# New Metal–Sulphur–Nitrogen Compounds from Reactions in Liquid Ammonia. The *X*-Ray Structures of *trans*-Bis(acetophenone dimethylhydrazone-$N^{\alpha}$)-dichloropalladium(II) and [Di(azathien)-1-yl-$S^1N^4$][2-(hydrazonoethyl)-phenyl]palladium(II)†

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Reaction of $[S_4N_3]Cl$ or $[S_3N_2Cl]Cl$ in liquid ammonia with $[PtCl_2(PR_3)_2]$ or $[(L–L')PdCl_2Pd(L–L')]$ (L–L' = C–N ligand) gives $[Pt(S_2N_2)(PR_3)_2]$ and $[Pd(S_2N_2H)(L–L')]$ respectively; in some cases complexes containing $S_3N^-$ ligands were also obtained. An alternative route to $[Pd(S_3N)(L–L')]$ complexes using $[HgPh(S_7N)]$ is also reported. Reaction of $S_8$–$NH_3$(l) solutions with $[PtCl_2(PR_3)_2]$ gives $[PtS_4(PR_3)_2]$. The new complexes were characterised by microanalyses, i.r., n.m.r., and mass spectroscopy, and *X*-ray crystallography.

It is clear from a number of recent publications[1–3] that there is a complex set of equilibria involved when $S_8$ or simple sulphur–nitrogen compounds are dissolved in liquid ammonia. The dissolution of sulphur is believed to result in $S_7N^-$, $S_4N^-$, $S_3N^-$, $S_6{}^{2-}$, and $S_4{}^{2-}$ which on work up give sulphur imides such as $S_7NH$ and $S_6(NH)_2$. The compounds $S_4N_4$ or $(NSCl)_3$ yield $[NH_4][S_4N_5]$ after work up[3] whilst it was reported over 30 years ago[4] that $[S_4N_3]Cl$ gives an explosive brown solid on evaporation of its ammonia solution.

A number of groups[5] are interested in the preparation of metal–sulphur–nitrogen complexes and we have been successful[6–10] in synthesising complexes of the type $[Pt(S_2N_2)(PR_3)_2]$ (**1**) and $[Pt(S_2N_2H)(PR_3)_2]X$ (**2**) ($X = PF_6{}^-$, $BF_4{}^-$ or $Cl^-$) by a variety of routes. To date, the most useful route has been the reaction of $S_4N_4H_4$ with $[PtCl_2(PR_3)_2]$ in the presence of dbu (1,8-diazabicyclo[5.4.0]undec-7-ene) to give (**1**) which can be protonated by HX to give (**2**). Compounds (**2**) exhibit interesting solid-state packing properties[8–10] with the cations and anions in columns or 'stacks'. Virtually all of the routes to (**1**) (and related metal–sulphur–nitrogen compounds) involve the use, at some stage, of explosive $S_4N_4$. For example, $S_4N_4H_4$ is prepared by reduction of $S_4N_4$ with $SnCl_2$ in methanol.

Recently,[11] we have found that if ammonia solutions of $[S_3N_2Cl]Cl$ (**3**) are evaporated to dryness and extracted into tetrahydrofuran (thf) a reactive intermediate suitable for the preparation of (**1**) is obtained. Unfortunately, the intermediate is not stable. It would obviously be of advantage to develop preparative routes to metal–sulphur–nitrogen compounds (and indeed other SN heterocycles) which do not involve explosive species. Additionally, we hoped to use $[PtCl_2(PR_3)_2]$ complexes to trap reactive SN fragments from liquid ammonia and gain insight into the solution equilibria. In this regard there have been preparations[12,13] of $Pb(S_2N_2)\cdot NH_3$ from $Pb(NO_3)_2$ and $S_4N_4$ in liquid ammonia, and the synthesis of $[(H_3N)HgSN_2]_2$ from reaction of $S_4N_4$ with $HgI_2$ in chloroform with gaseous ammonia.

Here we report on the development of a new route to $[Pt(S_2N_2)(PR_3)_2]$ complexes together with the preparation of a wide range of $[Pd(S_2N_2H)(L–L')]$ complexes (L–L' = chelate organometallic ligand). These latter complexes extend the range of mixed-ligand sulphur–nitrogen complexes to include palladium and contain virtually planar ligands thus offering the possibility of improved stacking properties compared with (**2**). The *X*-ray crystal structure of one example is reported and compared with that of the simple *trans*-dichloro complex $[PdCl_2(HL–L')_2]$ (HL–L' = acetophenone dimethylhydrazone). Nitrogen-15 labelling experiments have been used to probe the reaction pathway and to aid assignment of the vibrational spectra.

## Experimental

All reactions were performed in an inert atmosphere using standard Schlenk-line techniques. Ammonia was used as supplied (BOC, anhydrous). Drying of solvents, spectroscopic methods, and the preparation of $[MCl_2(PR_3)_2]$ was as previously reported.[6,9,10] I.r. spectra were measured as KBr discs on a Perkin-Elmer 1720 spectrometer, mass spectra using either fast atom bombardment (f.a.b.) or electron impact (e.i.) with a VG 2020 instrument. The compounds $[S_3N_2Cl]Cl$, $[S_4N_3]Cl$, and the $^{15}N$-labelled compounds were prepared by literature methods.[14] The palladium chloro-bridged dimers were synthesised from $Na_2[PdCl_4]$ or $Pd(O_2CMe)_2$ (Aldrich) with the appropriate ligand by standard procedures.[15–23] The compound $[HgPh(S_7N)]$ and $[Hg(S_7N)_2]$ were prepared by the literature method and stored at −20 °C in the dark prior to use.[24]

*Preparation of* $[M(S_2N_2)(PR_3)_2]$ *and* $[Pd(S_2N_2H)(L–L')]$ *from Reactions in Liquid* $NH_3$.—In a typical reaction, $[S_4N_3]Cl$ (0.037 g, 0.15 mmol) was added to liquid ammonia (5 $cm^3$) at −78 °C. The appropriate $[MCl_2(PR_3)_2]$ complex (0.17 mmol) was added and the reaction stirred at −78 °C for 30 min. After this time the reaction was allowed to warm to room temperature with the ammonia being blown off under a stream of nitrogen. The remaining brown solid was extracted with chloroform (2 × 5 $cm^3$), filtered through Celite, and purified by preparative thin-layer chromatography (p.t.l.c.) on silica using $CH_2Cl_2$ as eluant. Typically, 0.07 mmol of $S_4N_4$ ($R_f$ 0.8) and 0.11 mmol of complex (**1**) ($R_f$ 0.1) were separated.

The organometallic palladium complexes were prepared by a similar route. For example, in the preparation of the benzyldimethylamine complex, $[S_4N_3]Cl$ (0.61 g, 3 mmol) was added to liquid ammonia (10 $cm^3$) at −78 °C. Di-μ-chloro-bis[(benzyldimethylamine)palladium(II)] (0.94 g, 1.7 mmol) was added and the solution was stirred for 2 h at −78 °C before being allowed to warm to room temperature (r.t.) under a stream of $N_2$. The resultant red-brown solid was extracted with

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

dichloromethane (2 × 5 cm$^3$) to give a red solution, filtered through Celite, and purified by passage down a Bio-bead column (SX-8, 30 × 2 cm) with $CH_2Cl_2$ as eluant. The first red band gave upon removal of the solvent *in vacuo* [Pd($S_2N_2H$)(L–L′)] (0.81 g, 82%) and a second yellow band, $S_4N_4$ (0.12 g, 0.76 mmol). This route gave compounds (**4**)—(**14**) whose microanalytical and spectroscopic data are given in Tables 1—3. In the cases of (**7**), (**9**), and (**14**) a small amount of the $S_3N$ complex was also detected by mass spectroscopy.

*Preparation of* [Pt($S_2N_2$)($PR_3$)$_2$] *and* [Pd($S_2N_2H$)(L–L′)] *from* [$S_4N_3$]Cl *in* $CH_2Cl_2$.—In a typical reaction, ammonia was passed through a stirred suspension of [$S_4N_3$]Cl (0.050 g, 0.24 mmol) in $CH_2Cl_2$ (15 cm$^3$) at 20 °C until the yellow-green suspension had changed colour through black to dark red to orange with a white precipitate. The complex [$PtCl_2$($PR_3$)$_2$] (0.18 mmol) was added generating a dark red colour in solution. Ammonia was passed through the solution for a further 5 min, the solution stirred for 30 min then filtered through Celite and the filtrate reduced to about 2 cm$^3$ *in vacuo*. P.t.l.c. on silica using $CH_2Cl_2$ as eluant typically gave 0.02 mmol $S_4N_4$ ($R_f$ 0.8) and [Pt($S_2N_2$)($PR_3$)$_2$] (0.126 mmol, 70%; $R_f$ 0.1).

In the organometallic cases the same general reaction conditions were employed except purification was achieved by passage down a Bio-bead column (30 × 2 cm) using $CH_2Cl_2$ as eluant. In the case of L–L′ = acetophenone dimethylhydrazone, apart from (**14**) we also obtained (as the first fraction) the *trans* complex (**26**).

*Reaction of* $S_8$–$NH_3$ *with* [$PtCl_2$($PR_3$)$_2$].—In a typical reaction, sulphur (0.300 g, 1.165 mmol) was added to liquid ammonia at −78 °C. The mixture was sealed and allowed to warm to room temperature and left in the light for 6 h until all of the sulphur had dissolved yielding a dark blue solution. After cooling to −78 °C, [$PtCl_2$(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$) (0.150 g, 0.226 mmol) was added. The reaction mixture was stirred for 1 h and the ammonia blown off under a stream of nitrogen. Extraction with $CH_2Cl_2$ (6 cm$^3$) followed by Celite filtration yielded a yellow solution. This was reduced in volume to 2 cm$^3$ *in vacuo* and layered with diethyl ether–hexane (10:15 cm$^3$) to give orange crystals of [$PtS_4$(dppe)] (0.130 g, 0.18 mmol, 80%).

In the case of [$PtCl_2$($PPr^n{}_3$)$_2$] the conditions were as above except the product was worked up on a Bio-bead column (30 × 2 cm) using $CH_2Cl_2$ as eluant to give [$PtS_4$($PPr^n{}_3$)$_2$] as the first brown band (0.068 g, 0.104 mmol). The other R group reactions were performed on the n.m.r. scale only ($^{31}$P n.m.r. data are given in Table 4, microanalytical data in Table 1).

*Preparation of* [Pd($S_3N$)(L–L′)] *from* [HgPh($S_7N$)].—In a typical reaction, [HgPh($S_7N$)] (0.191 g, 0.35 mmol) was added to a stirred suspension of [(L–L′)$PdCl_2Pd$(L–L′)] (0.176 mmol) in $CH_2Cl_2$ (30 cm$^3$). The initial yellow colour of the solution turned red after 10 min. The reaction mixture was stirred for 4 h at room temperature, filtered through Celite, and reduced in volume to *ca.* 3 cm$^3$ *in vacuo*. Purification was achieved by passage down a Bio-bead column (SX-8) (30 × 2 cm) using $CH_2Cl_2$ as eluant. This gave the products (**15**)—(**19**) by slow evaporation of the solvent from the first red band (microanalytical, mass spectral and n.m.r. data are given in Tables 1 and 2). The i.r. spectra include two ν(SN) vibrations of medium intensity at *ca.* 960 and 710 cm$^{-1}$, a weak ν(SS) at *ca.* 530 cm$^{-1}$, and a weak ν(PtS) at 330 cm$^{-1}$ along with the vibrations due to the organometallic species.

*Deuteriation of Complexes* (**7**) *and* (**14**).—Deuteriations were achieved by dissolving either complex (**7**) or (**14**) in $CH_2Cl_2$ and adding about a 100-fold excess of $CH_3OD$. The deuteriated compound was obtained upon pumping off the solvent.

*Crystallography.—Crystal data.* Complex (**14**), $C_{10}H_{14}N_4PdS_2$, $M$ = 360.8, monoclinic, $a$ = 17.723(2), $b$ = 9.028(1), $c$ = 18.986(3) Å, β = 116.74(1)°, $U$ = 2 713 Å$^3$, space group $P2_1/c$, $Z$ = 8 (two crystallographically independent molecules), $D_c$ = 1.77 g cm$^{-3}$, yellow, air-stable prisms, μ(Cu-$K_\alpha$) = 140 cm$^{-1}$, $\bar{\lambda}$ = 1.541 78 Å, $F$(000) = 1 440.

Complex (**26**), $C_{20}H_{28}Cl_2N_4Pd$, $M$ = 501.8, monoclinic, $a$ = 8.574(3), $b$ = 14.389(5), $c$ = 9.784(4) Å, β = 115.09(3)°, $U$ = 1 093 Å$^3$, space group $P2_1/a$, $Z$ = 2 (the molecule is disposed about a centre of symmetry), $D_c$ = 1.52 g cm$^{-3}$, yellow, air-stable prisms, μ(Cu-$K_\alpha$) = 94 cm$^{-1}$, $\bar{\lambda}$ = 1.541 78 Å, $F$(000) = 512.

*Data collection and processing.* Nicolet R3m diffractometer, ω-scan method [2θ ⩽ 110 and 116° for (**14**) and (**26**) respectively], graphite-monochromated Cu-$K_\alpha$ radiation; 3 411 and 1 471 independent measured reflections, 2 785 and 1 438 observed [$|F_o| > 3\sigma(|F_o|)$], corrected for Lorentz and polarisation factors; numerical absorption corrections (face-indexed crystals). The minimum and maximum transmission factors for complex (**14**) were 0.04 and 0.19 and for (**26**) were 0.06 and 0.30 respectively.

*Structure analysis and refinement.* The structures were solved by the heavy-atom method and all the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealised (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 $R$ = 0.046 and 0.047 [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$], $R'$ = 0.053 and 0.053 for (**14**) and (**26**) respectively [$w^{-1} = \sigma^2(F) + 0.000\,152F^2$ and $0.000\,8F^2$]. The maximum and minimum residual electron densities in the final Δ$F$ maps were 0.60, 1.66 and −0.58, −1.48 e Å$^{-3}$ and the mean and maximum shifts/error in the final refinement cycle were 0.02, 0.169 and 0.000, 0.001 for (**14**) and (**26**) respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system[25] and published scattering factors.[26]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

## Discussion

Upon dissolving [$S_3N_2Cl$]Cl or [$S_4N_3$]Cl in liquid ammonia at −78 °C a purple-red solution is formed. We have shown previously that if the ammonia is allowed to evaporate and the resulting solid is treated with [$PtCl_2$($PR_3$)$_2$] compounds (**1**) are obtained.[11] However, the intermediate solid is reported to be explosive and the products obtained from it are difficult to obtain pure. We thus attempted reactions in liquid ammonia directly. The reactions proceed smoothly, with the products being readily separated and purified by p.t.l.c. or passage down Bio-bead columns. Equation (1) *partially* represents the

$$[S_4N_3]Cl + NH_3(l) + [MCl_2(PR_3)_2] \longrightarrow [M(S_2N_2)(PR_3)_2] + S_4N_4 \quad (1)$$

reaction: a substantial quantity of $S_4N_4$ is formed but the amount isolated does not correspond to a simple stoicheiometric reaction. If the red-purple solution mentioned above is worked up a substantial amount of $S_4N_4$ is obtained suggesting that competitive reactions are occurring. If $S_4N_4$ in liquid ammonia is treated with [$MCl_2$($PR_3$)$_2$] under similar conditions to the above reaction, although some (**1**) is formed the reaction is much slower and we therefore do not believe that $S_4N_4$ is an intermediate. If $S_4N_4$ is allowed to react at the

**Table 1.** Microanalytical data and yields (%) of the new complexes

| Compound and HL–L′ | Yield | Colour | C | H | N |
|---|---|---|---|---|---|
| $[Pd(S_2N_2H)(L-L')]$ | | | | | |
| **(4)** 3,3′,5,5′-Tetramethylazobenzene | 80 | Red | 43.6<br>(44.0) | 4.0<br>(4.1) | 12.7<br>(12.6) |
| **(5)** Azobenzene | 90 | Red | 37.9<br>(37.9) | 2.5<br>(2.5) | 14.5<br>(14.3) |
| **(6)** 2-Phenylpyridine | 82 | Red | 37.4<br>(37.3) | 2.4<br>(2.5) | 11.8<br>(11.8) |
| **(7)** Benzyldimethylamine | 82 | Red | 32.5<br>(32.5) | 3.9<br>(3.9) | 12.4<br>(12.6) |
| **(8)** *N*-Benzylidenebenzylamine | 68 | Orange | 42.6<br>(42.6) | 3.1<br>(3.1) | 10.5<br>(10.7) |
| **(9)** 7,8-Benzoquinoline | 24 | Red | 40.9<br>(41.4) | 2.2<br>(2.4) | 10.7<br>(11.1) |
| **(10)** 2-Benzylpyridine | 80 | Yellow | 39.5<br>(39.2) | 3.1<br>(3.0) | 11.0<br>(11.4) |
| **(11)** 2-(1-Pyrrolyl)-pyrimidine | 21 | Red | 28.0<br>(28.0) | 2.0<br>(2.0) | 19.8<br>(20.4) |
| **(12)** 8-Methylquinoline | 32 | Red | 33.2<br>(33.8) | 2.6<br>(2.6) | 12.0<br>(11.0) |
| **(13)** *N*-1-Naphthyldimethylamine | 48 | Red | 38.9<br>(38.9) | 3.4<br>(3.5) | 10.9<br>(11.3) |
| **(14)** Acetophenone dimethylhydrazone | 83 | Yellow | 33.3<br>(33.7) | 3.9<br>(3.8) | 15.5<br>(14.9) |
| $[Pd(S_3N)(L-L')]$ | | | | | |
| **(15)** *N*-Benzylidenebenzylamine | 31 | Orange | 41.2<br>(41.0) | 2.8<br>(2.7) | 6.5<br>(6.8) |
| **(16)** 8-Methylquinoline | 32 | Purple | 33.4<br>(33.5) | 1.9<br>(2.2) | 7.8<br>(7.5) |
| **(17)** 2-Phenylpyridine | 28 | Red | 34.5<br>(35.5) | 2.1<br>(1.9) | 7.3<br>(7.6) |
| **(18)** Acetophenone oxime $0.5CH_2Cl_2$ solvate | 55 | Red | 26.7<br>(26.0) | 2.3<br>(2.5) | 6.2<br>(7.0) |
| **(19)** 2-Phenylpyrazole | 23 | Red | 30.0<br>(30.2) | 1.6<br>(1.9) | 11.7<br>(11.2) |
| $S_4^{2-}$ Complexes | | | | | |
| **(20)** $[PtS_4(dppe)]$ | 80 | Orange | 42.8<br>(43.2) | 3.2<br>(3.3) | |
| **(21)** $[PtS_4(PPr_3)_2]\cdot CH_2Cl_2$ | 65 | Orange | 30.9<br>(31.3) | 6.0<br>(6.1) | |

boiling point of ammonia (*ca.* −33 °C) for 2 h before the addition of *cis*-$[PtCl_2(PR_3)_2]$ then **(1)** is formed quantitatively according to $^{31}P$ n.m.r. spectroscopy. This indicates that there is a slow reaction between liquid ammonia and $S_4N_4$ and preliminary $^{14}N$ n.m.r. studies of the liquid ammonia solution[27] suggest that the reactive species in solution is $S_3N_3^-$. The ease of reaction (1) led us to extend its use to the synthesis of a new class of mixed-ligand palladium complexes containing chelate C–N ligands by use of dimeric chloro-bridged $[(L-L')PdCl_2Pd(L-L')]$ complexes as starting materials. Microanalytical data for compounds prepared by this route are given in Table 1.

The most obvious difference between the products obtained from the phosphine complexes and the organometallic palladium dimers is that the latter contain the protonated ligand $S_2N_2H^-$ rather than $S_2N_2^{2-}$. In the preparation of complexes **(4)**—**(14)** we have noticed that after the ammonia has been allowed to evaporate when the solids are first placed under vacuum there is a distinct colour change and ammonia is liberated. It is possible that the initial product is of the type $[NH_4][Pd(S_2N_2)(L-L')]$ and that this readily disproportionates to $[Pd(S_2N_2H)(L-L')]$ and ammonia. An alternative route for this protonation is for the molecule to react with HCl from the $CH_2Cl_2$ used in the work up, but the quantities used seem inadequate for this purpose. We have shown (see below) that the protons in **(4)**—**(14)** are readily exchanged. In a few cases we have obtained $S_3N^-$ complexes [(2-ethoxy-2-methylpropyl)-dimethylamine **(22)**, benzyldimethylamine **(23)**, 2-benzylpyridine **(24)** and acetophenone dimethylhydrazone **(25)**] in low yield (*ca.* 5—10%) usually together with the $S_2N_2H^-$ complex. These compounds have been identified by mass spectroscopy, which is very characteristic (Table 2). Their presence further underlines the complex nature of the reactive liquid ammonia solution used. In particular it should be noted that in the formation of **(22)** none of the isoelectronic $S_2N_2H^-$ complex was observed.

We have also carried out reaction (1) using $^{15}N$-labelled $[S_4N_3]Cl$. Mass and $^{31}P$ n.m.r. spectroscopy enables the degree of $^{15}N$ labelling in the final product to be established. In the phosphine complexes **(1)** the final product contains 70—75% $^{15}N$ (*i.e.* there is a 70—75% chance of either nitrogen being $^{15}N$); in **(7)** and **(14)** this figure is reduced to 55—60%. The final labelling in the phosphine case suggests inclusion of one nitrogen from the liquid ammonia and suggests a reactive intermediate of $S_3N_3^-$ as in the equilibrium (2). This is

$$7S_4N_3^+ + 6NH_3 \rightleftharpoons 9S_3N_3^- + H_2S + 16H^+ \quad (2)$$

consistent with $^{14}N$ n.m.r. measurements[27] whilst the labelling in the other cases may imply the involvement of $S_4N_5^-$. Further work in this area is underway.

Dissolution of sulphur in liquid ammonia gives a dark blue solution which reacts with $[PtCl_2(PR_3)_2]$ to give complexes of the $S_4^{2-}$ ligand in good yield [equation (3)]; two examples [**(20)**

$$[PtCl_2(PR_3)_2] + S_8 + NH_3 \longrightarrow [PtS_4(PR_3)_2] + NH_4Cl + S_2N_2^{2-} \quad (3)$$

and **(21)**] were characterised fully (Tables 1 and 4) and the generality of the reaction established by $^{31}P$ n.m.r. spectroscopy. In the cases of $PR_3$ = $PMe_2Ph$ and $PMePh_2$ we also observed in the $^{31}P$ n.m.r. spectra small amounts (*ca.* 10%) of **(1)**. Equation (3) probably partially represents the reaction, however, $S_2N_2^{2-}$ has never been isolated and probably reacts rapidly to form other SN species. Several workers[1–3] have reported that solutions of sulphur in liquid ammonia contain a variety of species including polysulphide anions and sulphur–nitrogen anions in a complex series of equilibria. The utility of these solutions in the synthesis of metal complexes has not previously been reported. The observation of almost exclusively $S_4^{2-}$ complexes is consistent with current knowledge[2] about the constitution of $S_8$–$NH_3$ solutions providing we assume similar rates of reaction for polysulphide and sulphur–nitrogen anions with $[PtCl_2(PR_3)_2]$.

In view of the ease of formation of organometallic complexes containing $S_2N_2H^-$ ligands we have also studied the preparation of complexes containing the isoelectronic $S_3N^-$ ligand. Thus, reaction (4) of $[HgPh(S_7N)]$ or $[Hg(S_7N)_2]$ with

$$[(L-L')PdCl_2Pd(L-L')] + 2[HgPh(S_7N)] \longrightarrow 2[Pd(S_3N)(L-L')] + 2HgPhCl + S_8 \quad (4)$$

chloro-bridged palladium dimers gave $[Pd(S_3N)(L-L')]$, **(15)**—**(19)**, characterised by microanalyses (Table 1), n.m.r., mass (Table 2), and i.r. spectroscopy, although in the case of the latter technique many of the S–N bands are obscured by organic ligand modes.

Compounds **(4)**—**(14)** were characterised by several techniques. In the i.r. spectra all of the complexes show the expected vibrations due to the organic fragment together with bands due

**Table 2.** N.m.r. and mass spectral data for the new complexes

| | $^1$H N.m.r. | | *m/z* | | |
|---|---|---|---|---|---|
| Compound | δ(NH) | L–L′ protons | $M^+$ | $M^+ - NS$ | $M^+ - S_2N_2H$ |
| $S_2N_2H^-$ Complexes | | | | | |
| **(4)** | 8.62 | 2.28 (s, 3), 2.40 (s, 6), 2.55 (s, 3)<br>7.05(1), 7.15(1), 7.35(2), 7.80(1) | 436 | | 343 |
| **(5)** | 8.62 | 7.7 (m, 9) | 380 | 334 | 287 |
| **(6)** | 8.72 | 7.6 (m, 8) | 353 | 307 | 260 |
| **(7)** | 8.55 | 2.82(6), 3.91(3), 6.9 (m, 3), 7.3 (1) | 333 | 287 | |
| **(8)** | 8.10 | 4.98(2), 5.23(1), 7.2 (m, 9) | 393 | 347 | 300 |
| **(9)** | 9.24 | 7.5 (m, 5), 8.9 (dd, 1), 9.22 (d, 1) | 377 | 330 | 384 |
| **(10)** | 8.58 | 2.8(2), 7.4 (m, 9) | 367 | | |
| **(11)** | 9.24 | 7.7 (m, 3), 8.3 (m, 2), 8.6 (m, 1) | 343 | 297 | 250 |
| **(12)** | 8.70 | 2.8(2), 7.4 (m, 4), 8.1 (dd, 1), 8.8 (dd, 1) | | | |
| **(13)** | 8.42 | 3.4(6), 7.4 (m, 6) | 369 | | 276 |
| **(14)** | 8.95 | 2.52(3), 2.62(6), 7.37(1), 7.56(1) | 360 | | 267 |
| $S_3N^-$ Complexes | | | $M^+$ | $M^+ - NS$ | $M^+ - S_3N$ |
| **(15)** | | 5.12(2), 5.28(1), 7.35 (m, 9) | 410 | 364 | 300 |
| **(16)** | | 2.90(2), 7.4 (m, 4), 8.05 (dd, 1), 8.88 (dd, 1) | | | |
| **(17)** | | 7.3 (m, 4), 7.78(1), 7.83(2), 8.69 (d, 1) | 370 | 324 | 260 |
| **(18)** | | 2.2(3), 3.1(1), 7.4 (m, 4) | 350 | 314 | |
| **(19)** | | 7.4 (m, 7) | 359 | 313 | 249 |
| **(22)** | | | 360 | 314 | 250 |
| **(23)** | | | 350 | | 240 |
| **(24)** | | | 384 | 338 | |
| **(25)** | | | 377 | 331 | 267 |

**Table 3.** I.r. data (cm$^{-1}$) for $S_2N_2^{2-}$ and $S_2N_2H^-$ complexes

| Compound | ν(NH) | δ(NH) | ν(NS) | | | δ(NH), ν(PtN) | ν(MS), δ(NS) | |
|---|---|---|---|---|---|---|---|---|
| $[Pt(S_2N_2)(PMe_3)_2]$ | | | 1 046s | 679s | 605m | 459m | 367m | |
| $[Pt(S_2{}^{15}N_2)(PMe_3)_2]$ | | | 1 030m | 667m | 601m | 455m | 355m | |
| $[Pt(S_2N_2)(PMe_2Ph)_2]$ | | | 1 046s | 685(sh) | 613m | 435s | 362m | |
| $[Pt(S_2{}^{15}N_2)(PMe_2Ph)_2]$ | | | 1 027m | 672m | 604m | 432m | 354m | |
| $[Pd(S_2N_2)(dppe)]$ | | | 1 046s | 680s | 612w | 470m | 365m | 351(sh) |
| $[Pd(S_2{}^{15}N_2)(dppe)]$ | | | 1 022s | 667m | 605m | | 355w | 348(sh) |
| **(4)** | 3 195m, br | 1 099m | 1 043s | 895m | 689s | 606w | 380vw | 343m |
| **(5)** | 3 284m | 1 116m | 1 034m | 866m | 692s | 595w | | 332m |
| **(6)** | 3 140s | 1 105w | 1 038m | 878m | 701s | 615w | 384w | 337m |
| **(7)** | 3 295s | 1 146w | 1 033s | 878m | 691s | 575m | 332w | 341s |
| **(7)**[a] | 2 444 | 916 | 1 033 | 820 | 686 | 389 | 332 | 325 |
| **(7)**[b] | 3 287 | 1 146 | 1 014 | 858 | 676 | 503 | 330 | |
| **(7)**[c] | 2 441 | 914 | 1 011 | 809 | 671 | 387 | 326 | 321 |
| **(8)** | 3 293m | 1 154m | 1 037m | 881m | 705s | 612w | 364m | 334m |
| **(9)** | 3 136m, br | 1 133w | 1 037m | 882w | 711m | 618m | 360w | 332m |
| **(10)** | 3 104m | | 1 039s | 872m | 693w | 595w | | 334m |
| **(11)** | 3 146m, br | 1 130w | 1 042m | 897w | 696w | | | 336m |
| **(12)** | 3 171m | 1 113w | 1 036m | 874m | 689w | 619w | | 341m |
| **(13)** | 3 174m | 1 115w | 1 037s | 872w | 688(sh) | | 365w | 344m |
| **(14)** | 3 168m | 1 092m | 1 040m | 885m | 689m | 602m | 354w | 344m |
| **(14)**[a] | 2 369 | 806 | 1 030 | 838 | 687 | 398 | 351 | 338 |
| **(14)**[b] | 3 165 | 1 054 | 1 018 | 861 | 671 | 551 | 346 | 335 |
| **(14)**[c] | 2 340 | 1 017 | | | 669 | | 342 | 326 |

In the case of the phosphine complexes the degree of $^{15}N$ labelling is 70—75%; there are no NH vibrations and the low-frequency vibrations at *ca.* 440 cm$^{-1}$ are assigned as ν(PtN). For complexes **(7)** and **(14)** the degree of $^{15}N$ labelling is 55—60%. [a] Deuteriated. [b] $^{15}N$-Labelled. [c] $^{15}N$-Labelled and deuteriated.

**Table 4.** $^{31}P$ N.m.r. spectral data for $[PtS_4(PR_3)_2]$ complexes and other products of reaction of $[PtCl_2(PR_3)_2]$ and $S_8$–$NH_3(l)$

| | $[PtS_4(PR_3)_2]$ | | | $SPR_3$ | | Other products | |
|---|---|---|---|---|---|---|---|
| Phosphine | Yield (%) | δ | $^1J$(Pt–P)/Hz | Yield (%) | δ | Yield (%) | Compound |
| Platinum complexes | | | | | | | |
| $PPh_3$ | 40 | 16.3 | 2 964 | 55 | 43.3 | | |
| $PPh_2Me$ | 40 | −0.6 | 2 870 | 50 | 35.9 | 10 | $[Pt(S_2N_2)(PR_3)_2]$ |
| $PPhMe_2$ | 45 | −13.9 | 2 802 | 50 | 32.5 | 5 | $[Pt(S_2N_2)(PR_3)_2]$ |
| $PMe_3$ | 80 | −24.6 | 2 760 | 20 | 59.1 | | |
| $PEt_3$ | 95 | 12.2 | 2 835 | 5 | 54.9 | | |
| $PPr^n{}_3$ | 95 | 3.1 | 2 785 | 5 | 47.8 | | |
| $PBu^n{}_3$ | 90 | 4.2 | 2 792 | 10 | 48.9 | | |
| dppe | 95 | 48.9 | 2 809 | 5 | 46.8 | | |
| Palladium complexes | | | | | | | |
| dppe | 40 | 56.8 | — | 25 | 44.4 | | |

All chemical shifts are referred to 85% $H_3PO_4$. The complexes $[PtS_4(PPr^n{}_3)_2]$ and $[PtS_4(dppe)]$ were isolated; all other reactions were studied by $^{31}P$ n.m.r. spectroscopy only.

**Table 5.** Atom co-ordinates ( × $10^4$) with estimated standard deviations (e.s.d.s) in parentheses for complex (**14**)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd | 8 536(1) | 10 007(1) | 6 415(1) |
| N(1) | 8 008(4) | 10 943(7) | 5 279(3) |
| S(1) | 7 984(2) | 9 966(2) | 4 580(1) |
| N(2) | 8 384(5) | 8 406(8) | 4 885(4) |
| S(2) | 8 752(2) | 8 001(2) | 5 838(1) |
| C(1) | 9 055(4) | 9 053(8) | 7 469(4) |
| C(2) | 9 350(5) | 7 607(9) | 7 682(5) |
| C(3) | 9 649(5) | 7 108(10) | 8 438(5) |
| C(4) | 9 724(5) | 8 028(11) | 9 034(6) |
| C(5) | 9 453(5) | 9 497(11) | 8 859(5) |
| C(6) | 9 110(5) | 10 011(8) | 8 079(4) |
| C(7) | 8 751(4) | 11 480(8) | 7 848(4) |
| C(8) | 8 779(5) | 12 607(9) | 8 441(4) |
| N(3) | 8 418(4) | 11 725(7) | 7 098(3) |
| N(4) | 8 029(4) | 13 148(7) | 6 847(3) |
| C(9) | 8 479(5) | 13 992(8) | 6 499(4) |
| C(10) | 7 148(4) | 12 910(9) | 6 313(4) |
| Pd′ | 6 309(1) | 9 904(1) | 7 574(1) |
| N(1′) | 7 307(4) | 9 034(7) | 8 568(3) |
| S(1′) | 7 688(2) | 9 922(2) | 9 367(1) |
| N(2′) | 7 227(5) | 11 398(8) | 9 236(4) |
| S(2′) | 6 453(1) | 11 868(2) | 8 340(1) |
| C(1′) | 5 328(4) | 10 784(8) | 6 672(4) |
| C(2′) | 5 002(5) | 12 246(9) | 6 593(5) |
| C(3′) | 4 286(5) | 12 673(9) | 5 938(5) |
| C(4′) | 3 867(5) | 11 676(11) | 5 351(5) |
| C(5′) | 4 153(5) | 10 258(10) | 5 381(5) |
| C(6′) | 4 898(5) | 9 816(8) | 6 052(5) |
| C(7′) | 5 254(4) | 8 357(9) | 6 124(4) |
| C(8′) | 4 854(5) | 7 178(9) | 5 518(4) |
| N(3′) | 5 968(4) | 8 172(6) | 6 763(3) |
| N(4′) | 6 372(4) | 6 748(7) | 6 860(4) |
| C(9′) | 6 232(5) | 5 917(9) | 7 451(5) |
| C(10′) | 7 262(4) | 6 971(9) | 7 072(5) |

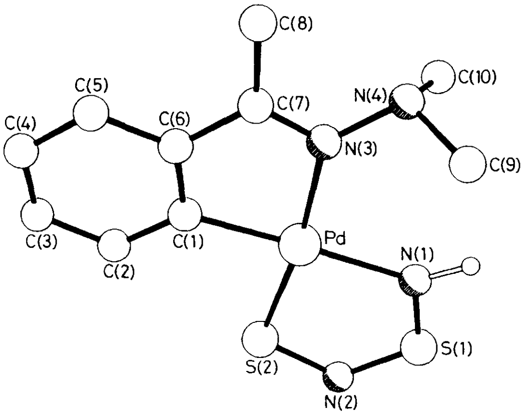

**Figure 1.** The *X*-ray crystal structure of complex (**14**)

to the $S_2N_2H^-$ ligand (Table 3). The most characteristic features are ν(NH) vibrations (3 300—3 100 cm$^{-1}$) and three ν(NS) vibrations at *ca.* 1 040, 880, and 695 cm$^{-1}$. At lower frequencies there are two bands at *ca.* 355 and 340 cm$^{-1}$ which may be assigned as ν(MS) and δ(NS) although it is not possible to discriminate these two vibrations. To aid our assignment, deuteriations and $^{15}$N-labelling experiments were carried out for complexes (7) and (**14**) and these data are included in Table 3. On deuterium labelling the ν(NH) vibration [3 295 and 3 168 cm$^{-1}$ (7) and (**14**) respectively] is lowered in frequency (2 444 and 2 369 cm$^{-1}$) as expected. The δ(NH) modes are similarly affected although the reduction in frequency is not as great as anticipated [1 146 to 916 cm$^{-1}$ for (7) and 1 092 to 806 cm$^{-1}$ for (**14**)]. However, ν($S^2$–$N^1$) is also lowered by *ca.* 60 cm$^{-1}$ on deuteriation indicating that these two vibrations are strongly coupled. The other two ν(NS) vibrations decrease slightly in frequency upon deuteriation (*ca.* 5 cm$^{-1}$) suggesting only slight coupling in this part of the ring. The higher-frequency band (*ca.* 1 040 cm$^{-1}$) is assigned as ν($S^2$–$N^2$) consistent with previous studies on bis-complexes.[28] $^{15}$N-Labelling experiments further confirm the above assignments for (7) and (**14**) as well as (**1**). For example, the ν(NS) modes all shift to lower frequencies by *ca.* 15—22 cm$^{-1}$ whilst the ν(NH) vibrations are lowered by about 5 cm$^{-1}$. The identification of the lower-frequency vibrations is not easy; the band at 332 cm$^{-1}$ of (7) is probably ν(PdS) since it is least affected by deuteriation and $^{15}$N labelling. The δ(NS) vibration at 341 cm$^{-1}$ is presumably similar in nature to the band seen in the spectrum of $S_4N_4$ at 340 cm$^{-1}$. The i.r. spectra of $^{15}$N-labelled examples of (**1**) are also given in Table 3; as expected those vibrations which involve the nitrogen atom are lowered in frequency.

N.m.r. and mass spectroscopic data are given in Table 2. The

**Table 6.** Selected bond lengths (Å) and angles (°) for complex (**14**)

| | | | |
|---|---|---|---|
| Pd–N(1) | 2.104(6) | Pd–S(2) | 2.237(3) |
| Pd–C(1) | 1.984(7) | Pd–N(3) | 2.092(6) |
| N(1)–S(1) | 1.579(7) | S(1)–N(2) | 1.566(7) |
| N(2)–S(2) | 1.665(8) | | |
| | | C(7)–N(3) | 1.292(9) |
| N(3)–N(4) | 1.435(8) | N(4)–C(9) | 1.459(12) |
| N(4)–C(10) | 1.444(8) | Pd′–N(1′) | 2.074(5) |
| Pd′–S(2′) | 2.234(2) | Pd′–C(1′) | 1.977(6) |
| Pd′–N(3′) | 2.085(6) | N(1′)–S(1′) | 1.575(6) |
| S(1′)–N(2′) | 1.524(8) | N(2′)–S(2′) | 1.690(6) |
| C(7′)–N(3′) | 1.311(8) | N(3′)–N(4′) | 1.442(9) |
| N(4′)–C(9′) | 1.462(13) | N(4′)–C(10′) | 1.456(10) |
| N(1)–Pd–S(2) | 85.3(2) | N(1)–Pd–C(1) | 177.5(3) |
| S(2)–Pd–C(1) | 92.2(2) | N(1)–Pd–N(3) | 102.4(2) |
| S(2)–Pd–N(3) | 172.2(2) | C(1)–Pd–N(3) | 80.0(3) |
| Pd–N(1)–S(1) | 118.0(3) | N(1)–S(1)–N(2) | 110.8(4) |
| S(1)–N(2)–S(2) | 119.3(5) | Pd–S(2)–N(2) | 106.6(3) |
| Pd–C(1)–C(2) | 129.9(6) | Pd–C(1)–C(6) | 113.0(5) |
| | | C(6)–C(7)–N(3) | 114.2(7) |
| C(8)–C(7)–N(3) | 123.6(6) | Pd–N(7)–C(7) | 115.6(5) |
| Pd–N(3)–N(4) | 128.7(4) | C(7)–N(3)–N(4) | 115.7(6) |
| N(3)–N(4)–C(9) | 109.8(6) | N(3)–N(4)–C(10) | 107.8(5) |
| C(9)–N(4)–C(10) | 113.6(6) | N(1′)–Pd′–S(2′) | 84.7(2) |
| N(1′)–Pd′–C(1′) | 176.3(3) | S(2′)–Pd′–C(1′) | 92.5(2) |
| N(1′)–Pd′–N(3′) | 103.5(2) | S(2′)–Pd′–N(3′) | 170.6(2) |
| C(1′)–Pd′–N(3′) | 79.1(3) | Pd′–N(1′)–S(1′) | 120.3(4) |
| N(1′)–S(1′)–N(2′) | 108.8(3) | S(1′)–N(2′)–S(2′) | 121.1(4) |
| Pd′–S(2′)–N(2′) | 105.0(3) | Pd′–C(1′)–C(2′) | 128.5(5) |
| Pd′–C(1′)–C(6′) | 114.5(5) | C(8′)–C(7′)–N(3′) | 123.2(7) |
| Pd′–N(3′)–C(7′) | 115.2(5) | Pd′–N(3′)–N(4′) | 127.7(4) |
| C(7′)–N(3′)–N(4′) | 116.7(6) | N(3′)–N(4′)–C(9′) | 108.1(7) |
| N(3′)–N(4′)–C(10′) | 109.0(6) | C(9′)–N(4′)–C(10′) | 113.3(6) |

**Table 7.** Atom co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for complex (**26**)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd | 0 | 0 | 0 |
| Cl | 1 820(1) | 1 229(1) | 1 141(1) |
| N(1) | 1 849(4) | −550(2) | −563(3) |
| N(2) | 1 700(5) | −446(3) | −2 071(4) |
| C(3) | 1 034(8) | −1 305(4) | −2 932(6) |
| C(4) | 612(8) | 337(5) | −2 835(6) |
| C(5) | 3 262(5) | −933(3) | 361(5) |
| C(6) | 4 658(7) | −1 230(5) | −88(6) |
| C(7) | 3 518(5) | −1 150(3) | 1 934(5) |
| C(8) | 4 982(5) | −848(4) | 3 135(5) |
| C(9) | 5 266(7) | −1 074(4) | 4 576(6) |
| C(10) | 4 153(9) | −1 637(4) | 4 849(6) |
| C(11) | 2 699(8) | −1 963(4) | 3 668(7) |
| C(12) | 2 377(6) | −1 722(4) | 2 193(6) |

**Table 8.** Selected bond lengths and angles for complex (**26**)

| | | | |
|---|---|---|---|
| Pd–Cl | 2.309(1) | Pd–N(1) | 2.046(4) |
| Pd–Cl′ | 2.309(1) | Pd–N(1′) | 2.046(4) |
| N(1)–N(2) | 1.433(6) | N(1)–C(5) | 1.288(5) |
| N(2)–C(3) | 1.468(7) | N(2)–C(4) | 1.452(8) |
| Cl–Pd–N(1) | 89.1(1) | Cl–Pd–Cl(a) | 180.0 |
| N(1)–Pd–Cl(a) | 90.9(1) | Cl–Pd–N(1a) | 90.9(1) |
| N(1)–Pd–N(1a) | 180.0 | Cl(a)–Pd–N(1a) | 89.1(1) |
| Pd–N(1)–N(2) | 119.7(2) | Pd–N(1)–C(5) | 125.6(3) |
| N(2)–N(1)–C(5) | 114.5(4) | N(1)–N(2)–C(3) | 110.3(4) |
| N(1)–N(2)–C(4) | 111.6(5) | C(3)–N(2)–C(4) | 110.4(4) |
| N(1)–C(5)–C(6) | 123.1(4) | N(1)–C(5)–C(7) | 119.8(4) |

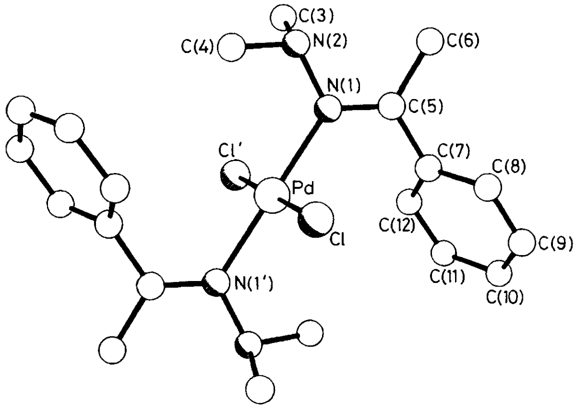

**Figure 2.** The *X*-ray crystal structure of complex (**26**)

n.m.r. spectra consist of the expected bands due to the organometallic ligand together with bands due to the NH proton on the $S_2N_2H^-$ ligand in the range 8.1—9.3. This compares with δ 9.5 for $[Ni(S_2N_2H)_2]$.[29] The mass spectra for (**4**)—(**14**) are characteristic and generally display $M^+$, $M - NS^+$, and $M - S_2N_2H^+$ ions with the parent ion being the most abundant.

As mentioned above we also observed minor amounts (5—10 mg) of $S_3N^-$ complexes (**22**)—(**25**) from some of the reactions in liquid ammonia and these were characterised by mass spectroscopy only (Table 2).

The crystal structures of complexes (**14**) and (**26**) have been determined. Atomic co-ordinates, bond lengths and angles are given in Tables 5—8 and the structures are shown in Figures 1 and 2. The structure of (**14**) is, with the exception of the hydrazone methyl groups, essentially planar. The degree of planarity differs for the two crystallographically independent molecules, being within 0.014 Å for N(4) in one molecule and 0.24 Å for C(8′) for the other. The central $PdSN_2C$ co-ordination is planar within 0.008 and 0.05 Å for palladium in each molecule respectively. In both molecules the hydrazine lone pair is directed towards C(8) and lies essentially within the co-ordination plane. The geometry of the $PdS_2N_2$ ring is similar to that reported[10] for $[Pt(S_2N_2H)(PR_3)_2]X$ and is consistent with the ligand being protonated, *i.e.* $S_2N_2H^-$. In the $PdC_3N$ metallacycle the metallated ligand has reduced angles at C(1) and N(3) in order to provide the 'bite' at palladium. The corresponding external angles at C(1) and N(3) are 129.9(6), 128.5(5) and 128.7(4), 127.7(4)° respectively. The C(7)–N(3) bond is, as expected, localised [1.292(9), 1.311(8) Å]. All four Pd–N bonds are within statistical significance the same, averaging 2.09 Å. Despite the planarity of the molecules they do not stack parallel to each other though there is a weak N(1)–H(1) ··· N(2′) hydrogen bond between the crystallographically independent molecules [N ··· N′ 3.02, H ··· N′ 2.11 Å; N–H ··· N′ 155°]. The absence of stacking despite both the planarity and the presence of an electron-rich $PdS_2N_2$ ring underlines the requirement for ionic structures[10] and it is possible that the deprotonated analogue will form a stacked structure. Work to this end is in progress.

The structure of complex (**26**) is as expected with a *trans* square-planar geometry (the palladium atom lying on a crystallographic centre of symmetry). The Pd–N bond is slightly shortened at 2.046(4) Å relative to that in (**14**) whilst the ligand is no longer planar with both the phenyl ring and the N(2) lone pair rotated significantly out of the N(1)–N(2)–C(5)–C(6) plane. The degree of bond ordering in the ligand is similar to that in (**14**) with a localised C(5)–N(1) double bond of 1.288(5) Å. There are no significant intermolecular packing interactions other than weak edge-to-face phenyl–phenyl electrostatic interactions.

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