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THE COORDINATION CHEMISTRY OF SILYL–SULPHURDIIMIDES

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Abstract—Reaction of $RNSNSiMe_3$ (R = Me_3Si, ^{t}Bu, *p*-$O_2NC_6H_4S$-) with $PtCl_2$(dppe) gives, in the case of R = *p*-$O_2NC_6H_4S$-, [Pt($NSNSC_6H_4NO_2)_2$(dppe)]. Reaction of $(Me_3Si)_2N_2S$ (1) or $Bu^tNSNSiMe_3$ (4) with $Pt(C_2H_4)(PPh_3)_2$ gives $Pt(NSNR)_2(PPh_3)_2$ (R = Me_3Si or ^{t}Bu). The X-ray structure of *p*-$O_2NC_6H_4SNSNSiMe_3$ reveals an essentially coplanar arrangement of the aryl and SNSN fragments. The bond lengths in the S_2N_2 chain are more closely related to those in $S_2N_2^{2-}$ ligands than those in $S_2N_2H^-$ ligands. The X-ray crystal structure of [Pt($NSNSC_6H_4NO_2$)(dppe)] (5) confirms the expected *cis* square-planar coordination of the platinum by the chelate phosphine and two *p*-$O_2NC_6H_4SNSN^-$ ligands. Of the atoms in the S—N ligand only the terminal nitrogen atoms lie in the platinum coordination plane. The rest of these ligands are essentially planar with their backbones *trans*-axial and approximately normal with respect to the PtN_2P_2 plane.

There have been several reports[1] on the coordination properties of sulphurdiimides, RNSNR, but it was only quite recently that the use of a silyl sulphurdiimide, $(Me_3Si)_2N_2S$ (1), in the preparation of the σ-bonded diimido complex *cis*-$Pt(NSNSiMe_3)_2(PPh_3)_2$ (2) was described.[2] Here we report full details of the preparation of **2** together with the results of our investigations into the reactivity of substituted silyl diimides $RNSNSiMe_3$ [R = *p*-$O_2NC_6H_4S$- (3), ^{t}Bu, (4)]. As part of these studies we have characterized *p*-$O_2NC_6H_4$ $SNSNSiMe_3$ (3) and the platinum complex $Pt(NSNSC_6H_4NO_2)_2(PPh_3)_2$ (5) by X-ray crystallography. The geometry of the S_2N_2 group in **3** is compared with that of the related $S_2N_2H^-$ and $S_2N_2^{2-}$ ligands.[3–5]

EXPERIMENTAL

All procedures were carried out under an inert atmosphere (Ar or N_2) unless stated otherwise. Solvents were dried before use; CH_2Cl_2 was distilled from CaH_2; diethyl ether, tetrahydrofuran (THF), toluene and *n*-hexane were distilled from sodium–benzophenone. $^{31}P\text{-}\{^1H\}$ NMR spectra were obtained using a JEOL FX90Q spectrometer operating at 36.21 MHz and are referred to external 85% H_3PO_4. IR spectra were recorded using a PE 683 as pressed KBr discs or Nujol mulls. Elemental analyses were performed by the microanalytical service at Imperial College.

The compounds, *cis*-$[PtCl_2(PR_3)_2]$, were obtained from $PtCl_2COD$ whilst $MCl_2(CH_3CN)_2$ (M = Pd, Pt) and $Pt(C_2H_4)(PPh_3)_2$ were prepared by standard methods.[6–8] Bis(trimethylsilyl)sulphurdiimide and *p*-$O_2NC_6H_4SNSNSiMe_3$ were prepared by adaptation of the literature methods.[9,10] *t*-$BuNSNSiMe_3$ was obtained[11] from the reaction of *t*-BuNSO with $(Me_3Si)_2NLi$.

p-$O_2NC_6H_4SNSNSiMe_3$ (3)

Bis(trimethylsilyl)sulphurdiimide (2.66 g, 0.013 mol) was dissolved in dichloromethane (75 cm^3) and cooled in an ice bath. To this stirred solution was added over 30 min, *p*-$O_2NC_6H_4SCl$ (2.46 g, 0.013 mol) in dichloromethane (60 cm^3). During this time the solution changed colour from pale yellow to red–orange. The solvent was removed *in vacuo* and the resulting solid was extracted with hexane (80 cm^3) which upon cooling to −20°C gave the product as pale orange–yellow needles. Yield

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1.1 g, 29%. Found: C, 37.8; H, 4.4; N, 14.5. Calc.: C, 37.6; H, 4.6; N, 14.6%. Crystals suitable for X-ray analysis were obtained by slow crystallization from a hexane solution.

$Pt(NSNSiMe_3)_2(PPh_3)_2$

$(Me_3Si)_2N_sS$ (0.3 cm^3, 0.28 g, 1.3 mmol) was added to a solution of $Pt(C_2H_4)(PPh_3)_2$ (1.0 g, 1.3 mmol) in benzene (25 cm^3). The reaction was stirred at room temperature for 2 h and then all volatile material was removed under reduced pressure to give a yellow solid which was triturated with hexane, redissolved in benzene (20 cm^3) and filtered through Celite. The volume of benzene was reduced to *ca* 10 cm^3 and 20 cm^3 of *n*-hexane were added. The product crystallized as pale yellow plates. Yield 0.32 g, 50%. ^{31}P-$\{^1H\}$: $\delta = 11.76$, $^1J(Pt—P) = 3098$ Hz. IR: $\nu(NSN)_a$ 1167, $\nu(NSN)_s$ 1022w, $\delta(NSN)$ 835br cm^{-1}. Found: C, 50.4; H, 4.6; N, 5.3. Calc.: C, 51.2; H, 4.9; N, 5.7%.

$Pt(NSN^tBu)_2(PPh_3)_2$

Me_3SiNSN^tBu (0.1 g, 0.13 mmol) and $Pt(C_2H_4)(PPh_3)_2$ (0.51 g, 0.056 mmol) were stirred together in toluene (5 cm^3) for 2 h. The solvent was removed *in vacuo* and the product extracted into *n*-hexane (2 × 20 cm^3). The hexane was reduced to *ca* 5 cm^3 and cooled (−20°C) to give the product. Yield 11 mg, 9%. ^{31}P-$\{^1H\}$: $\delta = 11.76$, $^1J = 3101$ Hz. Found: C, 53.0; H, 5.2; N, 5.4. Calc.: C, 52.9; H, 5.0; N, 5.7%.

$Pt(NSNSC_6H_4NO_2)_2(dppe)$

$PtCl_2(dppe)$ (0.024 g, 0.03 mmol) and *p*-$O_2NC_6H_4SNSNSiMe_3$ (0.077 g, 0.16 mmol) were stirred together in chloroform for 1 month. After this time the solvent was removed *in vacuo* and the remaining solid extracted with benzene (10 cm^3). Addition of hexane (10 cm^3) gave the product as a red precipitate. Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a benzene solution. Yield 25 mg, 70%. Found: C, 44.7; H, 3.7; N, 7.1. Calc. for $[Pt(NSNSC_6H_4NO_2)_2(dppe) \cdot C_6H_6]$: C, 44.7; H, 3.9; N, 7.1%. ^{31}P-$\{^1H\}$ ($CDCl_3$): $\delta = 33.43$ ppm, $^1J(Pt—P) = 3130$ Hz.

$Pd(HNSNSC_6H_4NO_2)Cl_2$

A solution of *p*-$O_2NC_6H_4SNSNSiMe_3$ (0.3 g, 1 mmol) in benzene (5 cm^3) was added to a solution of $PdCl_2(PhCN)_2$ (0.4 g, 1 mmol) in benzene (80 cm^3). On mixing, the solution became cloudy and after stirring for 1 week an orange–brown precipitate was formed together with a lightening of the solution from red to orange. The solid was filtered off, washed with hexane (3 × 10 cm^3) and dried *in vacuo*. Yield 0.3 g, 75%. Found: C, 16.7; H, 1.5; N, 10.4. Calc.: C, 18.4; H, 1.3; N, 10.7%.

Crystal data

$C_9H_{13}N_3O_2S_2Si$ (**3**). $M = 287.4$, triclinic, $a = 5.839(4)$, $b = 11.574(6)$, $c = 11.598(10)$ Å, $\alpha = 111.84(5)$, $\beta = 110.08(6)$, $\gamma = 100.00(5)°$, $U = 691$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.39$ g cm^{-3}. Yellow air-stable irregular polyhedron, crystal dimensions 0.1 × 0.1 × 0.1 mm. $\mu(Cu\text{-}K_\alpha) = 43$ cm^{-1}, $\lambda = 1.54178$ Å, $F(000) = 300$.

$C_{38}H_{32}N_6O_4P_2PtS_4$ (**5**). $M = 1022.0$, monoclinic, $a = 16.760(4)$, $b = 17.581(6)$, $c = 27.517(9)$ Å, $\beta = 90.73(2)°$, $U = 8107$ Å^3, space group $P2_1/c$, $Z = 8$ (two crystallographically independent molecules), $D_c = 1.68$ g cm^{-3}. Red–orange air-stable irregular polyhedron, crystal dimensions 0.15 × 0.1 × 0.2 mm. $\mu(Cu\text{-}K_\alpha) = 96.0$ cm^{-1}, $\lambda = 1.54178$ Å, $F(000) = 4047$.

Data collection and processing for 3 *and* 5

Nicolet R3m diffractometer, ω-scan method, ($2\theta \leqslant 116°$ for **3** and 100° for **5**), graphite monochromated Cu-K_α radiation, 1843 and 8322 independent measured reflections of which 1273 and 6655 were considered observed $[|F_o| > 3\sigma(|F_o|)]$ for **3** and **5**, corrected for Lorentz and polarization factors. For both **3** and **5** empirical absorption corrections based on 360 azimuthal scans were applied.

Structure analysis and refinement for 3

The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The methyl groups were refined as rigid bodies, the positions of all the other hydrogen atoms were idealized (C—H = 0.96 Å), assigned isotropic thermal parameters, $[U(H) = 1.2U_{eq}(C)]$ and allowed to ride on their parent carbons. Refinement was by block-cascade full-matrix least-squares to give $R = 0.069$, $R_w = 0.068$ ($w^{-1} = \sigma^2(F) + 0.00093F^2$) ($R = \Sigma[|(F_o - F_c)|]/\Sigma|F_o|$). The maximum residual electron density in the final ΔF map was 0.37 e Å^{-3}. The mean and maximum shifts/error in the final refinement cycle were 0.012 and 0.057, respectively. Computations were carried out on an Eclipse S140 computer using the *SHELXTL* program system.[12]

Structure analysis and refinement for 5

The structure was solved by the heavy-atom method and all non-hydrogen atoms refined anisotropically. Refinement (for two separate data collections on different crystals) showed the structure to be subject to severe anisotropic thermal motion in all of the aryl rings in both independent molecules. This disorder/anisotropic thermal motion could not be resolved into alternate partial occupancy orientations so refinement was terminated at $R = 0.115$.

RESULTS AND DISCUSSION

Sulphur diimides are known to coordinate in a variety of ways.[1] With organic substituents such as ^{t}Bu or Ph the complexes are bonded through one or both nitrogen atoms except in those cases where fragmentation to RNS complexes occurs. We have investigated the reactivity of $(Me_3Si)_2N_2S$ and $RNSNSiMe_3$ [R = ^{t}Bu, p-$O_2NC_6H_4S$ (**3**)] with simple metal phosphine halides and with $Pt(C_2H_4)(PPh_3)_3$ since the Si—N bond is relatively weak particularly in comparison to the Si—Cl bond. It was hoped that this would provide a rational synthetic route to diimido complexes. The formation of **3** from **1** [eq. (1)] is a typical example of the reactivity of this molecule.

$$(Me_3Si)_2N_2S + p\text{-}O_2NC_6H_4SCl \rightarrow p\text{-}O_2NC_6H_4SNSNSiMe_3 + Me_2SiCl. \quad (1)$$

Elimination of Me_3SiCl provides the driving force for the reaction although it should be noted that a significant side product is the insoluble bis compound RSNSNSR and **3** is only obtained in *ca* 30% yield.

The X-ray structure of **3** (Fig. 1, Table 1) reveals a planar S_2N_2 chain [maximum deviation from the mean plane 0.007 Å for S(1)] which is rotated slightly with respect to the aromatic ring (C(2)—C(1)—S(2)—N(2) torsion angle 5°). The bond distances and angles within the S_2N_2 chain closely resemble those in the metallacycle $Pt(S_2N_2)(PMe_3)_2$,[13] but are markedly dissimilar from those in $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$[4] (Table 2).

Of particular interest is the packing arrangement adopted by **3** in the crystal (Fig. 2). The molecules form infinite parallel stacks along the crystallographic *a* direction with their planes inclined. The interplanar separation between the S_2N_2 groups is 3.75 Å; the closest contact is C(1)—S(1)′ 3.65 Å. Within each stack, the S(1)—N(2) bond of one molecule lies over the aryl ring of the next.

Reaction of **1**, **3** or **4** with *cis*-$[PtCl_2(PR_3)_2]$ ($PR_3 = PPh_3$, PEt_3, PMe_2Ph and 1/2dppe) does not proceed as hoped except in the case of treatment of $PtCl_2$(dppe) with **3**, which gives $Pt(NSNSC_6H_4NO_2)$(dppe) (**5**). The latter product was characterized by IR, NMR and X-ray crystallography, however, it is not obtained via a smooth, simple reaction. The reaction takes 1 month at room temperature in chloroform and is insensitive to more vigorous conditions (e.g. reflux in toluene). ^{31}P NMR spectra were taken at time intervals during the course of the reaction. Thus after 1 week, the spectrum consists of *ca* 25% unreacted starting material, 25% of **5** and a third compound **6** with $\delta = 35.1$ ($^1J = 3014$ Hz), $\delta = 38.0$ ($^1J = 3798$ Hz) and $^2J(^{31}P—^{31}P) = 9$ Hz. For comparison, **5** has $\delta = 33.4$ and $^1J = 3130$ Hz and **2** has $\delta = 11.76$ ppm and $^1J = 3098$ Hz. It has been proposed[16] that

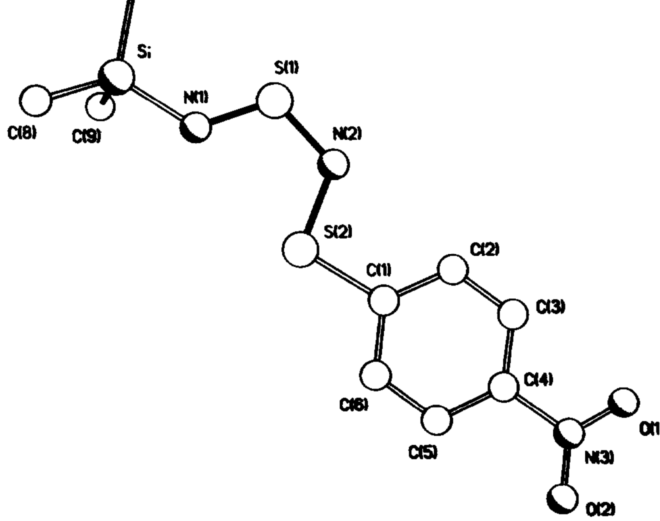

Fig. 1. The X-ray crystal structure of p-$O_2NC_6H_4$ $SNSNSiMe_3$ (**3**).

Table 1. Selected bond distances (Å) and angles (°) in **3**

S(1)—N(1)	1.503(5)	S(1)—N(2)	1.558(7)
S(2)—N(2)	1.653(7)	S(2)—C(1)	1.761(7)
Si(1)—N(1)	1.749(6)	Si(1)—C(7)	1.851(8)
Si(1)—C(8)	1.817(7)	Si(1)—C(9)	1.849(10)
O(1)—N(3)	1.213(9)	O(2)—N(3)	1.199(13)
N(3)—C(4)	1.493(11)		
N(1)—S(1)—N(2)	114.1(4)	N(2)—S(2)—C(1)	100.5(3)
N(1)—Si(1)—C(7)	110.2(3)	N(1)—Si(1)—C(8)	107.9(4)
C(7)—Si(1)—C(8)	110.8(4)	N(1)—Si(1)—C(9)	105.5(4)
C(7)—Si(1)—C(9)	111.2(5)	C(8)—Si(1)—C(9)	111.0(4)
S(1)—N(1)—Si(1)	128.8(4)	S(1)—N(2)—S(2)	116.1(3)
O(1)—N(3)—O(2)	125.6(8)	O(1)—N(3)—C(4)	117.0(9)
O(2)—N(3)—C(4)	117.4(6)	S(2)—C(1)—C(2)	124.5(6)
S(2)—C(1)—C(6)	115.3(4)		

Table 2. Comparative SN bond distances (Å) and angles (°) in **3**, $S_2N_2^{2-}$ and $S_2N_2H^-$ complexes. Because of their poor precision comparative distances for **5** have not been included

Compound	N(1)—S(1)	S(1)—N(2)	N(2)—S(2)	N(1)—S(1)—N(2)	S(1)—N(2)—S(2)
3	1.503(5)	1.558(7)	1.656(7)	114.1(4)	116.1(3)
$Pt(S_2N_2)(PMe_3)_2$[4]	1.492(13)	1.576(16)	1.668(17)	117.7(8)	115.0(8)
$Pt(S_2N_2)(PPh_3)_2$[13]	1.546(16)	1.567(19)	1.682(16)	116.0(9)	116.1(11)
$[Pt(S_2N_2H)(PEt_3)_2][Me_3SnCl_2]$[14]	1.572(12)	1.554(10)	1.667(10)	109.4(5)	119.8(7)
$[Pt(S_2N_2H)(PMe_2Ph)_2]Cl$[15]	1.582(8)	1.561(8)	1.647(8)	108.2(4)	120.5(5)

in $Pt(PPh_3)_2(PhNSNPh)$ (**7**) the diimide coordinates assymmetrically in an edge-on fashion through one N=S bond. In the ^{31}P NMR of **7** the ^{31}P—^{195}Pt coupling constants are 3368 and 4320 Hz and $\delta = 17.4$ ppm (both ^{31}P resonances). Since both **5** and **6** involve a different phosphine to **2** and **7** direct comparison of δ values is not possible but the coupling constants are quite dissimilar. The most plausible structure for intermediate **6** is $PtCl(dppe)(NSNSC_6H_4NO_2)$.

The X-ray structure of **5** (which has been briefly reported elsewhere[17]) although of limited precision because of disorder/thermal anisotropy problems reveals (Fig. 3) square-planar coordination of the platinum by the chelate phosphine and two anionic p-$O_2NC_6H_4SNSN^-$ ligands. Each of the independent molecules has approximate non-crystallographic C_2 symmetry about an axis bisecting the N—Pt—N and P—Pt—P angles. The p-$O_2NC_6H_4SNSN^-$ ligands are essentially planar with a *syn,syn* conformation about the N_2S group as might be expected from recent calculations.[18] In contrast to **2** the backbones of the *cis* diimido ligands are *trans*-axial relative to the coordination plane of the platinum with resulting pseudo-octahedral coordination of the Pt^{II} atom by the distal S_2N_2 sulphur atoms. The apical Pt···S contacts for both independent molecules are 3.19, 3.44, 3.25 and 3.37 Å. The mean inclination of the Pt···S vectors to the PtP_2N_2 plane is *ca* 60°.

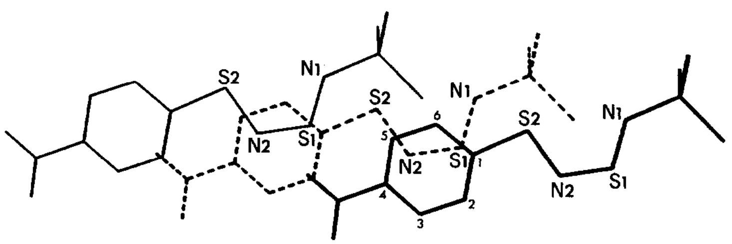

Fig. 2. Viewed parallel to the S_2N_2 plane showing the continuous stepped stacking of lattice translated molecules of (**3**) in the crystal. Uppermost molecule is shown heavy, middle dashed and lower light.

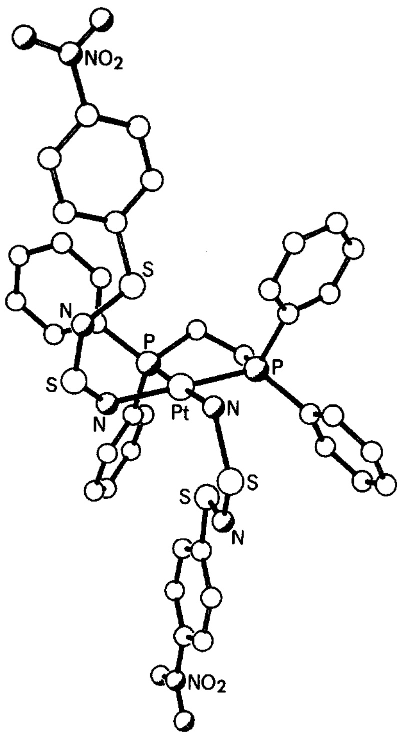

Fig. 3. The X-ray crystal structure of Pt(NSNSC$_6$H$_4$NO$_2$)$_2$(PPh$_3$)$_2$ (**5**).

The similarity of the ^1J values for **2** and **5** is as expected if the R group in RNSN$^-$ is only of marginal importance but we do not believe this to be the case. It should be noted[13,14] that in [Pt(S$_2$N$_2$H)(dppe)][PF$_6$] the phosphorus *trans* to nitrogen has $\delta = 38.6$ ppm and $^1J = 3162$ Hz whilst in Pt(S$_2$N$_2$)(dppe) the signal is at $\delta = 41.1$ and has $^1J = 2784$ Hz. We would have expected that the S$_2$N$_2^{2-}$ complex would have been more directly comparable with the *p*-O$_2$NC$_6$H$_4$SNSN$^-$ complex as was the case with Pt(S$_2$N$_2$)(PPh$_3$)$_2$ and **2**. It thus seems likely that changing from R = Me$_3$Si to *p*-O$_2$NC$_6$H$_4$S and from PPh$_3$ to dppe has mutually opposed effects on the magnitude of ^1J resulting in **2** and **5** fortuitously having remarkably similar parameters. This observation serves to underline the difficulties in making use of ^{31}P NMR data in an empirical fashion!

Pt(C$_2$H$_4$)(PPh$_3$)$_2$ reacts smoothly with the bis-silyldiimide to give Pt(NSNSiMe$_3$)$_2$(PPh$_3$)$_2$. With Me$_3$SiNSN^{t}Bu the reaction appears clean by NMR but the product [Pt(NSN^{t}Bu)$_2$(PPh$_3$)$_2$ (**8**)] is extremely soluble and could only be isolated in low yield. **3** gives a mixture of products which, to date, we have been unable to separate. The structure of **2** has been established by X-ray crystallography. It consists of a square-planar Pt^{II} with *cis* σ-bonded NSNSiMe$_3$ ligands.[15] Comparison of the ^{31}P NMR of **2** and **3** reveals almost identical chemical shifts and coupling constants as expected.

Reaction of PdCl$_2$(PhCN)$_2$ with **3** gives a complex with a microanalysis corresponding to PdCl$_2$(HNSNSC$_6$H$_4$NO$_2$) (**9**). The IR spectrum of **9** is significantly different from both the starting material and the simple σ-bonded complexes (Table 3). Apart from the variation in frequency of the ν(NSN) vibrations the most obvious feature is the presence of bands due to NH. We speculate that **9** contains an edge-on coordinated HNSNSC$_6$NO$_2$ ligand.

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REFERENCES

1. P. F. Kelly and J. D. Woollins, *Polyhedron* 1986, **5**, 607.
2. N. P. C. Walker, M. B. Hursthouse, C. P. Warrens

Table 3. Selected vibrational bands in **3** and its complexes

3		**5**	**9**		
IR	Raman	IR	IR	Raman	
			3190m		ν(NH)
			1408m		δ(NH)
1194m,br	1197w	1090m	1059s	1063m	ν(NSN)$_{as}$
1000w	998m	960w	968w	985m 966m	ν(NSN)$_s$
850br,vs	857w	824w			δ(NSN)
655m	—				ν(NS)
			620s		δ(NH)
—	541w				
			355w		ν(PdN)
			330m		ν(PdCl)

and J. D. Woollins, *J. Chem. Soc., Chem. Commun.* 1985, 227.

3. R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *Polyhedron* 1985, **4**, 1947.
4. R. Jones, P. F. Kelly, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.* 1986, 711.
5. R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.* 1985, 1325.
6. J. C. Bailar and H. Itanani, *Inorg. Chem.* 1965, **4**, 1618.
7. F. R. Hartley, *The Chemistry of Platinum and Palladium.* Applied Science, New York (1973).
8. C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.* 1968, **90**, 1464.
9. C. P. Warrens and J. D. Woollins, *Inorg. Synth.*, in press.
10. J. Kuyper and G. B. Street, *J. Am. Chem. Soc.* 1977, **99**, 7848.
11. R. Appel and M. Montenarh, *Z. Naturforsch.* 1975, **30B**, 847.
12. G. M. Sheldrick, *SHELXTL,* An integrated system for solving, refining and displaying crystal structures from diffraction data. University of Göttingen, F.R.G. (1978); Revision 4.1 (1983).
13. P. A. Bates, M. B. Hursthouse, P. F. Kelly and J. D. Woollins, *J. Chem. Soc., Dalton Trans.* 1986, 2367.
14. R. Jones, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.* 1987, 907.
15. R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, submitted.
16. R. Meij, D. J. Stufkens, K. Vrieze, E. Roosndaal and H. Schenk, *J. Organomet. Chem.* 1978, **155**, 323.
17. P. F. Kelly, I. P. Parkin and J. D. Woollins, *Phosphorus Sulphur*, accepted.
18. H. R. Rzepa and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, in press.