\mu\text{-}Cl)_2(Me_2SNR)_2]$ (**1**) in which the sulphimide appears to co-ordinate through the ylide nitrogen according to ^1H n.m.r. studies. Reaction of $[MCl_2(PhCN)_2]$ with Me_2SNPh gives a bis(sulphimide) complex *trans*-$[MCl_2(Me_2NSPh)_2]$ (**2**) when M = Pd but when M = Pt a phenylnitrene derivative *cis*-$[PtCl_2(Me_2SNPh)(NPh)]$ (**3**) is obtained. Reactions of complexes (**1**) with phosphines L = PEt_3, PMe_2Ph, $PMePh_2$, or PPh_3 give 1:1 adducts $[MCl_2L(Me_2SNR)]$ [M = Pd; R = 2-pyridyl, L = PEt_3, PMe_2Ph, $PMePh_2$, or PPh_3, (**4a**)—(**4d**); M = Pt, R = 2-pyridyl, L = PEt_3 (**4e**); M = Pd, R = 2-pyrimidinyl, L = PPh_3 (**4f**)]. An *X*-ray analysis of *cis*-$[PdCl_2(PPh_3)(Me_2SNC_4H_3N_2)]\cdot CH_2Cl_2$ (**4f**) revealed that the pyrimidine rather than the sulphimide N atom is the point of attachment of the sulphimide ligand to Pd. Conformational energy calculations suggest that electronic rather than steric factors determine which N atom acts as donor to Pd. The crystals are monoclinic, space group $P2_1/n$, with a = 17.307(6), b = 9.182(1), c = 17.960(2) Å, β = 97.15(2)°, R = 0.024 for 1 999 independent reflections with $I > 3\sigma(I)$. N.m.r. studies suggest a *trans* structure for complex (**4e**) with sulphimide co-ordination *via* the pyridyl nitrogen. The isomerism and fluxional behaviour of (**4c**) and (**4d**) was studied by variable-temperature n.m.r. spectroscopy.

The successful clinical exploitation of Cisplatin, *cis*-$[PtCl_2(NH_3)_2]$,[1] has encouraged studies on the synthesis and biological evaluation of structural analogues which might possess similar chemotherapeutic activity but reduced toxicity;[2] included in this category are complexes $[PtCl_2L_2]$ (L = heterocyclic ligand).[3] In an effort to develop new complexes with antitumour activity we have embarked on studies of the co-ordination chemistry of dipolar ligands and recently described the synthesis of 1-oxidopyridinium-2-thiolato complexes of palladium and platinum.[4]

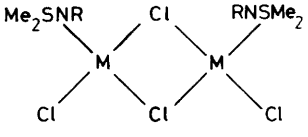
Ylides are versatile ligands for transition metals but attention has focused mainly on phosphorus–carbon[5] and sulphur–carbon[6] types. Transition-metal sulphimide complexes are mainly restricted to $[PdCl_2\{(CH_2)_4SNCOR\}]$ (R = Me or aryl) and $[PdCl_2\{(CH_2)_4SNCOR\}(PPh_3)]$ (R = Me or Ph), and also complexes $[MCl_2\{(CH_2)_4SNCOC_5H_4N\text{-}2\}]$ (M = Pd or Pt) in which the ylide functions as a bidentate ligand.[7] Related copper complexes have also been characterised.[8] We now report extension of our work to include palladium and platinum complexes of sulphimide ligands.

Results and Discussion

Reactions of a range of sulphur–nitrogen ylides Me_2SNR (R = heteroaromatic group) with palladium(II), $[PdCl_2(PhCN)_2]$, and platinum(II) complexes, $K_2[PtCl_4]$ and $[PtCl_2(PhCN)_2]$, gave insoluble orange or yellow powders which analysed in most cases as 1:1 adducts $[MCl_2(Me_2SNR)]$ [R = 2-pyridyl, M = Pd (**1a**) or Pt (**1b**); R = 4-methyl-2-pyridyl, M = Pd (**1c**) or Pt (**1d**); R = 2-pyrimidinyl, M = Pd (**1e**) or Pt (**1f**); R = 4-methyl-2-pyrimidinyl, M = Pd (**1g**) or Pt (**1h**); R = 2-pyrazinyl, M = Pd (**1i**) or Pt (**1j**)]. However in some cases, (**1f**), (**1h**), and (**1i**), analytically pure complexes were not obtained despite repeated washing and, where possible, precipitation from dimethyl sulphoxide (dmso) with ethanol. The insolubility of the complexes in less polar organic solvents prevented other methods of purification from being used. In the case of the 2-pyridyl sulphimide derivative (**1b**) an impure product was obtained using $K_2[PtCl_4]$ in water whereas $[PtCl_2(PhCN)_2]$ in refluxing dichloromethane gave an analytically pure product. In other cases (see Experimental section) pure products were obtained from both platinum precursors. The reactions also appear to be insensitive to stoicheiometry since both 1:1 and 1:2 molar ratios of 'MCl_2' and *N*-(2-pyridyl) sulphimide yielded the same 1:1 adducts.



(i)

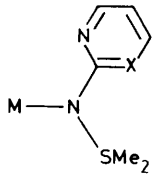


(ii)

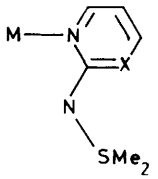
R		M		M
2-Pyridyl	(**1a**)	Pd	(**1b**)	Pt
4-Methyl-2-pyridyl	(**1c**)	Pd	(**1d**)	Pt
2-Pyrimidinyl	(**1e**)	Pd	(**1f**)	Pt
4-Methyl-2-pyrimidinyl	(**1g**)	Pd	(**1h**)	Pt
2-Pyrazinyl	(**1i**)	Pd	(**1j**)	Pt

The insolubility of these derivatives in many cases prevented full characterisation by spectroscopic means. In some cases, (**1d**), (**1e**), and (**1g**)—(**1j**), ^1H n.m.r. spectra could only be obtained in dmso and in every case a large number of signals was

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



(iii)



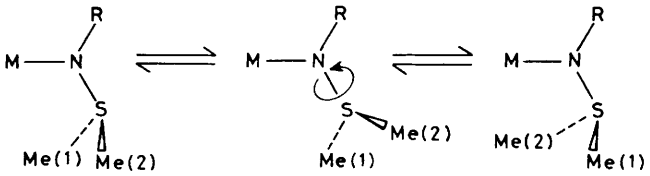
(iv)

X = CH,N

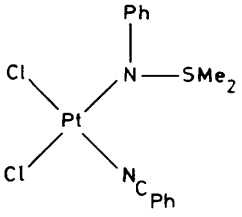
observed indicative of decomposition and the possible formation of dmso complexes[9] as a result of solvation. Where spectra could be obtained in a non-co-ordinating solvent (CD_2Cl_2) well resolved peaks corresponding to one hetero-aromatic nucleus and two sulphimide methyl groups were observed. In each case only one SMe_2 methyl resonance is present indicating equivalence of the Me groups and this was accompanied by platinum satellites for the platinum derivatives (**1b**) and (**1f**).

The high insolubility of the complexes is not consistent with a monomeric structure containing a bidentate ylide although this could not be confirmed by molecular weight measurements in solution. A dinuclear structure with chloride bridges and *cis* or *trans* ylides, (**i**) or (**ii**), seems more likely in view of the wide range of palladium(II) and platinum(II) complexes with such a structure.[10] The i.r. spectra of complexes (**1**) are broadly in agreement with this proposal since, for example, (**1a**) and (**1b**) exhibited three distinct bands at *ca.* 350, 330, and 290 cm^{-1} in the ν(M–Cl) region consistent with the *trans* structure (**1i**).[10,11] The remaining structural problem concerns the mode of ylide co-ordination since attachment can occur *via* the ylidic nitrogen, (**iii**), or alternatively through a heteroaromatic ring nitrogen, (**iv**). The n.m.r. spectra do not resolve this question unequivocally but two points are notable. First the SMe_2 methyls are equivalent which in view of the proposed structure requires that equivalence is achieved by a fluxional process involving inversion at sulphur accompanied by rotation about the N–S bond (see Scheme). However the poor solubility of the complexes prevented low-temperature spectra being recorded. Secondly, the presence of Pt–CH_3 coupling in the SMe_2 signal, J = *ca.* 30 Hz, may be significant. Unfortunately no comparators are available in the literature to distinguish between the two modes of bonding, *i.e.* whether this is a ^6J(Pt–H) or ^4J(Pt–H) value. Intuitively the coupling seems large for a ^6J(Pt–H) value pointing tentatively towards the ylide-bound form (**iii**). Evidence supporting the latter conclusion will now be described.

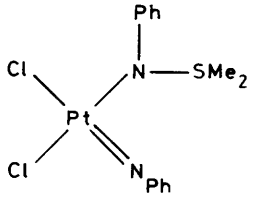
In an attempt to identify the mode of ylide co-ordination in complexes (**1**), reactions of palladium and platinum halides were carried out with $PhNSMe_2$ where the absence of a donor site on the aromatic ring restricts the ligand to N-ylide co-ordination. However, this apparently simple change in the N-bound substituent results in quite different complexes being formed. For example the reaction of $[PdCl_2(PhCN)_2]$ with 1 molar equivalent of $PhNSMe_2$ in dichloromethane unexpectedly gave a soluble product which analyses as the 2:1 adduct $[PdCl_2(Me_2NSPh)_2]$ (**2**). The ^1H n.m.r. spectrum is similarly consistent with this formulation showing a sharp SMe_2 singlet and interestingly three well resolved phenyl group multiplets, ratio 2:2:1. The i.r. spectrum shows only one ν(Pd–Cl) band at 330 cm^{-1} indicating a *trans* rather than a *cis* geometry about the metal centre. The comparable reaction of $PhNSMe_2$ with $[PtCl_2(PhCN)_2]$ does not yield a similar product. Instead the analytical data are consistent with either of two closely related formulae $[PtCl_2(Me_2SNPh)(PhCN)]$ (**3a**) or $[PtCl_2(Me_2SNPh)(NPh)]$ (**3b**) but unfortunately do not distinguish between them. The ^1H n.m.r. spectrum shows complex aromatic



Scheme.



(3a)



(3b)

signals near δ 7 and an SMe_2 singlet, ratio 10:6, consistent with either formulation. The SMe_2 methyls also show coupling to the ^{195}Pt nucleus, J(Pt–H) = 31.3 Hz which is comparable to that of (**1b**), J(Pt–H) = 31.5 Hz, and (**1f**), J(Pt–H) = 32.5 Hz. This provides good evidence for the N-ylide mode of co-ordination in these two complexes and possibly in other complexes of type (**1**).

The structure proposed for (**3a**) can be considered to result from displacement of one benzonitrile ligand from $[PtCl_2(PhCN)_2]$ by $PhNSMe_2$ and since the i.r. spectrum of (**3**) shows two ν(Pt–Cl) modes the *cis* isomer is indicated. However, no ν(C≡N) band is observed in the region 2 200—2 400 cm^{-1} and on this basis the presence of a co-ordinated benzonitrile ligand seems unlikely although this conclusion is not unequivocal. The alternative formulation (**3b**) suggests the presence of a phenyl nitrene ligand possibly resulting from elimination of dimethyl sulphide from *e.g.* a bis(sulphimide) complex $[PtCl_2(Me_2SNPh)_2]$ similar to the palladium derivative (**2**). Although we have no direct spectroscopic evidence for a nitrene structure we note that the SMe_2 methyl resonance in the ^1H n.m.r. spectrum exhibits a significant low-field shift relative to those of all the other sulphimide complexes isolated. This may reflect co-ordination to a higher-oxidation-state metal, Pt^{IV}, which is required for this structure. We note that one of the main preparative routes to sulphimides involves coupling of a nitrene with dialkyl sulphides[12] so that a reversal of this reaction is not inconceivable in the presence of a metal ion. Moreover a wide range of routes to nitrene complexes have been developed, some of which employ related phosphine imides R_3PNR' as the nitrene source.[13]

It was of interest to develop further the co-ordination chemistry of these ylide ligands and with a view to splitting the halogen bridges in complexes (**1a**)—(**1j**), reactions with phosphines L = PEt_3, PMe_2Ph, $PMePh_2$, and PPh_3 were carried out. The palladium complex (**1a**) readily afforded 1:1 adducts (**4a**)—(**4d**) with all four phosphines whereas the analogous platinum derivatives gave complex mixtures and a pure 1:1 complex (**4e**) was obtained only with PEt_3. Proton n.m.r. studies indicated that in some bases bis(phosphine) adducts *cis*- and *trans*-$[PtCl_2L_2]$ were present in the product mixtures along with 1:1 adducts, thus preventing purification. A pure 1:1 complex (**4f**) was also obtained from the reaction of (**1e**) with PPh_3 whereas impure products were obtained with PEt_3. Reactions of complex (**1i**) with PEt_3, PMe_2Ph, $PMePh_2$, and PPh_3 and of (**1j**) with PMe_2Ph, $PMePh_2$, and PPh_3 similarly gave intractable product mixtures.

Complexes (**4a**)—(**4f**) are yellow crystalline compounds

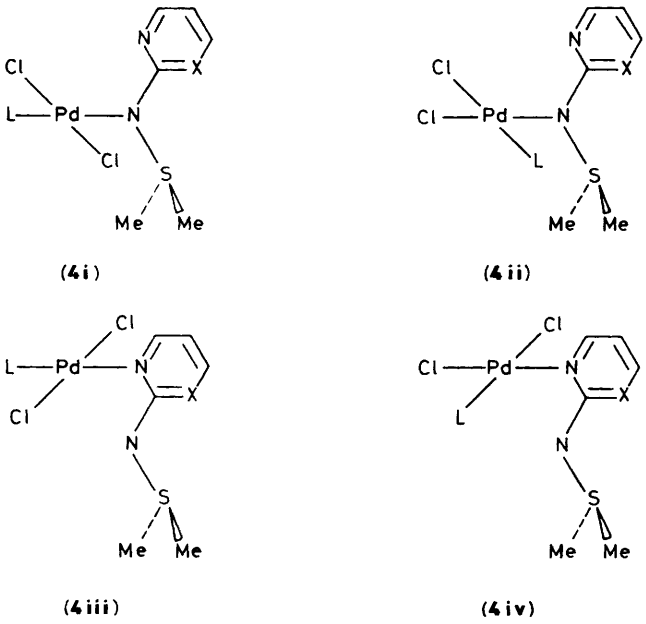


Figure 1. Isomeric forms of $[PdCl_2L(Me_2SNR)]$ (**4**) (L = tertiary phosphine, R = 2-pyridyl or 2-pyrimidinyl, X = CH,N)

soluble in polar organic solvents such as dichloromethane and chloroform but insoluble in non-polar solvents such as hexane. Four isomeric forms of this type of complex are possible (see Figure 1) based on (*a*) *cis* and *trans* dispositions of the chloride ligands about the square planar co-ordination of the metal and (*b*) sulphimide co-ordination *via* the ylide nitrogen [(**4i**) or (**4ii**)] or *via* a heteroaromatic ring nitrogen [(**4iii**) and (**4iv**)]. Since ^1H n.m.r. data did not distinguish between these forms *X*-ray diffraction studies of two derivatives exhibiting different n.m.r. features, (**4a**) and (**4b**), were carried out. The results of these studies have already been reported for the triethylphosphine complex $[PdCl_2(PEt_3)(Me_2SNC_5H_4N)]$ (**4a**) where a *trans* configuration of ligands about the metal centre was found and the sulphimide was observed to co-ordinate through the ylide nitrogen.[14] This corresponds to isomer (**4i**) and illustrates that the ylide adopts a conformation such that the R–N–S plane is approximately normal to the square plane of the complex. The ^1H n.m.r. spectrum of (**4a**) is consistent with such a structure in solution showing four pyridyl CH signals at δ 6.6—8.1, an SMe_2 singlet at δ 3.18, and one CH_2 and one CH_3 multiplet at δ 1.93 and 1.28 due to the phosphine ligand. The dimethylphenylphosphine derivative (**4b**) shows comparable spectroscopic features and a similar structure is therefore proposed.

The ^1H n.m.r. spectrum of the triphenylphosphine pyrimidinyl complex (**4f**), in contrast with (**4a**) and (**4b**), exhibits two equal-intensity methyl signals centred at δ 2.68 consistent with a less symmetric structure in which the two SMe_2 methyls are in different environments. Consequently *X*-ray diffraction studies of (**4f**) were carried out in order to establish the structural origin of this asymmetry. Suitable crystals were obtained in slow crystallisation from dichloromethane solution.

Structure Analysis of cis-$[PdCl_2(PPh_3)(Me_2SNC_4H_3N_2)]\cdot CH_2Cl_2$.—The crystals contain well separated molecules of (**4f**) and of dichloromethane in 1:1 molar ratio. The palladium atom is surrounded, as expected, by a *cis* square planar Cl_2PN donor set (see Figure 2). The donor nitrogen atom, N(1), is incorporated in the pyrimidine ring of the $Me_2SNC_4H_3N_2$ ligand. The Pd–N bond length [2.022(5) Å] is appreciably shorter than the corresponding value of 2.078(4) Å in *cis*-$[PdCl_2(Bu^t_2PCH_2C_{10}H_8N)]$; intramolecular overcrowding in the latter complex, the only *cis*-$PdCl_2PN$ sp^2 species to be structurally characterised,[15] may explain this difference. The Pd–P and Pd–Cl distances in (**4f**) (Table 1) agree well with the values in other *cis*-$PdCl_2PN$ species[15,16] and the greater *trans* influence of the phosphine, compared with a nitrogen donor, is illustrated by the lengthening of Pd–Cl(2) by 0.085(3) Å relative to Pd–Cl(1). The geometry of the PPh_3 ligand is unexceptional; in particular, the Pd–P–C–C torsion angles [16.0(5), 28.1(5), and 59.0(5)°] are similar to corresponding values in solid PPh_3 [l.p.–P–C–C 21.7, 32.7, and 56.2° where l.p. = lone pair],[17] suggesting that the phosphine conformation is little affected by its co-ordination to the metal.

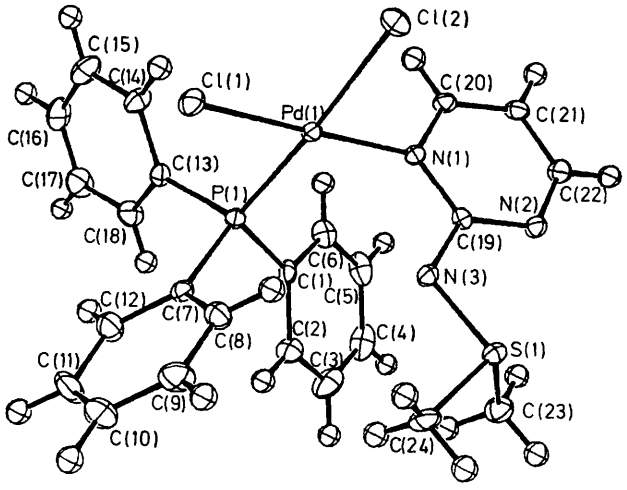


Figure 2. A view of *cis*-$[PdCl_2(PPh_3)(Me_2SNC_4H_3N_2)]$ (**4f**), showing 50% probability ellipsoids

The attachment of the metal atom to the pyrimidine N(1) atom in complex (**4f**), rather than to the sulphimide N(3) atom, contrasts with the situation in *trans*-$[PdCl_2(PEt_3)(Me_2SNC_5H_4N)]$ (**4a**) where the palladium atom bonds preferentially to the sulphimide, rather than to the pyridine, nitrogen atom.[14] Steric factors do not appear to explain the site of metal attachment in (**4f**): a plot of the conformation energy[18] of (**4f**) as a function of the torsion angles ω_1 = N(1)–Pd(1)–P(1)–C(1) and ω_2 = P(1)–Pd(1)–N(1)–C(19) had its lowest local minimum close to the conformation found in the crystal structure of (**4f**), where ω_1 = 2.7(3) and ω_2 = −79.6(4)°. A similar minimum energy, with no abnormally short non-bonded contacts, is found for a hypothetical model of (**4f**) with Pd bonded to N(3). We conclude that electronic factors probably determine the choice of donor nitrogen in complexes (**4f**) and (**4a**) but cannot assess the relative importance of the nature of the *trans* ligand (PR_3 or Cl) compared with the donor properties of sulphimide *versus* pyridine and pyrimidine nitrogen atoms. We note that pyridine is appreciably more basic than pyrimidine (pK_a = 5.6 for pyridine, pK_{a1} = 1.3 for pyrimidine).[19] Distances and angles in the sulphimide ligand of complex (**4f**) in general agree well with corresponding values in (**4a**) and in free sulphimides.[14,20] The most notable differences are the shortness of the N(3)–C(19) bond length in (**4f**) [1.332(7) Å compared with 1.366(6)—1.395(6) Å] and in the C–N–S–Me torsion angles [−77.4(5) and −179.6(5)° in (**4f**) compared with 92—100 and 157—164° in (**2a**) and uncomplexed sulphimides].

The structure of complex (**4f**) in the solid state corresponds to isomer (**4iv**) in Figure 1. This structure is also consistent with the ^1H n.m.r. spectrum where two SMe_2 methyl signals are observed suggesting retention of this structure in solution. However we note that this does not preclude the possibility of

Table 1. Selected distances (Å) and angles (°) in *cis*-[$PdCl_2(PPh_3)(Me_2SNC_4H_3N_2)$]·$CH_2Cl_2$

Pd(1)–Cl(1)	2.289(2)	Pd(1)–Cl(2)	2.374(2)
Pd(1)–P(1)	2.246(2)	Pd(1)–N(1)	2.022(5)
Cl(3)–C(25)	1.724(10)	Cl(4)–C(25)	1.740(10)
S(1)–N(3)	1.656(5)	S(1)–C(23)	1.786(7)
S(1)–C(24)	1.767(7)	P(1)–C(1)	1.819(6)
P(1)–C(7)	1.815(6)	P(1)–C(13)	1.836(6)
N(1)–C(19)	1.372(7)	N(1)–C(20)	1.332(8)
N(2)–C(19)	1.352(8)	N(2)–C(22)	1.333(8)
N(3)–C(19)	1.332(7)	C(1)–C(2)	1.387(9)
C(1)–C(6)	1.379(9)	C(2)–C(3)	1.391(11)
C(3)–C(4)	1.361(13)	C(4)–C(5)	1.375(13)
C(5)–C(6)	1.371(10)	C(7)–C(8)	1.396(9)
C(7)–C(12)	1.367(9)	C(8)–C(9)	1.365(10)
C(9)–C(10)	1.356(11)	C(10)–C(11)	1.368(12)
C(11)–C(12)	1.374(11)	C(13)–C(14)	1.382(9)
C(13)–C(18)	1.377(8)	C(14)–C(15)	1.381(10)
C(15)–C(16)	1.375(11)	C(16)–C(17)	1.350(12)
C(17)–C(18)	1.394(9)	C(20)–C(21)	1.370(9)
C(21)–C(22)	1.355(9)		

Cl(1)–Pd(1)–Cl(2)	92.2(1)	Cl(1)–Pd(1)–P(1)	86.8(1)
Cl(1)–Pd(1)–N(1)	175.9(2)	Cl(2)–Pd(1)–P(1)	176.0(1)
Cl(2)–Pd(1)–N(1)	84.8(2)	P(1)–Pd(1)–N(1)	96.4(2)
N(3)–S(1)–C(23)	108.8(3)	N(3)–S(1)–C(24)	97.6(3)
C(23)–S(1)–C(24)	99.0(3)	Pd(1)–P(1)–C(1)	115.5(2)
Pd(1)–P(1)–C(7)	112.3(2)	Pd(1)–P(1)–C(13)	114.0(2)
C(1)–P(1)–C(7)	106.1(3)	C(1)–P(1)–C(13)	101.2(3)
C(7)–P(1)–C(13)	106.8(3)	Pd(1)–N(1)–C(19)	120.0(4)
Pd(1)–N(1)–C(20)	120.9(4)	C(19)–N(1)–C(20)	117.8(5)
C(19)–N(2)–C(22)	116.9(5)	S(1)–N(3)–C(19)	112.2(4)
P(1)–C(1)–C(2)	122.8(5)	P(1)–C(1)–C(6)	118.8(5)
C(2)–C(1)–C(6)	118.5(6)	C(1)–C(2)–C(3)	119.9(7)
C(2)–C(3)–C(4)	120.5(8)	C(3)–C(4)–C(5)	119.8(8)
C(4)–C(5)–C(6)	120.0(7)	C(1)–C(6)–C(5)	121.2(7)
P(1)–C(7)–C(8)	118.1(5)	P(1)–C(7)–C(12)	124.2(5)
C(8)–C(7)–C(12)	117.7(6)	C(7)–C(8)–C(9)	120.2(6)
C(8)–C(9)–C(10)	120.8(7)	C(9)–C(10)–C(11)	120.2(8)
C(10)–C(11)–C(12)	119.1(7)	C(7)–C(12)–C(11)	121.9(6)
P(1)–C(13)–C(14)	120.7(5)	P(1)–C(13)–C(18)	120.0(5)
C(14)–C(13)–C(18)	119.2(6)	C(13)–C(14)–C(15)	119.6(6)
C(14)–C(15)–C(16)	120.6(7)	C(15)–C(16)–C(17)	120.3(7)
C(16)–C(17)–C(18)	119.8(7)	C(13)–C(18)–C(17)	120.4(6)
N(1)–C(19)–N(2)	122.3(5)	N(1)–C(19)–N(3)	115.7(5)
N(2)–C(19)–N(3)	122.0(5)	N(1)–C(20)–C(21)	122.2(6)
C(20)–C(21)–C(22)	116.7(6)	N(2)–C(22)–C(21)	124.0(6)
Cl(3)–C(25)–Cl(4)	112.0(6)		

rearrangement to the alternative *cis* form (**4ii**) [*cf.* (**4a**)] which, if stereochemically rigid, would also show inequivalent SMe_2 methyl groups.

The observation of both geometric (*cis*/*trans*) and linkage isomerism in complexes (**4**) now enables us to attempt an explanation of the n.m.r. spectra of complexes (**4c**) and (**4d**) where both isomerism and fluxional behaviour are indicated. The spectrum of (**4c**) is quite simple at 20 °C, showing, in addition to overlapping phenyl resonances, an SMe_2 singlet and a $PMePh_2$ methyl group doublet. However as the temperature is reduced the SMe_2 signal broadens and splits into one large singlet and two equal-intensity but weak resonances at −60 °C. The $PMePh_2$ doublet also broadens at low temperature and at −60 °C a shoulder can also be discerned along with additional pyridyl *CH* signals. These data suggest that two isomeric forms exist at low temperature: a symmetric form and an unsymmetric form, integrated ratio 8:1 at −60 °C. The variable-temperature ^1H n.m.r. spectra of the triphenylphosphine derivative (**4d**) show corresponding but more marked changes and these will be discussed in detail. However the ^{31}P-$\{^1H\}$ n.m.r. spectrum which was recorded at +60 °C ($CD_3C_6D_5$) and over the

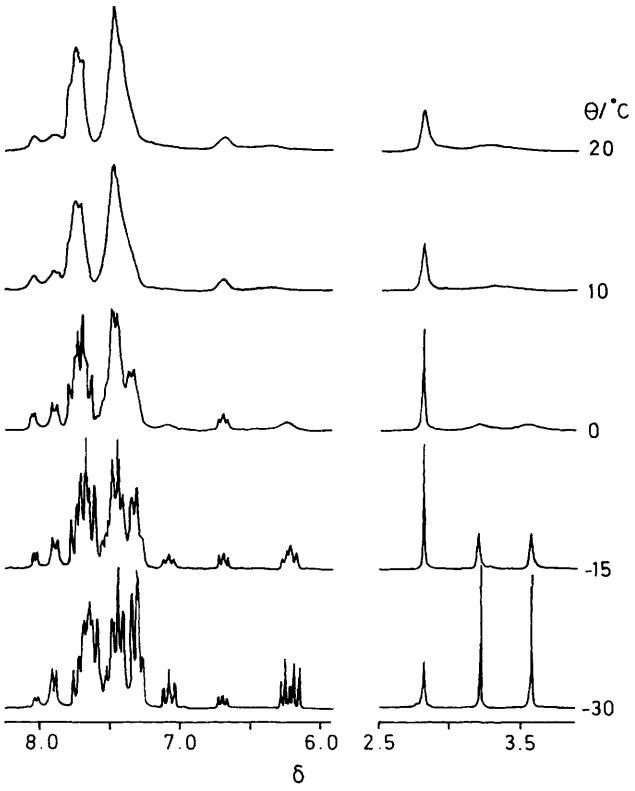


Figure 3. Variable-temperature ^1H n.m.r. spectrum of [$PdCl_2(PPh_3)(Me_2SNC_5H_4N)$] (**4d**) in CD_2Cl_2

temperature range +40 to −60 °C (CD_2Cl_2) will be described first.

At −60 °C a sharp singlet δ 26.6, (**A**), is present accompanied by a very weak resonance at δ 28.5, (**B**), consistent with the presence of two isomers. As the temperature is raised the minor isomer signal, (**B**), increases in intensity at the expense of the major isomer peak, (**A**), indicating a temperature-dependent equilibrium. Above −20 °C the peak at δ 26.6 also begins to broaden followed subsequently by the other peak and both coalesce at *ca.* 40 °C. At +60 °C a singlet sharp peak is observed indicating rapid exchange between the two isomeric forms (**A**) and (**B**). The ^1H n.m.r. spectra (Figure 3) show corresponding changes but the SMe_2 resonances provide more detailed information. At −60 °C the major isomer (**A**) exhibits two equal-intensity singlets whilst the minor isomer (**B**) shows only one. Moreover the two resonances of isomer (**A**) broaden markedly above −20 °C and coalesce at *ca.* 12 °C indicating fluxional behaviour which equilibrates the two inequivalent methyl environments. At higher temperatures the signals of both isomers broaden and begin to coalesce, again indicating rapid exchange between the two isomers.

The simplest explanation for these observations is that the major isomer (**A**) with inequivalent methyls has structure (**4iv**) similar to (**4f**) and the minor isomer (**B**) (equivalent methyls) has the *trans* structure (**4i**) found with (**4a**). However, since (**4i**) and (**4ii**) would have similar n.m.r. spectra as would (**4iii**) and (**4iv**), other permutations are possible which would give rise to the observed spectra.

We note that the fluxional behaviour of isomer (**A**), involving exchange of the two SMe_2 methyl groups, presumably results from an inversion–rotation process proceeding *via* a planar N–SMe_2 group as illustrated in the Scheme. Inversion at sulphur has been observed in free sulphimides and related ligands where it leads to racemisation[21] and in particular it has been noted

that protonation of the sulphimide nitrogen reduces the inversion barrier. By analogy it might be expected that co-ordination of the sulphimide nitrogen as in isomers (**4i**) and (**4ii**) would similarly reduce the barrier to inversion relative to that in the isomeric forms (**4iii**) and (**4iv**). We have already noted the presence of only one SMe_2 signal in the spectra of complexes (**1**) where evidence has been obtained for the N ylide mode of co-ordination, thus supporting the suggestion that this type of bonding produces low inversion barriers. If this conclusion is valid we note that isomer (**B**) in complex (**4d**) which shows one SMe_2 methyl signal down to −60 °C could have the alternative form (**4ii**) which exhibits a very low barrier to inversion at sulphur.

Thus two explanations can be proposed to explain the dynamic n.m.r. data for complex (**4d**) and hence for (**4c**). The first is that the two isomers correspond to *cis* (**A**) and *trans* (**B**) forms of the molecule with either mode of sulphimide co-ordination to the metal. Alternatively both isomers have a *cis* arrangement about the metal but in one the sulphimide is bound *via* the heteroaromatic ring [isomer (**A**) = (**4iv**)] and in the other *via* the sulphimide nitrogen [isomer (**B**) = (**4ii**)]. The latter explanation requires that the exchange between (**A**) and (**B**) involves flipping of the metal between the two nitrogen donor atoms of the ligand, a process which has many precedents in inorganic chemistry.[22]

The first explanation implies that *cis–trans* isomerisation may be involved and although this is frequently observed in square planar complexes it is not normally rapid on the n.m.r. time-scale.[10,13a,23] It may be significant that the low-temperature n.m.r. spectra of (**4a**)—(**4d**) at −60 °C indicate that only one isomeric form (**B**) is present with (**4a**) and (**4b**); a small quantity of the second isomer (**A**) was observed with (**4c**) and this becomes the dominant form with (**4d**). As noted earlier, steric effects do not appear to be significant in the *cis* structure which indicates that the *trans* form is stabilised by alkylphosphines as in the case of (**4a**).

In contrast with the palladium complexes (**1**) the only pure complex isolated from reactions of platinum derivatives of type (**1**) with phosphines was $[PtCl_2(PEt_3)(Me_2SNC_5H_4N)]$ (**4e**). The ^1H n.m.r. spectrum of this derivative is in most respects very similar to that of *trans*-$[PdCl_2(PEt_3)(Me_2SNC_5H_4N)]$ (**4a**) apart from minor differences in the ligand δ values. Although this suggests a similar structure, significantly we note the absence of platinum–hydrogen coupling in the SMe_2 singlet. Thus the alternative hetero ring mode of co-ordination found in (**2**) is indicated although in this case a *trans* arrangement of the ligands about the metal [isomer (**4iii**)] appears to be favoured. Accordingly a single ν(Pt–Cl) mode is observed in the i.r. spectrum at 334 cm^{-1}.

Conclusions

The phenylsulphimide molecule $PhNSMe_2$ has been found to function as a simple monodentate ligand towards palladium(II) and platinum(II) in complexes $[PdCl_2(Me_2SNPh)_2]$ and $[PtCl_2(Me_2SNPh)(PhN)]$. The sulphimide also appears to function as a phenyl nitrene source in the formation of the latter complex. Heteroaromatic substituted sulphimides $RNSMe_2$ (R = heteroaromatic radical) with two or more donor sites available are able to co-ordinate *via* either the heteroaromatic ring donor atom or the ylide nitrogen. The factors controlling this preference for co-ordination *via* a particular donor atom appear to be electronic rather than steric and may be related to the nature of the other ligands on the metal. The particular combinations of ligands available also influence the isomeric form of the complexes since *e.g.* with phosphine derivatives $[MCl_2L(Me_2SNR)]$ *trans* structures are observed with alkylphosphines L = PEt_3 and *cis* isomers with arylphosphines such as PPh_3.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer calibrated against polystyrene. Hydrogen-1 and ^{31}P n.m.r. spectra were recorded at 200.1 and 80 MHz respectively on a Bruker WP200SY spectrometer with $SiMe_4$ and H_3PO_4 (85%) as references. All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over powdered calcium hydride (diethyl ether, hexane, and dimethyl sulphoxide) and P_2O_5 (dichloromethane) under nitrogen and distilled just before use. Elemental analyses were carried out by the Department of Chemistry, University of Manchester Institute of Science and Technology.

The compounds $K_2[PtCl_4]$, $PtCl_2$, and $PdCl_2$ were purchased from Johnson Matthey and used without further purification; $[PdCl_2(PhCN)_2]$ and $[PtCl_2(PhCN)_2]$ were prepared as previously described[25] as were the ylides *S,S*-dimethyl-*N*-(2-pyridyl)sulphimide,[24–26] *S,S*-dimethyl-*N*-(4-methyl-2-pyridyl)sulphimide,[26] *S,S*-dimethyl-*N*-(2-pyrimidinyl)sulphimide,[25] *S,S*-dimethyl-*N*-(4-methyl-2-pyrimidinyl)-sulphimide,[25] *S,S*-dimethyl-*N*-(2-pyrazinyl)sulphimide, and *S,S*-dimethyl-*N*-phenylsulphimide.[27] The amines required for such syntheses were purchased from Aldrich and used after recrystallisation from hot hexane, where necessary.

Preparations.—*Dichloro*[S,S-*dimethyl*-N-(2-*pyridyl*)-*sulphimide*]*palladium*(II) (**1a**). Bis(benzonitrile)dichloropalladium(II) (0.23 g, 0.59 mmol) in dichloromethane (10 cm^3) was added to *S,S*-dimethyl-*N*-(2-pyridyl)sulphimide (0.1 g, 0.64 mmol) in dichloromethane (5 cm^3). The orange precipitate (0.1 g) was filtered off and washed several times with dichloromethane, then diethyl ether, and finally dried *in vacuo*. The filtrate was reduced in volume and on standing gave a second crop of the required compound (0.05 g, total yield 76%) (Found: C, 24.6; H, 3.0; N, 8.0. $C_7H_{10}Cl_2N_2PdS$ requires C, 25.3; H, 3.0; N, 8.4%). I.r.: $\nu_{max.}$(KBr) 3 005, 2 995, 2 905, 1 540, 1 460, 1 435, 1 335, 1 285, 1 155, 1 120, 1 040, 855, 795, 775, 620, 530, 435, 351, 335, and 290 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 3.38 (s, 6 H, SMe_2), 6.69 (t, 1 H, *J* 8, H^4 or H^5), 6.98 (d, 1 H, *J ca.* 8, H^3), 7.57 (t, 1 H, *J ca.* 8, H^4 or H^5), and 8.65 (d, 1 H, *J ca.* 8 Hz, H^6).

Dichloro[S,S-*dimethyl*-N-(2-*pyridyl*)*sulphimide*]*platinum*(II) (**1b**). (*a*) *From* $K_2[PtCl_4]$. *S,S*-Dimethyl-*N*-(2-pyridyl)-sulphimide (0.10 g, 0.66 mmol) in water (3 cm^3) was added to dipotassium tetrachloroplatinate (0.27 g, 0.64 mmol) in water (6 cm^3). The mixture was stirred for 4 h during which time the red solution turned yellow and a precipitate formed (0.20 g). It proved impossible to obtain an analytically pure product from this material after trituration with, separately, water, ethanol, dichloromethane, or diethyl ether (Found: C, 18.5; H, 2.2; N, 5.8. $C_7H_{10}Cl_2N_2PtS$ requires C, 20.0; H, 2.4; N, 6.7%). The remaining filtrate was reduced in volume and allowed to stand for several days. A second crop of yellow material (0.03 g) was purified as above to give a product believed to be the impure required compound with an identical i.r. spectrum [see (*b*) below].

(*b*) *From* $[PtCl_2(PhCN)_2]$. *S,S*-Dimethyl-*N*-(2-pyridyl)-sulphimide (0.05 g, 0.31 mmol) in dichloromethane (4 cm^3) was added to bis(benzonitrile)dichloroplatinum(II) (0.135 g, 0.28 mmol) in dichloromethane (10 cm^3). The solution was heated under reflux for 48 h during which period a yellow precipitate formed. This material was removed by periodic filtration of the mixture and was washed with dichloromethane to give the compound (**1b**) (0.075 g, 62%) (Found: C, 19.5; H, 2.2; N, 6.0%). I.r.: $\nu_{max.}$(KBr) 3 005, 2 990, 2 985, 1 610, 1 540, 1 460, 1 430,

1 335, 1 280, 1 240, 1 150, 1 120, 1 040, 1 020m, 865, 800, 775, 625, 530, 435, 350, 330, and 305 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 3.45 [s, 6 H, J(Pt–H) 31.5, SMe_2], 6.67 (td, 1 H, J 8.0 and 1.0, H^4 or H^5), 7.08 [dd, 1 H, J 8.0 and 1.0, J(Pt–H) 15.0, H^3 or H^6], 7.60 (td, 1 H, J 8.0 and 1.0, H^4 or H^5), and 8.95 [dd, 1 H, J 8.0 and 1.0, J(Pt–H) 31.5 Hz, H^3 or H^6].

Dichloro[S,S-*dimethyl*-N-(4-*methyl*-2-*pyridyl*)*sulphimide*]-*palladium*(II) (**1c**). *S,S*-Dimethyl-*N*-(4-methyl-2-pyridyl)-sulphimide (0.15 g, 0.87 mmol) in dichloromethane (5 cm^3) was added dropwise to a stirred solution of $[PdCl_2(PhCN)_2]$ (0.33 g, 0.86 mmol) in dichloromethane (10 cm^3). The orange product was purified by the method given for compound (**1a**) to give compound (**1c**) (0.12 g, 40%) (Found: C, 28.2; H, 3.6; N, 8.1. $C_8H_{12}Cl_2N_2PdS$ requires C, 27.8; H, 3.5; N, 8.1%). I.r.: $\nu_{max.}$(KBr) 3 000, 2 980, 1 620, 1 540, 1 525, 1 475, 1 445—1 400 (br), 1 325, 1 310, 1 285, 1 230, 1 180, 1 105, 920, 860, 805, 755, 645, 590, 560, 445, 355, 335, and 320 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 2.30 (s, 3 H, 4-Me), 3.40 (s, 6 H, SMe_2), 6.50 (dd, 1 H, J 8.0, < 1.0, H^5), 6.80 (s, 1 H, H^3), and 8.47 (d, 1 H, J 8.0 Hz, H^6).

Dichloro[S,S-*dimethyl*-N-(4-*methyl*-2-*pyridyl*)*sulphimide*]-*platinum*(II) (**1d**). Dipotassium tetrachloroplatinate (0.39 g, 0.98 mmol) and *S,S*-dimethyl-*N*-(4-methyl-2-pyridyl)sulphimide (0.17 g, 0.98 mmol) in water (17 cm^3) were stirred at room temperature for 4 h. The product was filtered off and washed with water, ethanol, and dichloromethane, and finally diethyl ether to give the required yellow compound (0.33 g, 77%) (Found: C, 21.6; H, 2.6; N, 6.2. $C_8H_{12}Cl_2N_2PtS$ requires C, 22.1; H, 2.7; N, 6.4%). I.r.: $\nu_{max.}$(KBr) 3 000, 2 910, 1 640, 1 560, 1 535, 1 475, 1 445, 1 415, 1 325, 1 285, 1 260, 1 235, 1 180, 1 145, 1 030, 970, 860, 800, 450, and 325 cm^{-1}. The complex was too insoluble for measurement of a satisfactory ^1H n.m.r. spectrum.

Dichloro[S,S-*dimethyl*-N-(2-*pyrimidinyl*)*sulphimide*]-*palladium*(II) (**1e**). *S,S*-Dimethyl-*N*-(2-pyrimidinyl)sulphimide (0.1 g, 0.64 mmol) and $[PdCl_2(PhCN)_2]$ (0.25 g, 0.64 mmol) in dichloromethane (15 cm^3) were allowed to react as described for (**1c**). Purification by the method given for (**1a**) gave the required compound (0.19 g, 86%) (Found: C, 21.3; H, 2.6; N, 11.2. $C_6H_9Cl_2N_3PdS$ requires C, 21.6; H, 2.7; N, 12.6%). I.r.: $\nu_{max.}$(KBr) 3 040, 2 990, 2 910, 1 585, 1 555, 1 458, 1 430, 1 265, 1 180, 1 040, 985, 955, 920, 800, 780, 765, 690, 640, 450, and 340 cm^{-1}. Proton n.m.r. [$(CD_3)_2SO$]: δ 2.95 (br d, 6 H, SMe_2), 6.6 (distorted t, 1 H, H^5), and 8.30 (br s, 2 H, H^4 and H^6).

Dichloro[S,S-*dimethyl*-N-(2-*pyrimidinyl*)*sulphimide*]-*platinum*(II) (**1f**). (*a*) *From* $[PtCl_2(PhCN)_2]$. Bis(benzonitrile)-dichloroplatinum(II) (0.221 g, 0.46 mmol) and *S,S*-dimethyl-*N*-(2-pyrimidinyl)sulphimide (0.079 g, 0.51 mmol) were refluxed in dichloromethane (20 cm^3) for 48 h when a yellow precipitate formed. This was separated, washed with dichloromethane followed by diethyl ether, and dried *in vacuo* to give complex (**1f**) (0.151 g, 78%) (Found: C, 17.6; H, 2.1; N, 9.8. $C_6H_9Cl_2N_3PtS$ requires C, 17.1; H, 2.1; N, 9.9%). Proton n.m.r. (CD_2Cl_2): δ 3.55 [s, 6 H, J(Pt–H) 32.5, SMe_2], 6.75 (t, 1 H, J 8.0, H^5), 8.50 (dd, 1 H, J 7.0, 1.0, H^4 or H^6), and 9.20 (dd, 1 H, J 7.0, 1.0 Hz, H^6 or H^4). I.r.: $\nu_{max.}$(KBr) 3 070, 2 995, 2 965, 1 620, 1 590, 1 540, 1 455, 1 420, 1 355, 1 260, 1 180, 1 140, 1 030, 985, 955, 930, 780, 630, 445, and 334 cm^{-1}.

(*b*) *From* $K_2[PtCl_4]$. Dipotassium tetrachloroplatinate (0.27 g, 0.64 mmol), *S,S*-dimethyl-*N*-(2-pyrimidinyl)sulphimide (0.1 g, 0.65 mmol), and water (10 cm^3) were stirred at room temperature for 4 h. The yellow precipitate (0.13 g) was separated and triturated with acetonitrile. It was dissolved in dimethyl sulphoxide and then reprecipitated with ethanol but this did not give an analytically pure compound (Found: C, 18.4; H, 2.7; N, 10.8%).

Dichloro[S,S-*dimethyl*-N-(4-*methyl*-2-*pyrimidinyl*)*sulphimide*]*palladium*(II) (**1g**). *S,S*-Dimethyl-*N*-(4-methyl-2-pyrimidinyl)sulphimide (0.17 g, 0.10 mmol) and $[PdCl_2(PhCN)_2]$ (0.37 g, 0.097 mmol) were allowed to react in dichloromethane (15 cm^3) as described for (**1c**). Purification by the method described for (**1a**) gave the required compound (0.28 g, 84%) (Found: C, 24.2; H, 3.5; N, 12.3. $C_7H_{11}Cl_2N_2PdS$ requires C, 24.2; H, 3.2; N, 12.1%). I.r.: $\nu_{max.}$(KBr) 3 070, 2 990, 2 920, 2 850, 1 585, 1 545, 1 430, 1 405, 1 370, 1 315, 1 255, 1 060, 1 030, 980, 965, 920, 880, 855, 795, 665, 585, 475, 360, and 335 cm^{-1}. Proton n.m.r. [$(CD_3)_2SO$]: δ 2.25 (br s, 3 H, ring Me), 2.90 (br s, 6 H, SMe_2), 6.50 (br d, 1 H, pyrimidinyl H), and 8.12 (d, 1 H, pyrimidinyl H).

Dichloro[S,S-*dimethyl*-N-(4-*methyl*-2-*pyrimidinyl*)-*sulphimide*]*platinum*(II) (**1h**). Dipotassium tetrachloroplatinate (0.13 g, 0.30 mmol), *S,S*-dimethyl-*N*-(4-methyl-2-pyrimidinyl)-sulphimide (0.11 g, 0.64 mmol), and water (15 cm^3) were stirred at room temperature for 6 h. The yellow precipitate (0.07 g) was separated and washed several times with acetonitrile. It was dissolved in dimethyl sulphoxide and reprecipitated with ethanol but this treatment did not give an analytically pure compound (Found: C, 17.7; H, 2.2; N, 8.7. $C_7H_{12}Cl_2N_3PtS$ requires C, 19.3; H, 2.5; N, 9.6%). I.r.: $\nu_{max.}$(KBr) 3 050, 3 000, 2 900, 1 630, 1 580, 1 530, 1 485, 1 405, 1 340, 1 280, 1 210, 1 140, 1 040, 1 010, 980, 945, 935, 800, 720, 640, 440, and 330br cm^{-1}. The compound was too insoluble for measurement of a satisfactory ^1H n.m.r. spectrum.

Dichloro[S,S-*dimethyl*-N-(2-*pyrazinyl*)*sulphimide*]-*palladium*(II) (**1i**). *S,S*-Dimethyl-*N*-(2-pyrazinyl)sulphimide (0.13 g, 0.85 mmol) and bis(benzonitrile)dichloropalladium(II) (0.32 g, 0.82 mmol) were stirred in dichloromethane (15 cm^3) at room temperature. The orange product (0.06 g) was filtered off and washed with acetonitrile. This material was dissolved in dimethyl sulphoxide and reprecipitated with ethanol. The resultant orange solid remained analytically impure (Found: C, 18.6; H, 2.6; N, 10.2. $C_6H_9Cl_2N_3PdS$ requires C, 21.6; H, 2.7; N, 12.6%). I.r.: $\nu_{max.}$(KBr) 3 050, 3 000, 2 910, 1 630—1 570br, 1 500—1 455br, 1 405, 1 285, 1 205, 1 150, 1 080, 1 040, 1 020, 985, 950, 810, 450, and 350 cm^{-1}. The compound was too insoluble for measurement of a satisfactory ^1H n.m.r. spectrum.

Dichloro[S,S-*dimethyl*-N-(2-*pyrazinyl*)*sulphimide*]*platinum*-(II) (**1j**). Dipotassium tetrachloroplatinate (0.4 g, 0.87 mmol), *S,S*-dimethyl-*N*-(2-pyrazinyl)sulphimide (0.15 g, 0.97 mmol), and water (15 cm^3) were stirred at room temperature for 6 h. The precipitate was separated by filtration and washed successively with water, ethanol, dichloromethane, and finally diethyl ether to give the required compound (0.24 g, 60%) (Found: C, 17.2; H, 2.1; N, 9.8. $C_6H_9Cl_2N_3PtS$ requires C, 17.1; H, 2.1; N, 9.9%). I.r.: $\nu_{max.}$(KBr) 3 050, 3 000, 2 900, 1 630, 1 580, 1 530, 1 485, 1 405, 1 340, 1 230, 1 210, 1 140, 1 040, 1 010, 980, 945, 935, 800, 720, 640, 440, and 330 cm^{-1}. The complex was too insoluble for measurement of a satisfactory ^1H n.m.r. spectrum.

Dichlorobis(S,S-*dimethyl*-N-*phenylsulphimide*)*palladium*(II) (**2**). Bis(benzonitrile)dichloropalladium(II) (0.11 g, 0.29 mmol) in dichloromethane (10 cm^3) was added to *S,S*-dimethyl-*N*-phenylsulphimide (0.05 g, 0.32 mmol) in dichloromethane (5 cm^3). The colour changed from orange to dark red. The mixture was stirred for 20 min and the volume reduced to *ca.* 5 cm^3 by evaporation. On standing at −12 °C a red-brown oily product formed. This was separated and triturated with cold hexane to give a powder which was then recrystallised several times from dichloromethane–hexane. The product (0.052 g, 37%) was finally purified by washing several times with dry diethyl ether (Found: C, 38.6; H, 4.6; N, 5.6. $C_{16}H_{22}Cl_2N_2PdS_2$ requires C, 39.7; H, 4.5; N, 5.8%). I.r.: $\nu_{max.}$(KBr) 3 000, 2 920, 2 850, 1 590, 1 480, 1 420, 1 375, 1 240, 1 030, 990, 945, 830, 755, 690, 510, and 330 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 3.15 (s, 6 H, SMe_2), 7.00 (m, 1 H, aryl H), 7.30 (m, 2 H, aryl H), and 7.65 (m, 2 H, aryl H).

Dichloro(S,S-*dimethyl*-N-*phenylsulphimide*)(*phenylimido*)-*platinum* (**3**). *S,S*-Dimethyl-*N*-phenylsulphimide (0.1 g, 0.68

mmol) and bis(benzonitrile)dichloroplatinum(II) (0.28 g, 0.58 mmol) were heated under reflux for 1 h in dichloromethane (20 cm^3). The product was filtered off and the filtrate was evaporated to low volume to precipitate a yellow solid. This was separated, recrystallised from dichloromethane–n-hexane, and finally washed with diethyl ether to give the required complex (0.05 g; total yield with second crop 0.077 g, 22%) (Found: C, 33.6; H, 2.8; N, 5.3. $C_{14}H_{16}Cl_2N_2PtS$ requires C, 32.9; H, 3.1; N, 5.5%). I.r.: $\nu_{max.}$(KBr) 3 000, 2 905, 1 490, 1 465, 1 430, 1 415, 1 370, 1 130, 1 070, 1 040, 990, 945, 850, 750, 690, 510, 370, and 340 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 3.62 [6 H, *J*(Pt–H) 31.3 Hz, SMe_2], 6.95 (m, 2 H, aryl H), and 7.15 (m, 8 H, aryl H).

Dichloro[S,S-*dimethyl*-N-(2-*pyridyl*)*sulphimide*](*triethylphosphine*)*palladium*(II) (**4a**). Triethylphosphine (0.03 g, 0.27 mmol) and dichloro[*S*,*S*-dimethyl-*N*-(2-pyridyl)sulphimide]-palladium(II) (0.10 g, 0.30 mmol) were heated under reflux for 1 h in dichloromethane (12 cm^3). The product was cooled, filtered off, and the filtrate was evaporated to leave an oily residue. This was washed with diethyl ether and redissolved in dichloromethane (5 cm^3). Addition of n-hexane (1 cm^3) caused separation of an unidentified orange oil. This was separated and the residual solution was allowed to evaporate slowly to deposit yellow needles of the required compound (0.04 g, 29%) (Found: C, 34.6; H, 5.4; N, 6.2. $C_{13}H_{25}Cl_2N_2PPdS$ requires C, 34.7; H, 5.6; N, 6.2%). I.r.: $\nu_{max.}$(KBr) 3 000, 2 980, 1 590, 1 555, 1 460, 1 430, 1 300, 1 295, 1 150, 1 105, 1 040, 1 000, 980, 955, 910, 850, 780, 760, 735, 725, 635, 620, 530, 485, 440, 360, and 335 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 1.28 [dt, 9 H, *J*(P–H) 17, *J*(H–H) 7, PCH_2CH_3], 1.93 [dq, 6 H, *J*(P–H) 12, *J*(H–H) 7, PCH_2CH_3], 3.18 (s, 6 H, SMe_2), 6.65 (ddd, *J* 7.1, 5.1, 1.0, pyridyl H), 7.47 (ddd, *J* 8.4, 7.1, 2.0, pyridyl H), and 8.01 (d, 1 H, *J* 5.1 Hz, pyridyl H).

Dichloro(*dimethylphenylphosphine*)[S,S-*dimethyl*-N-(2-*pyridyl*)*sulphimide*]*palladium*(II) (**4b**). Dimethylphenylphosphine (0.06 g, 0.42 mmol) and dichloro[*S*,*S*-dimethyl-*N*-(2-pyridyl)sulphimide]palladium(II) (0.13 g, 0.38 mmol) in dichloromethane (10 cm^3) were heated for 16 h under reflux. Work up as in the preceding experiment gave the required yellow microcrystalline compound (0.08 g, 50%) (Found: C, 37.6; H, 4.4; N, 5.6. $C_{15}H_{21}Cl_2N_2PPdS$ requires C, 38.3; H, 4.5; N, 5.9%). I.r.: $\nu_{max.}$(KBr) 3 100, 3 000, 2 905, 1 585, 1 550, 1 460, 1 420, 1 330, 1 285, 1 160, 1 148, 1 110, 1 030, 995, 980, 950, 910, 855, 780, 740, 730, 665, 635, 620, 520, 485, 440, and 355 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 1.83 [d, 6 H, *J*(P–H) 12.5, PMe_2], 3.1 (s, 6 H, SMe_2), 6.65 (t, 1 H, *J* 8, pyridyl H), 7.52 (m, 4 H, aryl H), 7.72 (d, 1 H, *J* 10, pyridyl H), 7.86 (m, 2 H, aryl H), and 8.02 (d, 1 H, *J* 8 Hz, pyridyl H).

Dichloro[S,S-*dimethyl*-N-(2-*pyridyl*)*sulphimide*](*methyldiphenylphosphine*)*palladium*(II) (**4c**). Methyldiphenylphosphine (0.049 g, 0.21 mmol) in dichloromethane (3 cm^3) was added dropwise to a stirred suspension of dichloro[*S*,*S*-dimethyl-*N*-(2-pyridyl)sulphimide]palladium(II) (0.06 g, 0.19 mmol) in dichloromethane (8 cm^3) and the mixture was heated under reflux for 16 h. The product was filtered off and the filtrate was reduced in volume by evaporation. Addition of n-hexane gave a yellow product which was recrystallised from dichloromethane–n-hexane to give the required compound (0.043 g, 45%) (Found: C, 44.2; H, 4.3; N, 5.0. $C_{20}H_{23}Cl_2N_2PPdS$ requires C, 45.1; H, 4.3; N, 5.2%). I.r.: $\nu_{max.}$(KBr) 3 050, 2 960, 1 600, 1 550, 1 470, 1 430, 1 330, 1 285, 1 105, 1 000, 980, 920, 900, 775, 740, 700, 515, 490, 450, and 340 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 2.05 [d, 3 H, *J*(P–H) 12.5, PMe], 3.15 (s, 6 H, SMe_2), 6.68 (t, 1 H, *J* 6.0, pyridyl H), 7.48 (m, 7 H, aryl H), 7.82 (m, 5 H, aryl H), and 8.02 (d, 1 H, *J* 4.0, pyridyl H).

Dichloro[S,S-*dimethyl*-N-(2-*pyridyl*)*sulphimide*](*triphenylphosphine*)*palladium*(II) (**4d**). Triphenylphosphine (0.11 g, 0.42 mmol) in dichloromethane (7 cm^3) was added dropwise to a suspension of dichloro[*S*,*S*-dimethyl-*N*-(2-pyridyl)sulphimide]-palladium(II) (0.13 g, 0.39 mmol) in dichloromethane (8 cm^3) and the mixture was stirred at room temperature for 10 h. The cloudy orange solution was filtered and the filtrate was reduced in volume by evaporation. Addition of n-hexane gave a yellow product which was recrystallised from dichloromethane–n-hexane at −12 °C to give the required compound (0.16 g, 69%) as a yellowish green solid (Found: C, 46.9: H, 4.0; N, 4.3. $C_{25}H_{25}Cl_2N_2PdS$ requires C, 50.5; H, 4.2; N, 4.7%). I.r.: $\nu_{max.}$(KBr) 3 050, 2 960, 2 920, 1 600, 1 540, 1 470, 1 425, 1 330, 1 285, 1 260, 1 095, 1 020, 975, 950, 915, 800, 750, 700, 535, 500, and 330 cm^{-1}. Proton n.m.r. (CD_2Cl_2): [isomer (**A**)], δ 3.20 (s, 6 H, SMe_2), 6.70 (br s, 1 H, pyridyl H), and 8.05 (br s, 1 H, pyridyl H); [isomer (**B**)], δ 2.62 (br s, 6 H, SMe_2), 6.35 (br s, *ca.* 2 H, pyridyl H), 7.10 (br s, *ca.* 1 H, pyridyl H), and 7.90 (br s, *ca.* 1 H, pyridyl H). The remaining aromatic protons give rise to multiplets centred on δ 7.45 and 7.75.

Dichloro[S,S-*dimethyl*-N-(2-*pyridyl*)*sulphimide*](*triethylphosphine*)*platinum*(II) (**4e**). Triethylphosphine (0.12 g, 0.10 mmol) and dichloro[*S*,*S*-dimethyl-*N*-(2-pyridyl)sulphimide]-platinum(II) (0.39 g, 0.09 mmol) were heated under reflux in dichloromethane (7 cm^3) for 1 h. The product was filtered off and the filtrate reduced in volume by evaporation. Addition of n-hexane precipitated a yellow material which was purified by repeated precipitation from dichloromethane–n-hexane to give the required complex (0.14 g, 28%) (Found: C, 29.1; H, 4.4; N, 5.0. $C_{13}H_{25}Cl_2N_2PPtS$ requires C, 28.9; H, 4.6; N, 5.2%). I.r.: $\nu_{max.}$(KBr) 2 960, 2 925, 1 555, 1 460, 1 335, 1 150, 1 035, 1 000, 980, 950, 905, 865, 780, 765, 530, 420, and 334 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 1.22 [dt, 9 H, *J*(H–H) 7.0, *J*(P–H) 17.0, PCH_2CH_3], 1.90 [dq, 6 H, *J*(H–H) 7.0, *J*(P–H) 11.0, PCH_2CH_3], 3.20 (s, 6 H, SMe_2), 6.68 (ddd, 1 H, *J* 1.0, 5.1, 7.1, H^4 or H^5), 7.48 (ddd, 1 H, *J* 2.0, 6.4, 7.0, H^4 or H^5), 7.91 (br d, H^3 or H^6), and 8.40 (ddd, *J* 0.9, 1.8, 5.1 Hz, H^3 or H^6).

Dichloro[S,S-*dimethyl*-N-(2-*pyrimidinyl*)*sulphimide*]-(*triphenylphosphine*)*palladium*(II) (**4f**). Triphenylphosphine (0.06 g, 0.22 mmol) in dichloromethane (3 cm^3) was added dropwise to a suspension of dichloro[*S*,*S*-dimethyl-*N*-(2-pyrimidinyl)sulphimide]palladium(II) (0.07 g, 0.20 mmol) in dichloromethane (7 cm^3) and the mixture was stirred at room temperature for 16 h. The product was filtered off and the filtrate reduced in volume by evaporation. Addition of diethyl ether caused precipitation of a yellow solid which was recrystallised from dichloromethane–diethyl ether to give the mono(dichloromethane) solvate of the required compound (0.045 g, 31%) (Found: C, 42.5; H, 3.6; N, 6.2. $C_{25}H_{26}Cl_4N_3PPdS$ requires C, 44.1; H, 3.8; N, 6.2%). I.r.: $\nu_{max.}$(KBr) 3 060, 3 000, 2 920, 1 590, 1 545, 1 480, 1 450, 1 435, 1 270, 1 190, 1 100, 1 035, 1 000, 960, 930, 800, 750, 735, 690, 530, 510, 450, 360 (sh), 340, and 285 cm^{-1}. Proton n.m.r. (CD_2Cl_2): δ 2.60 (br s, 3 H, SMe), 2.77 (br s, 3 H, SMe), 6.30 (m, 1 H, pyrimidinyl H), 7.40 (m, 7 H, PPh_3), 7.75 (m, 8 H, PPh_3), 7.90 (m, 1 H, pyrimidinyl H), and 8.20 (m, 1 H, pyrimidinyl H).

Crystallography.—*Crystal data.* $C_{25}H_{26}Cl_4N_3PPdS$, *M* = 679.8, monoclinic, *a* = 17.307(6), *b* = 9.182(1), *c* = 17.960(2) Å, β = 97.15(2)°, *U* = 2 832(1) $Å^3$, *Z* = 4, D_c = 1.594 g cm^{-3}, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 11.74 cm^{-1}, *F*(000) = 1 368, space group $P2_1/n$.

All measurements were made with Mo *X*-rays using an Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator. The specimen was a yellow crystal measuring 0.28 × 0.10 × 0.05 mm. Cell dimensions were determined by a least-squares refinement of the setting angles of 21 automatically centred reflections with $10 \leqslant \theta \leqslant 15°$. Intensities of 4 414 reflections with $2 \leqslant \theta \leqslant 22°$ were measured by continuous θ—2θ scans of 0.70° in θ, increased by 1/4 at each end to allow for background. Two intensity standards, measured every 2 h, showed no significant change. After correction for Lorentz polarisation and absorption effects [28] (transmission factors on *F*

Table 2. Fractional co-ordinates for *cis*-$[PdCl_2(PPh_3)(Me_2SNC_4H_3N_2)]\cdot CH_2Cl_2$

Atom	*X*/*a*	*Y*/*b*	*Y*/*c*
Pd(1)	0.134 84(2)	−0.025 86(5)	0.063 08(2)
Cl(1)	0.163 31(9)	−0.268 64(16)	0.056 38(9)
Cl(2)	0.027 78(9)	−0.072 32(18)	0.130 44(8)
Cl(3)	0.553 82(15)	−0.889 38(31)	0.223 58(19)
Cl(4)	0.533 35(18)	−0.608 39(33)	0.153 75(15)
S(1)	0.269 66(9)	0.313 25(17)	0.222 55(8)
P(1)	0.230 98(8)	0.012 52(17)	−0.007 84(7)
N(1)	0.108 6(3)	0.186 2(5)	0.076 8(2)
N(2)	0.130 3(3)	0.400 6(5)	0.151 6(3)
N(3)	0.222 8(3)	0.213 0(5)	0.154 8(2)
C(1)	0.253 8(3)	0.292 5(6)	−0.023 7(3)
C(2)	0.327 4(4)	0.261 0(7)	−0.003 5(4)
C(3)	0.341 1(5)	0.407 2(9)	−0.017 4(4)
C(4)	0.282 6(6)	0.494 1(8)	−0.049 7(4)
C(5)	0.209 7(5)	0.436 5(8)	−0.070 2(4)
C(6)	0.196 0(4)	0.291 9(7)	−0.058 0(4)
C(7)	0.321 8(3)	−0.072 1(6)	0.031 5(3)
C(8)	0.335 3(3)	−0.090 8(7)	0.109 1(3)
C(9)	0.402 3(4)	−0.155 5(9)	0.141 2(4)
C(10)	0.457 2(4)	−0.200 3(9)	0.098 6(5)
C(11)	0.446 1(4)	−0.180 7(10)	0.022 5(4)
C(12)	0.377 8(4)	−0.119 4(8)	−0.010 1(3)
C(13)	0.209 5(3)	−0.054 3(6)	−0.104 5(3)
C(14)	0.149 4(4)	−0.151 4(7)	−0.123 8(3)
C(15)	0.133 5(4)	−0.198 2(8)	−0.197 2(4)
C(16)	0.176 8(5)	−0.148 5(9)	−0.251 2(4)
C(17)	0.236 0(4)	−0.054 1(9)	−0.232 9(4)
C(18)	0.252 2(3)	−0.004 8(7)	−0.159 2(3)
C(19)	0.153 7(3)	0.269 2(6)	0.128 8(3)
C(20)	0.040 1(3)	0.240 4(7)	0.047 3(3)
C(21)	0.014 0(3)	0.373 6(7)	0.067 7(3)
C(22)	0.061 0(4)	0.448 2(6)	0.120 4(3)
C(23)	0.310 4(4)	0.468 0(7)	0.181 6(3)
C(24)	0.354 4(3)	0.205 0(7)	0.239 3(3)
C(25)	0.580 5(5)	−0.708 4(11)	0.228 2(5)

0.95—1.05), and merging of equivalent reflections, 3 463 unique reflections were obtained; of these 1 999 had $I \geqslant 3\sigma(I)$ and were used subsequently.

The structure was solved from Patterson and difference syntheses. Full-matrix least-squares refinement of 316 parameters, with $w^{-1} = \sigma^2(F) + 0.0023F^2$, converged with $R = 0.024$ and $R' = 0.028$ (see Table 2). Anisotropic thermal parameters were used for all non-H atoms. All H atoms were included in the final calculations, riding on the attached C atoms, with C–H 0.96 Å and $U(H) = 1.2U_{iso}(C)$. Conformational energy calculations were made on a Uman computer using the Chemmod package.[18] All other calculations were performed with the GX system.[29] Neutral atom scattering factors and complex anomalous dispersion corrections were taken from ref. 30.

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

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