Preparation, Properties, and *X*-Ray Photoelectron Spectra of Palladium(II) and Platinum(II) Complexes of Amine Imides (Aminimides) and Sulphur Ylides

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The reactions of amine imides $RR'_2\overset{+}{N}\overset{-}{N}COR''$ (R = $PhCH_2$ or *p*-$O_2NC_6H_4CH_2$, R′ = Me, R″ = Me, Et, or Ph) and the sulphur ylide $Me_2\overset{+}{S}(O)\overset{-}{C}HCOPh$ with halides of palladium(II) and platinum(II) give novel ylide–metal complexes $[MCl_2L_2]$, $[PtCl_2\{Me_2\overset{+}{S}(O)\overset{-}{C}HCOPh\}(SEt_2)]$, and $[PtCl_2\{Me_2\overset{+}{S}(O)\overset{-}{C}HCOPh\}]$. Infrared, ^1H and ^{13}C n.m.r., and *X*-p.e. data indicate that the co-ordination of the ylide to the metal is through the nucleophilic $\overset{+}{N}$ or $\overset{-}{C}$ atom as simple terminal ligands. The complex *cis*-$[PtCl_2\{Me_2\overset{+}{S}(O)\overset{-}{C}HCOPh\}(SEt_2)]$ releases diethyl sulphide in dimethyl sulphoxide and is transformed into the complex $[PtCl_2\{Me_2\overset{+}{S}(O)\overset{-}{C}HCOPh\}]$ which is chelated through the carbanion carbon and the sulphonium oxygen of the ylide. The thermal properties of the complexes have been examined by thermal gravimetric analysis, and the nature of the bonding is discussed.

RECENTLY many studies have been reported of the reactions of metals with ylides.[1] Most information available concerns phosphorus ylides, and only a few reports deal with sulphur and nitrogen ylides. Except for one study,[2] there are few reports on the reactions of amine imides (aminimides) with transition metals. Dias *et al.*[2] described the reactions of *N*-(1-pyridinio)benzamidate (pyridine *N*-benzoylimide) and related substances with halides of rhodium, iridium, palladium, and platinum. Their interest arose from a desire to examine the influence of metal ions on the thermal stability of the N–N bond and on *ortho*-metallation reactions.

There are reports which describe stable complexes of sulphur ylides. For example, Brovo *et al.*[3] reported bis(sulphonio-ylide) complexes with the *trans* configuration and Koezuka *et al.*[4] described the preparation of platinum and palladium complexes of a stable sulphur ylide and the structure determination by means of i.r. and ^1H n.m.r. On the other hand, few reports deal with sulphur ylides of the $RR'\overset{+}{S}(O)\overset{-}{C}HCOR''$ type, where the oxygen of the sulphonyl group is considered to interact with the transition metal. In addition, although one of the most remarkable features of ylide complexes is the unusually high thermal stability, little is known of the nature of the bonding in nitrogen ylide complexes. Hence, in this paper, the preparation and structure determination of several stable palladium and platinum complexes of amine imides and a sulphur ylide [benzoyl(dimethyloxosulphonio)methanide] are described, and the nature of the bonding is discussed based on *X*-p.e.,[5] i.r.,

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[1] A. Greco, *J. Organometallic Chem.*, 1972, **43**, 351; H. Schmidbauer, *Accounts Chem. Res.*, 1975, **8**, 62; W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer, and W. D. Korte, *J. Amer. Chem. Soc.*, 1974, **96**, 2847; S. Z. Goldberg, H. N. Duesler, and K. N. Raymond, *Inorg. Chem.*, 1972, **11**, 1397; H. H. Karsch, H. F. Klein, and H. Schmidbauer, *Chem. Ber.*, 1974, **107**, 93.

[2] S. A. Dias, A. W. Downs, and W. R. McWhinnie, *J.C.S. Dalton*, 1975, 162.

[3] P. Brovo, G. Fronza, G. Gaudiano, and C. Ticozzi, *Gazzetta*, 1973, **103**, 623.

[4] H. Koezuka, G. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, 1974, **13**, 443.

[5] M. Senō and S. Tsuchiya, *J. Electron Spectroscopy and Related Phenomena*, 1976, **8**, 165.

^{1}H and ^{13}C n.m.r., and thermal-gravimetric analysis (t.g.a.) measurements.

RESULTS AND DISCUSSION

Ylides combine with transition metals as either simple terminal ligands, bridging groups, or chelating moieties. Their co-ordination as simple terminal ligands and a bridging group has already been found, but the co-ordination as a chelating moiety is novel. Most of the complexes reported in this paper are of the simple terminal-ligand type, but one sulphur ylide complex is of the chelating type. First we describe the formation and structure determination of the complexes by means of i.r. and n.m.r. spectroscopy, conductivities, and ele-

TABLE 1

Analytical data, melting points, and conductivities of the ylides

	Analysis (%) [a]				Λ [b]
Complex	C	H	N	M.p. (θ_c/°C)	S cm^2 mol^{-1}
$[\mathrm{PdCl_2}\{p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COMe}\}_2]$ (1c)	39.65 (40.55)	4.40 (4.65)	12.6 (12.9)	215 (decomp.)	6.8
$[\mathrm{PdCl_2}\{(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{CO_2Et}\}_2]$ (2c)	41.55 (42.4)	5.00 (5.00)	11.9 (12.35)	169 (decomp.)	6.3
$[\mathrm{PdCl_2}\{p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COPh}\}_2]$ (3c)	48.2 (49.5)	4.60 (4.40)	11.05 (10.9)	185 (decomp.)	11.2
$[\mathrm{PdCl_2}\{(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COPh}\}_2]$ (4c)	56.0 (56.05)	5.20 (5.30)	8.15 (8.15)	184	7.2
$[\mathrm{PdCl_2}\{(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COMe}\}_2]$ (5c)	46.85 (47.05)	5.80 (5.80)	9.95 (9.95)	188	
$[\mathrm{PdCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}_2]$ (8)	42.2 (42.15)	4.30 (4.20)		180	3.2
$[\mathrm{PtCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}_2]$ (9)	36.15 (36.5)	3.85 (3.65)		156	2.5
$[\mathrm{PtCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}(\mathrm{SEt_2})]$ (10)	31.0 (30.85)	4.20 (4.15)		136	2.2
$[\mathrm{PtCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}]$ (11)	25.9 (25.95)	2.40 (2.60)		166	2.0

[a] Figures in parentheses are calculated values. [b] Measured in nitromethane at 20 °C.

TABLE 2

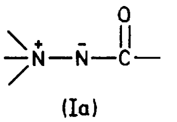
Infrared data (cm^{-1}) of the salts, ylides, and ylide complexes

Compound	ν(C=O)	ν(N–N)	ν(S=O)	ν(M–Cl)
$[(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\mathrm{NHCOMe]Br}$ (1a)	1 690	1 260		
$(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COMe}$ (1b)	1 580	1 350		
$[\mathrm{PdCl_2}\{(p\text{-}\mathrm{O_2NC_6H_5CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COMe}\}_2]$ (1c)	1 610	1 320		330
$[(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\mathrm{NHCO_2Et]Br}$ (2a)	1 740	1 250		
$(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{CO_2Et}$ (2b)	1 640	1 270		
$[\mathrm{PdCl_2}\{(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{CO_2Et}\}_2]$ (2c)	1 665	1 270		300
$[(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{HCOPh]Br}$ (3a)	1 690	1 275		
$(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COPh}$ (3b)	1 550	1 325		
$[\mathrm{PdCl_2}\{(p\text{-}\mathrm{O_2NC_6H_4CH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COPh}\}_2]$ (3c)	1 620	1 320		318
$[(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\mathrm{HCOPh]Br}$ (4a)	1 700	1 280		
$(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COPh}$ (4b)	1 570	1 340		
$[\mathrm{PdCl_2}\{(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COPh}\}_2]$ (4c)	1 620	1 310		312
$[(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\mathrm{NCOMe]Br}$ (5a)	1 700	1 270		
$(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COMe}$ (5b)	1 580	1 370		
$[\mathrm{PdCl_2}\{(\mathrm{PhCH_2)Me_2}\overset{+}{\mathrm{N}}\overset{-}{\mathrm{N}}\mathrm{COMe}\}_2]$ (5c)	1 610	1 320		325
$[\mathrm{Me_3}\overset{+}{\mathrm{S}}\mathrm{O]Cl}$ (6)			1 240	
$\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}$ (7)	1 530		1 175	
$[\mathrm{PdCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}_2]$ (8)	1 645		1 195	337
$[\mathrm{PtCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}_2]$ (9)	1 650		1 195	326
$[\mathrm{PtCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}(\mathrm{SEt_2})]$ (10)	1 650		1 230	318, 293
$[\mathrm{PtCl_2}\{\mathrm{Me_2}\overset{+}{\mathrm{S}}\mathrm{(O)}\overset{-}{\mathrm{C}}\mathrm{HCOPh}\}]$ (11)	1 660		1 140	323, 305

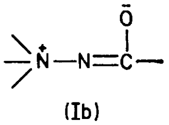
mental analyses, and then discuss the nature of the bonding by use of t.g.a. and X-p.e. spectroscopy.

Formation and Structure of some Palladium Complexes with Amine Imides.—Most of the ylides used were synthesized according to the literature,[6] but three amine imides were newly prepared. Amine imides reacted with disodium tetrachloropalladate(II) in ethanol at room temperature to afford crystalline products. The details of the reactions are described in the Experimental section. The products have the composition $[PdCl_2(ylide)_2]$ as revealed by the elemental analyses listed in Table 1.

The amine imides used in the present investigation may be described by the canonical formulae (I). As a simple terminal ligand an amine imide has two possible co-ordination sites: one is a carbonyl oxygen and the other is a nucleophilic nitrogen atom. Spectroscopic data for the palladium complexes are summarized in Table 2. The carbonyl bands of the amine imide complexes were observed 70—90 cm^{-1} to lower wavenumbers than those of the corresponding salts and 15—70 cm^{-1} to higher wavenumbers than those of the corresponding amine imide. As the above canonical structures suggest that co-ordination through the carbonyl oxygen would cause ν(C=O) to shift to a lower frequency, and co-ordination through the nucleophilic nitrogen ($\bar{N}$) would cause ν(C=O) to shift to a higher frequency, the latter mode of co-ordination is indicated in these complexes.



(Ia)



(Ib)

TABLE 3

N.m.r. data

(*a*) ^{1}H

Compound	Ph	CH$_2$	$\overset{+}{N}(CH_3)_2$	CH$_3$
	Chemical shift (δ/p.p.m.)			
(4a)	7.90, 7.40	5.60	3.90	
(4b)	7.90, 7.40	4.97	3.35	
(4c)	7.90, 7.40	5.10	3.40	
(5a)	7.45	5.45	3.80	2.20
(5b)	7.40	4.92	3.22	1.83
(5c)	7.50	5.35	3.77	3.00

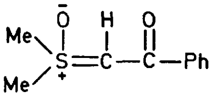
(*b*) ^{13}C

	CO	Ph	CH$_2$	$\overset{+}{N}(CH_3)_2$	CH$_3$
(5a)	166	130, 128, 126, 124	67	52	20
(5b)	168	128, 125, 124	65	51	23
(5c)	168	128, 125, 124	68	53	26

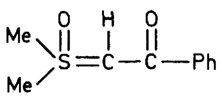
The n.m.r. results lead to the same conclusion. In Table 3, ^{1}H and ^{13}C n.m.r. spectra of the complex of *NN*-dimethylbenzylamine *N*-acetylimide (5c) are compared with those of the corresponding salt (5a) and aminimide (5b). All the peaks in the ^{1}H n.m.r. spectrum of complex (5c) appeared to lower field of those of ylide (5b) and were close to the peaks of salt (5a). Each of the complexes had a single far-i.r. absorption ascribed to the Pd–Cl bond, and this implies a *trans*-dichloro-structure. In addition, these complexes had low conductivities in nitromethane. We believe, therefore, that the complexes have a *trans*-bis(amine imide)dichloro-structure.

Dias *et al.*[2] reported *ortho*-metallation of *N*-(1-pyridinio)benzamidate through the phenyl ring, and therefore there is a possibility that complexes (3c) and (4c) possessing phenyl rings have a chelate structure. However, the i.r. and n.m.r. data do not provide any evidence for *ortho*-metallation; we observed two bands at *ca.* 690 and 720 cm^{-1} (Ph ring) in the i.r. spectra of complexes (3c) and (4c), and could not find any differences between the peak, due to the phenyl protons of complex (4c) and that of ylide (4b).

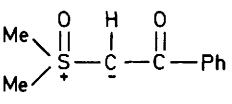
Formation and Structure of Palladium and Platinum Complexes with Sulphur Ylides.—In Table 2 are given the observed i.r. spectra of the sulphur ylide and its complexes. Benzoyl(dimethyloxosulphonio)methanide (7) may be described by four canonical structures as shown in (II). The i.r. spectrum of benzoylmethylenetriphenylphosphorane, $PPh_3(CHCOPh)$, shows strong bands at 1 524 and 1 382 cm^{-1} which appear to involve vibrations of the P⎓C⎓C⎓O moiety, and these bands are replaced by single carbonyl-stretching bands in the corresponding salt (1 660 cm^{-1}) and the mercury complex (1 632 cm^{-1}).[7] Two bands were also observed (at 1 530 and 1 390 cm^{-1}) for the sulphur ylide (7), which could be assigned to an S⎓C⎓C⎓O moiety. The low value of ν(C=O) suggests an important contribution from (IId). The S=O absorption band of ylide (7) was observed at 1 175 cm^{-1}, lower than that (1 240 cm^{-1}) of trimethylsulphonium chloride (6). This suggests a considerable contribution from (IIa). Hence, this ylide has three possible co-ordination sites: a carbonyl oxygen, a sulphoxide oxygen, and a methine carbon.



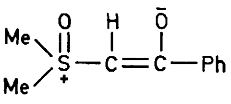
(IIa)



(IIb)



(IIc)



(IId)

As shown in Table 2, the ν(C=O) and ν(S=O) values of complexes (8)—(10) were observed at higher frequencies than those of ylide (7), and the band at 1 390 cm^{-1} disappeared. Hydrogen-1 n.m.r. peaks of the methine protons of all the sulphur-ylide complexes shifted to lower field, and the peak of the methine proton of complex (10) was accompanied by satellites due to spin–spin coupling with ^{195}Pt. The coupling constant $J(^{195}Pt–CH)$ is close to that of dichloro(diethyl sulphide) [(methylphenylsulphonio)(*p*-chlorobenzoyl)methanide]platinum-

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[6] A. W. Johnson, 'Ylide Chemistry,' Academic Press, New York, 1966; S. Wawzonek and E. Yeakey, *J. Amer. Chem. Soc.*, 1960, **82**, 5718.

[7] P. A. Arnup and M. C. Baird, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 65.

(II) reported previously[4] (Table 4). Hence, ylide (7) is believed to co-ordinate to the metal through the methine carbon. The single far-i.r. absorption due to Pd–Cl indicates that complexes (8) and (9) have a *trans*-dichlorobis(sulphur ylide) structure. The ν(Ph–Cl) band of complex (10) was observed at 318 and 293 cm^{-1} in the solid state, and suggests a *cis* configuration. This structure is supported by the ^{1}H n.m.r. spectra of complex (10) (Figure 1) which exhibited two kinds of signal with equal intensities due to hindered rotation of the diethyl sulphide around the Pt–S bond. Hence, complex (10) has a *cis*-dichloro(diethyl sulphide)(sulphur ylide) structure.

TABLE 4

Hydrogen-1 n.m.r. data of the sulphur-ylide complexes

	Chemical shifts (δ/p.p.m.)			
Compound	Ylide (S–CH$_3$)	Ylide (C–H)	CH$_2$*CH*$_3$	*J*(Pt–CH)/Hz
(7) [a]	3.50	5.05		
(8) [b]	3.50—4.00	6.20		
(9) [b]	3.70—4.00	6.50		
(10) [b]	3.70	6.85	1.15, 0.50	126
(11) [b]	3.90	6.65		114

[a] In CDCl$_3$ at 35 °C. [b] In [^{2}H$_6$]dmso at 35 °C.

When green-yellow complex (10) was dissolved in dimethyl sulphoxide (dmso), the diethyl sulphide ligand was released. This process was followed by ^{1}H n.m.r. spectroscopy (Figure 1); after dissolution the intensity of one methyl signal of SEt$_2$ decreased, the methyl peak of the ylide was split, and new methine and phenyl peaks appeared. Addition of benzene to the solution resulted in a white product (11), the ^{1}H n.m.r. spectra of which showed the absence of SEt$_2$. The ν(S=O) stretching band (1 140 cm^{-1}) of complex (11) is much lower than that (1 230 cm^{-1}) of (10), and lower than that (1 175 cm^{-1}) of the original ylide (7); the ν(C=O) band of complex (11) occurred at higher wavenumber than that of (10). It is of interest to note that the chemical shift (δ 6.65 p.p.m.) of the methine proton of complex (11) is higher, and the coupling constant (*J* 114 Hz) smaller, than the corresponding values of complex (10) (δ 6.85 p.p.m., *J* 126 Hz). These results indicate that the platinum is co-ordinated through the oxygen of the sulphoxide group of ylide (7); the conjugation of S=C–C=O is decreased and the Pt–C bond is weakened as a result of this mode of co-ordination. Complex (11) has the composition [PtCl$_2$(ylide)] as revealed by elemental analyses, and two bands for ν(Pt–Cl) were observed at 323 and 305 cm^{-1}. Hence, we conclude that complex (11) has the chelated structure shown below. Although attempts to obtain molecular-weight data by using a vapour-pressure osmometer failed due to the decomposition of complex (11) in *NN*-dimethylformamide (dmf) at 100 °C, dimerization does not occur since a low conductivity (2 S cm^2 mol^{-1}) was found in nitromethane.

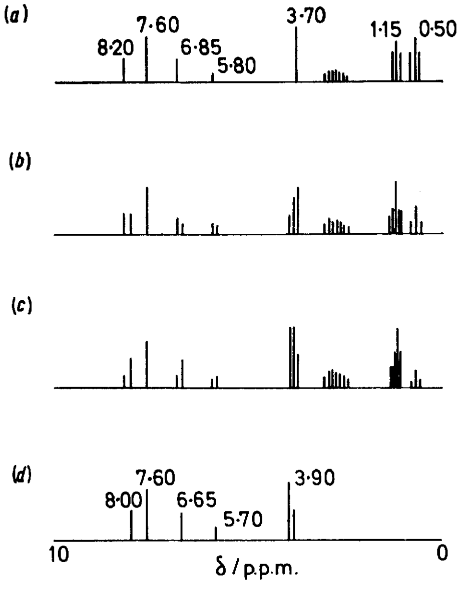
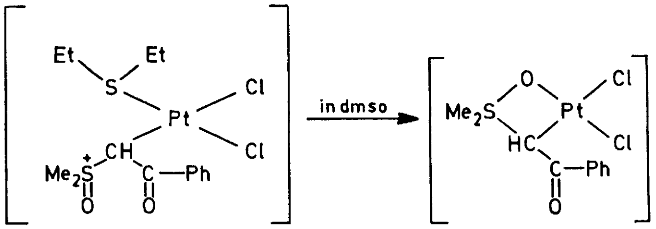


FIGURE 1 Variation of the ^{1}H n.m.r. spectra of complex (10) (*a*) in [^{2}H$_6$]dmso, (*b*) after 1 h, (*c*) after 2 h, and (*d*) complex (11)



(10)

(11)

Thermal Properties of the Ylide Complexes.—The bonding in ylide complexes is of interest since these compounds are found to be extremely stable. For example, Gillard *et al.*[8] described the stability of platinum complexes of $C_6H_5\overset{+}{N}$–$\overset{-}{C}$H(Et) in solution; no change was observed when the complexes were heated under reflux in either chloroform or benzene solution with high concentrations of benzoyl or acetyl chlorides. The complexes described in this paper are also thermally stable, *e.g.* the decomposition temperature of complex (8) is 240 °C. The t.g.a. results are summarized in Table 5. In the case of

TABLE 5

Thermal gravimetric analysis data of the ylide complexes

Complexes	θ$_c$/°C	Weight loss/g mol^{-1}
(1c)	215	492 (474 [a])
(2c)	169	512 (534 [a])
(3c)	185	571 (596 [a])
(4c)	195	515 (508 [a])
(5c)	200	390 (384 [a])
(8)	240	378 (392 [a])
(10)	180	87 (90 [b])
	240	189 (196 [c])
(11)	200	115 (118 [d])
	240	79 (78 [e])
cis-[PtCl$_2$(SEt$_2$)$_2$]	180	192 (180 [f])

[a] Twice the molecular weight of the ylide ligand. [b] *M* of SEt$_2$. [c] *M* of ligand ylide. [d] *M* of PhCOCH. [e] *M* of dmso. [f] Twice the molecular weight of SEt$_2$.

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[8] R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organometallic Chem.*, 1971, **33**, 247.

complex (10), SEt_2 was eliminated at 180 °C and the ylide molecule at 230 °C. Diethyl sulphide in *cis*-[$PtCl_2(SEt_2)_2$] is also eliminated at 180 °C. Complex (11) decomposes in two steps. The group released at 200 °C is one fragment (CHCOPh) of the co-ordinated ylide, and the group eliminated at 240 °C is another fragment (SMe_2O) of ylide. These results show that complex (10) does not decompose to (11) in a nitrogen atmosphere. This behaviour is different from the transformation in dmso, and reflects the large difference in decomposition temperatures; complex (11) decomposes at 200 °C in nitrogen, and at 100 °C in dmf.

TABLE 6

Nitrogen 1*s*, Pd 3*d*, Pt 4*f*, Cl 2*p*, and S 2*p* *X*-p.e. binding energies (eV) for the salts, ylides, ylide complexes, and related compounds

Compounds	N 1*s*	Pd 3*d* 3/2, 5/2	Pt 4*f* 5/2, 7/2	Cl 2*p*	S 2*p*
(1a)	405.0, 402.5, 400.1				
(1b)	405.1, 401.4, 397.5				
(1c)	405.0, 401.6, 398.4	342.1, 336.7		196.8	
(4a)	402.3, 399.8				
(4b)	401.4, 397.5				
(4c)	401.4, 398.5	342.2, 336.8		197.4	
(8)		342.2, 337.0		197.0	167.2
(9)			74.9, 71.1	196.7	166.6
(10)			75.1, 71.8	197.3	167.0, 163.4
(11)			75.5, 72.2	197.6	166.5
cis-[$PtCl_2(SEt_2)_2$]			75.3, 71.8	197.2	162.9
$K_2[Pt(MeCH{=}CH_2)Cl_3]$			75.7, 72.5	197.9	
$Na_2[PdCl_4]$		342.6, 337.2		198.5	
$K_2[PtCl_4]$			75.5, 72.1	198.0	

Comparison of the decomposition temperature of the amine imide–palladium complexes with that of the sulphur ylide–palladium complex suggests that the Pd–C bond strength is stronger than that of Pd–N.

Bonding Character of the Ylide Complexes.—As shown in Table 2, a ν(C=O) shift is observed in the i.r. data of the ylides and those of the corresponding complexes, and the difference in ν(C=O) between ylide (3b) and complex (3c) is the largest (70 cm^{-1}) found for the amine imides and their complexes. This suggests that the Pd–N bond in complex (3c) is the strongest of those in the amine imide complexes.

N.m.r. measurements on these complexes indicate changes in the electron distribution due to Pd–N bond formation. As shown in Table 3, ^1H and ^{13}C n.m.r. peaks of complex (5c) appear to lower field of those of ylide (5b). It is suggested that the electrons of the methyl and methylene carbons drift towards the co-ordinated nitrogen to compensate for the decrease in electron density at this atom. The difference in ν(C=O) between the sulphur ylides and their complexes (115—130 cm^{-1}) is larger than those found in the amine imides. This suggests a strong interaction between the metal and the methine carbon, and is consistent with the t.g.a. results.

The technique of *X*-ray photoelectron (*X*-p.e.) spectroscopy has recently been applied to transition-metal complexes with a primary object of probing the bonding between the ligand and the metal.[9] In an attempt to confirm the bonding, the *X*-p.e. spectra of the ylide complexes and related compounds were recorded. In Table 6 are given measured core-electron ionization potentials (binding energies), and the spectra of the related compounds are shown in Figure 2. The power of the *X*-p.e. method may be clearly seen from Figure 2. The multipeak structure of the N 1*s* spectra, owing to the difference in electrostatic environment, is evident. The N 1*s* spectra of (1a)—(1c) can be assigned as follows. The highest binding-energy peak is attributed to N 1*s* of a nitro-group, and the middle to $\overset{+}{N}$, and the lowest to $\overset{-}{N}$ or NH.

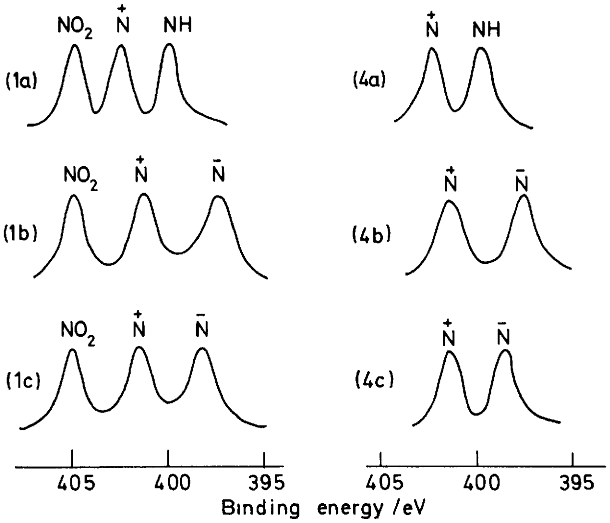

FIGURE 2 Nitrogen 1*s* *X*-p.e. spectra of salts (1a) and (4a), ylides (1b) and (4b), and complexes (1c) and (4c)

The higher binding energies of (4a)—(4c) are ascribed to $\overset{+}{N}$, while the lower binding energies are attributed to $\overset{-}{N}$ or NH. Nitrogen 1*s* binding energies of $\overset{-}{N}$ or NH in salts

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[9] J. Escard, G. Mavel, J. E. Guerchais, and R. Kergoat, *Inorg. Chem.*, 1974, **13**, 695; C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *ibid.*, 1973, **12**, 2770; K. T. Ng and D. Hercules, *J. Amer. Chem. Soc.*, 1975, **97**, 4168; G. A. Olah, G. Liang, G. D. Mattescu, and J. L. Riemenschneider, *ibid.*, 1973, **95**, 8698; C. E. Mixan and J. B. Lambert, *J. Org. Chem.*, 1973, **38**, 1350.

(1a) and (4a), ylides (1b) and (4b), and complexes (1c) and (4c) differ significantly from each other and decrease in the order salt > complex > ylide. A correlation has been established between the binding energy and the formal charge, and thus the substantial shift in binding energy clearly confirms a net electron transfer from nitrogen to palladium in these complexes. These results, which do not depend on a comparison of different compounds but involve a comparison of inequivalent nitrogens in one compound, are more reliable. Comparison of Pd 3*d* binding energies in the complexes with that of $Na_2[PdCl_4]$ seems to support the above interpretation; that is, slightly smaller values observed for palladium may be attributed to the co-ordination of the ylide, which would tend to increase the electron density on palladium, although the binding energies may be affected through the different contributions of the Madelung potentials due to differences in the crystal structures. This result also indicates that the metal halide is co-ordinated through the nucleophilic nitrogen ($\bar{\mathrm{N}}$) of the ylide, in agreement with the n.m.r. and i.r. results. Less reliable information, from a comparison of the binding energies in the salts, ylides, and complexes, now follows. If we assign unit negative charge to the ylide nitrogen ($\bar{\mathrm{N}}$) and zero charge to the nitrogen (NH) of the salt, transfer of $0.35e^-$ from the nitrogen of the ylide to the palladium in complex (1c), and $0.43e^-$ in complex (4c), may be proposed.

Similar results were obtained from measurements on the sulphur ylide complexes. The platinum 4*f* binding energies of complexes (9) and (10) are lower than that of $K_2[PtCl_4]$, indicating net electron transfer from carbon to metal. However, the Pt 4*f* binding energy of complex (11) was surprisingly high (75.5 eV).* Presumably, this represents back donation from platinum to the ligand. The fact that the S 2*p* binding energy of complex (11) (166.5 eV) is lower than that of complex (10) (167.0 eV) supports this interpretation. In order to substantiate these result *X*-p.e. measurements were made on the Zeise's salt $K_2[Pt(MeCH{=}CH_2)Cl_3]$ (13), which is stabilized by back donation. A glance at the high Pt 4*f* binding energy of Zeise's salt (75.7 eV) shows that the above conclusion is basically correct.

The 2*p* spectra of the two sulphur atoms in complex (10) exhibited a doublet owing to a difference in the nature of the bonding. The higher binding-energy peak is ascribed to the ylide sulphur, and the lower-energy peak to the sulphur of SEt_2. The lower binding energy for the sulphur of SEt_2 indicates the weak interaction between the platinum and the sulphur atom in this case and is in agreement with the t.g.a. results. The Pt–Cl bonds have partial ionic character, since the Cl 2*p* binding energies of the sulphur ylide complexes are lower than that of $K_2[PtCl_4]$.

EXPERIMENTAL

Preparation of the Amine Imides.—*NN*-Dimethyl-*p*-nitrobenzylamine *N*-acetylimide (1b) and *NN*-dimethylbenzylamine *N*-acetylimide were prepared according to the methods reported by Wawzonek and Yeakey.[6]

NN-*Dimethyl*-p-*nitrobenzylamine* N-*ethoxycarbonylimide* (2b). To *p*-nitrobenzyl bromide (1.6 g) in dry benzene, (10 cm^3) was added ethyl 3,3-dimethylcarbazate (1 g) and the mixture was heated under reflux for 3 h. 1,1-Dimethyl-1-*p*-nitrobenzyl-2-ethoxycarbonylhydrazinium bromide (2a, 1.5 g) was obtained by cooling. This salt (1 g) was dissolved in water (10 cm^3) and titrated to a phenolphthalein end-point with 1 N sodium carbonate. The solution was extracted three times with portions (20 cm^3) of chloroform and the extract was dried with $Na_2[SO_4]$ for 24 h. Removal of chloroform under reduced pressure gave (2b) as white *crystals* (0.54 g) which were purified by recrystallization from benzene. Calc. for $C_{12}H_{17}N_3O_4$: C, 53.95; H, 6.35; N, 15.7%; m.p. 147 °C (Found: C, 54.15; H, 6.40; N, 15.8%).

NN-*Dimethyl*-p-*nitrobenzylamine* N-*benzoylimide*. To *p*-nitrobenzyl bromide (2.63 g) in dry benzene (10 cm^3) was added 2,2-dimethylbenzohydrazide (2 g) in dry benzene (10 cm^3) and the mixture was heated under reflux for 5 h. 1,1-Dimethyl-1-*p*-nitrobenzyl-2-benzoylhydrazinium bromide (3a, 3.8 g) was obtained by cooling. The salt was treated as described in the preceding section. The yield of (3b) was 1.71 g (63.6%) and the solid *product* was recrystallized from benzene, m.p. 137 °C (Found: C, 64.4; H, 5.85; N, 14.3. Calc. for $C_{16}H_{17}N_3O_3$: C, 64.2; H, 5.75; N, 14.05%).

NN-*Dimethylbenzylamine* N-*benzoylimide* (4b). 2,2-Dimethylbenzohydrazide (10 g) in dry benzene (10 cm^3) was added to benzyl bromide (10.5 g) and the mixture was heated under reflux for 5 h. 1-Benzyl-1,1-dimethyl-2-benzoylhydrazinium bromide (4a) was obtained by cooling. The yield of the white crystals was 12 g after recrystallization from a mixture of absolute ethanol and light petroleum. The salt (4a) was treated as before. The yield of (4b) was 6.75 g (69.8%) and the solid *product* was recrystallized from chloroform–hexane. Calc. for $C_{16}H_{18}N_2O$: C, 75.6; H, 10.9; N, 7.10%; m.p. 122 °C (Found: C, 75.9; H, 10.5; N, 7.10%).

Preparation of Metal Complexes.—(a) *Amine imide complexes. Dichlorobis*(NN-*dimethyl*-p-*nitrobenzylamine* N-*acetylimide*)*palladium*(II), (1c). Disodium tetrachloropalladate(II) (0.30 g, 1 mmol) was dissolved in hot ethanol (10 cm^3) and the solution was filtered. Compound (1b, 0.4 g, 2 mmol) was added, and the mixture was allowed to stand at room temperature for 10 h. The amber-coloured *product* (1c) was washed with ethanol, dried *in vacuo*, and recrystallized from nitromethane, yield 0.297 g.

The other palladium *complexes* (2c), (3c), (4c), and (5c) were similarly prepared. Their colours, yields, and recrystallization solvents are summarized in the following Table.

Complex	Colour	Yield (%)	Solvent
(1c)	Amber	45.6	Nitromethane
(2c)	Amber	47.4	Nitromethane
(3c)	Amber	60.6	Nitromethane
(4c)	Orange	69.9	Chloroform–light petroleum
(5c)	Orange	62.0	Chloroform–light petroleum

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[10] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353; R. Kuhn and H. Trischmann, *Annalen*, 1958, **611**, 119; Horstkönig and H. Metzger, *Chem. Ber.*, 1965, **98**, 3743.

(b) *Sulphur-ylide complexes*. Benzoyl(dimethyloxosulphonio)methanide (7) used here was prepared according to the published method.[10]

Bis[benzoyl(dimethyloxosulphonio)methanide]dichloropalladium(II) (8). Disodium tetrachloropalladate(II) (0.22 g, 0.8 mmol) was dissolved in dry ethanol (10 cm^3) and the solution was filtered. The ylide (7; 0.3 g, 1.6 mmol) in dry ethanol (10 cm^3) was added. After standing at room temperature for 3 h, the reaction mixture was filtered to collect the precipitate, which was washed with dry ethanol and dried *in vacuo*. The yellowish *crystals* were recrystallized from nitromethane, yield 0.41 g (93%), m.p. 179—180 °C.

Bis[benzoyl(dimethyloxosulphonio)methanide]dichloroplatinum(II) (9). Dipotassium tetrachloroplatinate(II) (0.32 g, 0.8 mmol) in water (10 cm^3) was treated with the ylide (7; 0.3 g, 1.6 mmol) in water (10 cm^3), and the resulting mixture was set aside overnight. The yellowish *product* was collected by filtration and dried *in vacuo*, m.p. 155—156 °C, yield 0.39 g (76.0%).

[Benzoyl(dimethyloxosulphonio)methanide]dichloro(diethyl sulphide)platinum(II) (10). *cis*-Dichlorobis(diethyl sulphide)platinum(II) (0.68 g, 1.6 mmol) in dry ethanol (30 cm^3) was treated with the ylide (7; 0.3 g, 1.6 mmol) in dry ethanol (20 cm^3) and the reaction mixture was set aside for 3 d. The yellowish green *crystals* of (10) were collected and dried *in vacuo*. The reaction of (7) with *trans*-[PtCl$_2$(SEt$_2$)$_2$] also yielded the same product, m.p. 136 °C, yield 0.56 g (66.3%).

[Benzoyl(dimethyloxosulphonio)methanide]dichloroplatinum(II) (11). Complex (10) (0.4 g, 0.7 mmol) was dissolved in dmso (5 cm^3), and the mixture was set aside at room temperature for 2 d. Addition of benzene to the solution gave white crystals, which were filtered off and dried *in vacuo*. The *product* was purified by recrystallization from benzene–dimethyl sulphoxide, m.p. 166 °C, yield 0.23 g (70%).

Physical Measurements.—Infrared spectra (400—4 000 cm^{-1}) were recorded for KBr discs on a JASCO IRA-2 spectrometer. Far-i.r. spectra (200—400 cm^{-1}) were obtained for Nujol mulls on a JASCO DS, 701 G spectrometer. Hydrogen-1 n.m.r. spectra of the ylides (in CDCl$_3$) and of the complexes (in [^{2}H$_6$]dmso or CDCl$_3$) were recorded on a Hitachi R-22 spectrometer operating at 90 MHz, with SiMe$_4$ as internal standard at room temperature. Carbon-13 n.m.r. spectra were obtained on a Hitachi R-26 spectrometer in the Fourier-transform mode at 10 MHz. ^{13}C–H Coupling was eliminated by using a broad-band ^{1}H-noise-modulated decoupler. The measurements were made in saturated deuteriochloroform solutions of the salts, ylides, or complexes in 10-mm sample tubes, and SiMe$_4$ was used as the internal standard. Conductivity measurements were made in nitromethane solutions using a Toa model CM-2A conductimeter. Thermal gravimetric analyses (t.g.a.) were carried out on a Shimazu TGA 20 instrument.

X-Ray photoelectron (*X*-p.e.) spectra were recorded on a JASCO ESCA-1 spectrometer. Magnesium-K_α radiation (1 253.6 eV) was used as the source, and fine powdered samples were dispersed on Scotch tape, which was mounted on a copper sample holder. Nitrogen 1*s*, Pd 3*d*, Pt 4*f*, Cl 2*p*, and S 2*p* binding energies were referenced to the C 1*s* line of impurity carbon at 284 eV. An attempt was also made to reference the spectra to the Au $4f_{\frac{7}{2}}$ line at 83 eV by vacuum deposition of gold on to the sample. The binding energies were read at the midpoint of the full peak at half height. The final values of the binding energies for each complex were determined from measurements in triplicate on several sample preparations and their accuracy is within ±0.20 eV. Visual examination of the samples after measurements revealed no evidence of radiation damage.

[6/1015 *Received*, 27*th May*, 1976]