The Preparation and Characterisation of (Disulphur dinitrido)bis(phosphine) Complexes, $[M(S_2N_2)(PR_3)_2]$ ($M = Pt$, $PR_3 = PMe_3, PMe_2Ph, PMePh_2, PPh_3, PEt_3, PPr^n_3, PBu^n_3$, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$; $M = Pd$, $PR_3 = \frac{1}{2}Ph_2PCH_2CH_2PPh_2$). *X*-Ray Crystal Structure of $[Pt(S_2N_2)(PMe_3)_2]$†

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Reaction of $Na(S_3N_3)$ with $[MCl_2(PR_3)_2]$ ($M = Pt$, $PR_3 = PMe_3, PMe_2Ph, PMePh_2, PPh_3, PEt_3, PPr^n_3, PBu^n_3$, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$; $M = Pd$, $PR_3 = \frac{1}{2}Ph_2PCH_2CH_2PPh_2$) gives complexes of the type $[M(S_2N_2)(PR_3)_2]$ in high yield (quantitatively by ^{31}P n.m.r. > 60% isolated). The identity of the complexes was established by ^{31}P n.m.r., i.r., microanalysis and, in the case of $[Pt(S_2N_2)(PMe_3)_2]$, by *X*-ray crystallography.

The preparation of compounds containing sulphur–nitrogen ligands is currently an area of active interest[1–5] and their potential technological usefulness has previously been highlighted.[1,3] Complexes containing the $S_2N_2H^-$ ligand have been known for a number of years[4–6] but it is only quite recently that the existence of the disulphur dinitrido ligand, $S_2N_2^{2-}$, was established. Two routes to it have been reported. First,[7] deprotonation of $Ni(S_2N_2H)_2$ provides a rational, high-yield, synthesis of $K_2[Ni(S_2N_2)_2]$ and $[NR'_4][Ni(S_2N_2)(S_2N_2H)]$ ($R' = Me, Et$, or Bu^n). Alternatively, reactions of S_4N_4 have been employed; reaction with $Pb(NO_3)_2$[8] gives $Pb(S_2N_2)$, whilst $[Co(cp)(CO)_2]$ ($cp = \eta\text{-}C_5H_5$) and $[Ir(dppen)_2(CO)][BPh_4]$ [dppen = *cis*-1,2-bis(diphenylphosphino)ethene] yield $[Co(cp)(S_2N_2)]$ and $[Ir(dppen)_2(S_2N_2)][BPh_4]$ respectively.[9,10] We have recently found[3] that treatment of $[Pt(PPh_3)_3]$ with S_4N_4 gives $[Pt(S_2N_2)(PPh_3)_2]$ although use of $S_4N_4H_4$ (cyclotetra-azathiane) gives better yields since the reaction involving S_4N_4 is complicated with the products including a binuclear compound.[2,11]

In view of the relative dearth of $S_2N_2^{2-}$ complexes (in particular in compounds which also contain phosphine ligands) we have been investigating the synthesis of complexes containing this ligand. The deprotonation of $S_2N_2H^-$ cannot provide a general route since there are only a limited number of complexes containing this ligand. Reactions of S_4N_4 with metal centres are poorly understood and although they provide the majority of the known $S_2N_2^{2-}$ complexes they can be unpredictable, *e.g.* $[Ti(cp)_2(CO)_2]$ gives $[Ti(cp)_2(S_3N_4)]$.[12] We have investigated salt elimination reactions of *cis*-$[MCl_2(PR_3)_2]$ ($M = Pt$, $PR_3 = PMe_3, PMe_2Ph, PMePh_2, PPh_3, PEt_3, PPr^n_3, PBu^n_3$, or $\frac{1}{2}$dppe; $M = Pd$, $PR_3 = \frac{1}{2}$dppe) [dppe = 1,2-bis(diphenylphosphino)ethane] with $Na(S_3N_3)$ and report here that this reaction provides a general, high-yield route to complexes of the type $[M(S_2N_2)(PR_3)_2]$. The *X*-ray structure of $[Pt(S_2N_2)(PMe_3)_2]$ together with the spectroscopic properties (^{31}P n.m.r., i.r.) of the other complexes are reported.

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 and stored over 4A molecular sieves; diethyl ether, tetrahydrofuran (thf), toluene, and n-hexane were distilled from sodium–benzophenone; ethanol was dried and distilled from magnesium–iodine. $^{31}P\text{-}\{^1H\}$ N.m.r. spectra were obtained using a JEOL FX90Q spectrometer operating at 36.21 MHz and are referred to external 85% H_3PO_4. I.r. spectra were recorded as pressed KBr discs using a Perkin-Elmer 683 instrument. Elemental analyses were performed by the microanalytical service at Imperial College.

The compounds $Na(S_3N_3)$, $[PtCl_2(dppe)]$, $[PdCl_2(dppe)]$, and *cis*-$[PtCl_2(PPh_3)_2]$ were prepared by standard methods;[12–15] *cis*-$[PtCl_2(PR_3)_2]$ ($PR_3 = PMe_3, PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph$, or $PMePh_2$) were prepared from $[PtCl_2(cod)]$ [cod = cyclo-octa-1,5-diene][16] and a stoicheiometric quantity of the phosphine and were recrystallised from CH_2Cl_2–Et_2O.

Preparation of Disulphur Dinitrido Complexes.—**CAUTION:** $Na(S_3N_3)$ may explode when subjected to shock or rapid heating. A typical reaction is as follows. To $Na(S_3N_3)$ (0.2 mmol) in ethanol (10 cm^3) was added *cis*-$[MCl_2(PR_3)_2]$ (0.1 mmol) in dichloromethane (10 cm^3). The solution immediately darkened and then gradually lightened to pale orange (*ca.* 5—15 min). After this time the volume of the solution was reduced to *ca.* 1 cm^3 and a yellow solid precipitated by the addition of water (50 cm^3). After drying *in vacuo* this solid was washed with cyclohexane (20 cm^3) to remove S_4N_4 and then extracted into toluene (10 cm^3). After filtration the toluene solution was reduced to dryness *in vacuo* and the final product obtained by recrystallisation from dichloromethane–n-hexane.

The above procedure gave $[Pt(S_2N_2)(PR_3)_2]$ ($PR_3 = PMePh_2, PMe_2Ph, PEt_3$, or PPr^n_3) and $[Pd(S_2N_2)(dppe)]$. Good quality samples of $[Pt(S_2N_2)(dppe)]$ and $[Pt(S_2N_2)(PMe_3)_2]$ were obtained as above but without the toluene extraction step. Attempts to isolate $[Pt(S_2N_2)(PBu^n_3)_2]$ gave only oils. The triphenylphosphine complex was not isolated from the above reaction since we have previously reported it.[3] To date we have been unable to isolate a pure sample of $[Ni(S_2N_2)(dppe)]$.

The purity of the products could be assessed using t.l.c.; with silica plates a suitable eluant is methanol–dichloromethane (1:99). Isolated yields were 60—70%.

Crystals suitable for *X*-ray analysis were obtained by slow diffusion of n-hexane into a chloroform solution of the complex.

Crystal Data.—$C_6H_{18}N_2P_2PtS_2$, $M = 439.39$, monoclinic, $a = 8.962(2)$, $b = 11.667(8)$, $c = 7.046(2)$ Å, $\beta = 110.79(2)°$,

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† [Di(azathienyl)-S^1,N^4]bis(trimethylphosphine)platinum(II).

Supplementary data available (No. SUP 56618, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Selected bond lengths and angles in $[Pt(S_2N_2)(PMe_3)_2]$

Bond lengths (Å)

S(1)–Pt	2.268(6)	P(1)–Pt	2.268(5)
P(2)–Pt	2.261(6)	N(1)–Pt	2.083(14)
N(2)–S(1)	1.668(17)	N(1)–S(2)	1.492(13)
N(2)–S(2)	1.576(16)	C(1)–P(1)	1.828(18)
C(2)–P(1)	1.766(21)	C(3)–P(1)	1.837(24)
C(4)–P(2)	1.796(18)	C(5)–P(2)	1.778(18)
C(6)–P(2)	1.830(17)		

Bond angles (°)

P(1)–Pt–S(1)	170.6(3)	P(2)–Pt–S(1)	91.5(3)
P(2)–Pt–P(1)	98.0(3)	N(1)–Pt–S(1)	86.4(5)
N(1)–Pt–P(1)	84.2(5)	N(1)–Pt–P(2)	175.6(4)
N(2)–S(1)–Pt	105.5(6)	N(2)–S(2)–N(1)	117.7(8)
C(1)–P(1)–Pt	112.7(7)	C(2)–P(1)–Pt	122.6(7)
C(2)–P(1)–C(1)	100.4(10)	C(3)–P(1)–Pt	110.6(9)
C(3)–P(1)–C(1)	102.4(9)	C(3)–P(1)–C(2)	106.1(12)
C(4)–P(2)–Pt	112.9(7)	C(5)–P(2)–Pt	116.2(7)
C(5)–P(2)–C(4)	100.0(10)	C(6)–P(2)–Pt	117.8(8)
C(6)–P(2)–C(4)	106.1(10)	C(6)–P(2)–C(5)	101.8(9)
S(2)–N(1)–Pt	115.3(8)	S(2)–N(2)–S(1)	115.0(8)

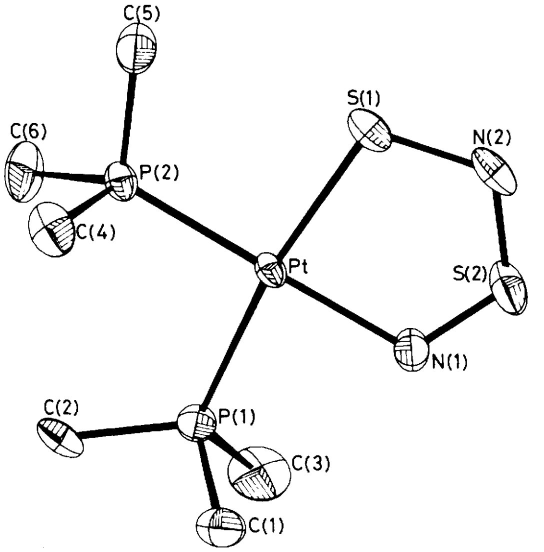

Figure 1. The *X*-ray crystal structure of $[Pt(S_2N_2)(PMe_3)_2]$ (hydrogen atoms omitted)

Table 2. Fractional atomic co-ordinates (× 10^4) for $[Pt(S_2N_2)(PMe_3)_2]$

Atom	*x*	*y*	*z*
Pt	2 749(1)	0	2 130(1)
S(1)	5 146(4)	214(7)	1 761(5)
S(2)	3 114(6)	1 701(4)	−939(7)
P(1)	224(4)	36(10)	2 148(5)
P(2)	3 700(4)	−1 443(4)	4 379(5)
N(1)	1 912(14)	1 251(11)	−108(18)
N(2)	4 854(15)	1 191(12)	−64(19)
C(1)	−1 254(17)	−445(14)	−255(25)
C(2)	−368(19)	−772(20)	3 880(31)
C(3)	−408(23)	1 517(19)	2 335(29)
C(4)	2 819(20)	−2 805(14)	3 418(26)
C(5)	5 753(20)	−1 785(16)	5 010(26)
C(6)	3 548(22)	−1 290(18)	6 889(21)

Table 3. Microanalytical data (%)*

Compound	C	H	N
$[Pt(S_2N_2)(PMePh_2)_2]$	43.95 (45.40)	4.05 (3.80)	3.80 (4.05)
$[Pt(S_2N_2)(PMe_2Ph)_2]$	33.65 (34.10)	3.85 (3.95)	4.55 (4.95)
$[Pt(S_2N_2)(PMe_3)_2]$	16.40 (16.40)	4.05 (4.15)	6.50 (6.40)
$[Pt(S_2N_2)(PEt_3)_2]$	27.65 (27.55)	5.70 (5.80)	5.25 (5.35)
$[Pt(S_2N_2)(PPr^n{}_3)_2]$	36.00 (35.60)	6.85 (6.95)	4.50 (4.60)
$[Pt(S_2N_2)(dppe)]$	45.00 (45.55)	3.45 (3.55)	3.85 (4.10)
$[Pd(S_2N_2)(dppe)]\cdot CH_2Cl_2$	47.95 (47.55)	4.35 (3.85)	4.10 (4.10)

* Calculated values are given in parentheses.

$U = 689$ Å^3, space group $P2_1$, $Z = 2$, $D_c = 2.12$ g cm^{-3}, $F(000) = 416$, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 102.6 cm^{-1}.

Data Collection.—Unit-cell parameters were determined and intensity data collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω—2θ scan procedure[18] to give 1 306 reflections ($3 \leqslant 2\theta \leqslant 50°$). On averaging ($R_{\text{av.}} = 0.015$) these yielded 1 201 unique reflections. A semi-empirical absorption correction[19] was applied to the data set; maximum and minimum transmission was 99.7 and 71.9% respectively.

Structure Solution and Refinement.—The structure was solved *via* the heavy-atom method. After isotropic refinement of all non-hydrogen atoms the DIFABS method of absorption correction[20] was applied. Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms. The final cycle of refinement included all the methyl hydrogen atoms in the calculated positions (C–H 0.96 Å, $U = 0.10$ Å^2). The final values of R and R' were 0.0253 and 0.0247 respectively for the 141 variables and 1 142 data for which $F^2 > 3\sigma(F^2)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, w, being defined as $1/[\sigma^2(F) + 0.000\,001F^2]$. All computations were made using SHELX 76[21] on a DEC VAX-11/750 computer. Figure 1 was drawn using SNOOPI.[22]

Selected final bond lengths and angles are given in Table 1 and fractional atomic co-ordinates, excluding hydrogens, in Table 2.

Results and Discussion

Reaction of two equivalents of $Na(S_3N_3)$ with *cis*-$[MCl_2(PR_3)_2]$ (M = Pd or Pt) proceeds cleanly to give disulphur dinitrido complexes (Tables 3—5) $[M(S_2N_2)(PR_3)_2]$. The reaction may be monitored by ^{31}P-$\{^1H\}$ n.m.r. and Figure 2 shows a typical spectrum from a crude reaction mixture (in this case $PR_3 = PMe_2Ph$). Only the final product is observed, indicating a very clean reaction; it is noticeable that no SPR_3 or phosphorus–nitrogen compounds are present. Apart from the disulphur dinitrido complex the reaction also gives S_4N_4: this was detected by t.l.c. and, after isolation from the cyclohexane washings in the work-up, by i.r. spectroscopy. This latter procedure also allowed us to quantify the S_4N_4 production and leads to the overall reaction shown in equation (1). It is difficult

$$[MCl_2(PR_3)_2] + 2Na(S_3N_3) \longrightarrow [M(S_2N_2)(PR_3)_2] + S_4N_4 + 2\,NaCl \quad (1)$$

to speculate about the mechanism of the reaction and in this regard it should be noted that S_4N_4 and $S_4N_4H_4$ are also sources of the $S_2N_2{}^{2-}$ ligand when reacted with zerovalent platinum complexes.[3] Since ethanolic solutions of $S_3N_3{}^-$ are known to give S_4N_4 on standing[23] we tested the reactivity of S_4N_4 with $[MCl_2(PR_3)_2]$ complexes. Under the conditions employed here no reaction was seen. Indeed it seems more likely

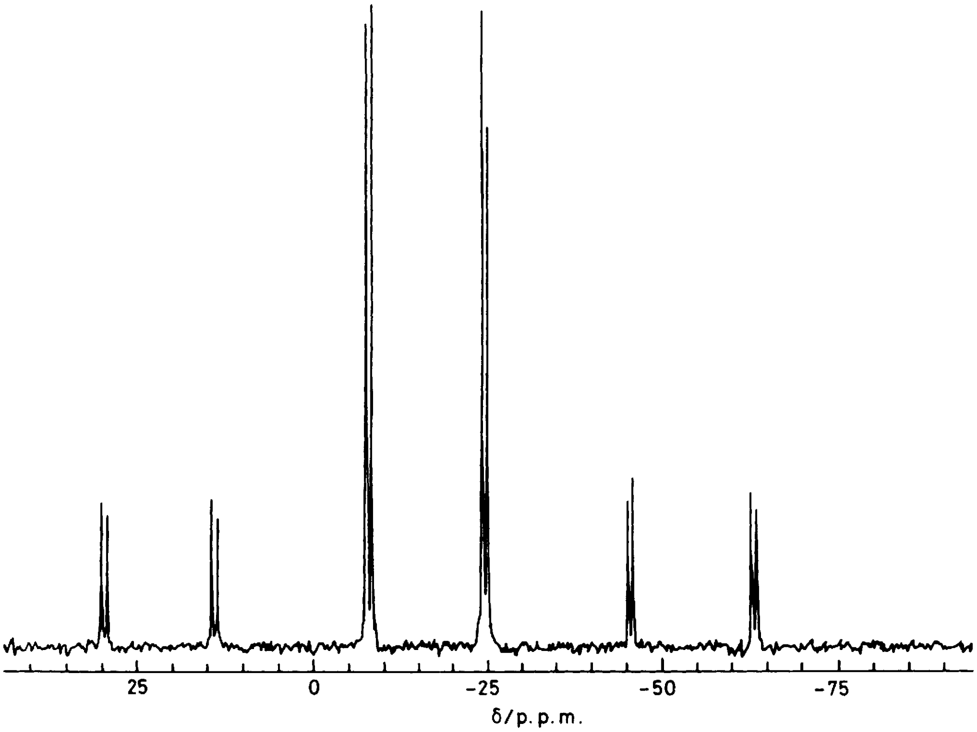

Figure 2. ^{31}P-{^{1}H} N.m.r. spectrum ($CDCl_3$) from the crude reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ and $Na(S_3N_3)$ (1:2)

Table 4. Infrared absorptions (cm^{-1}) for the $S_2N_2^{2-}$ ligand

Compound	ν_{SN}		δ_{SN}	ν_{PtN}	δ_{SN}	ν_{PtS}
$[Pt(S_2N_2)(PPh_3)_2]$	1 045s	*	610m	445m	360m	352 (sh)
$[Pt(S_2N_2)(PMePh_2)_2]$	1 046m	*	613w	436m	364w	345w
$[Pt(S_2N_2)(PMe_2Ph)_2]$	1 046s	*	613m	435s	362m	350 (sh)
$[Pt(S_2N_2)(PMe_3)_2]$	1 046s	679s	605m	459m	367m	
$[Pt(S_2N_2)(PEt_3)_2]$	1 054m	682s	610w	466m	360w	345w
$[Pt(S_2N_2)(PPr^n_3)_2]$	1 050s	683s	610w	469m	364w	350w
$[Pt(S_2N_2)(dppe)]$	1 046s	680s	612w	470m	365m	351 (sh)
$[Pd(S_2N_2)(dppe)]$	1 064s	664m	600w	439m	344m	340 (sh)

* Band obscured by phosphine absorption.

that the reverse situation applies, *i.e.* $S_4N_4H_4$ is known to yield $S_3N_3^-$ on deprotonation thus it may be that the trisulphur trinitride anion is an intermediate in the formation of the known $S_2N_2^{2-}$ and $S_2N_2H^-$ complexes. Interestingly, we have preliminary ^{31}P n.m.r. evidence which indicates that base deprotonation of $S_4N_4H_4$ does provide a route to the complexes reported here. The rate of the reactions reported here did not allow us to use n.m.r. to probe for intermediates whilst the lack of side reactions may imply a concerted rather than an equilibrium process. If this were the case then a bis complex, $[M(S_3N_3)_2(PR_3)_2]$, could be initially formed and subsequently disproportionate to the disulphur dinitrido complex and tetrasulphur tetranitride. Alternatively, the slow formation of S_4N_4 from $S_3N_3^-$ which we have already mentioned may involve an equilibrium (2) that is pushed to the right as the $S_2N_2^{2-}$ that is produced reacts with the $[MCl_2(PR_3)_3]$ complexes.

$$2\,S_3N_3^- \rightleftharpoons S_4N_4 + S_2N_2^{2-} \qquad (2)$$

Characterisation of the complexes was accomplished by microanalysis (Table 3), i.r. (Table 4), and ^{31}P n.m.r. (Table 5) and the features of interest are as follows. In the i.r. spectra there are strong characteristic absorptions at around 1 050, 680, and 360 cm^{-1}. These can be assigned as ν_{SN} and δ_{SN} by analogy with the spectra of $[M(S_2N_2H)_2]$ complexes.[24] The weaker ν_{MN} and ν_{MS} vibrations may be assigned similarly. Unlike the $[M(S_2N_2H)_2]$ complexes no ν_{SN} band is observed around 850 cm^{-1}, however a weak band is observed at *ca.* 615 cm^{-1}. We have tentatively assigned this low-frequency band as δ_{SN}. The absence of the band at 850 cm^{-1} may be due to the lack of any intensity enhancement of this SN stretch by mixing with δ_{NH} which is known to occur in the $[M(S_2N_2H)_2]$ complexes. The intensity of this band might also be affected on going from the bis to the heteroleptic complexes described here since coupling between the sulphur–nitrogen ligands obviously cannot occur in the latter compounds.

Table 5. Phosphorus-31 n.m.r. data[a]

Compound	δ_A	δ_X	$^{1}J_A$	$^{1}J_X$	^{2}J	$R = J_A/J_X$
$[Pt(S_2N_2)(PPh_3)_2]$	11.4	23.6	2 994	2 827	22	1.06
$[Pt(S_2N_2)(PMePh_2)_2]$	−9.7	8.9	2 886	2 781	24	1.04
$[Pt(S_2N_2)(PMe_2Ph)_2]$	−24.6	−7.9	2 799	2 731	24	1.025
$[Pt(S_2N_2)(PMe_3)_2]$	−38.0	−17.0	2 748	2 681	27	1.025
$[Pt(S_2N_2)(PEt_3)_2]$	0.7	16.4	2 828	2 679	22	1.06
$[Pt(S_2N_2)(PPr^n_3)_2]$	−8.2	7.8	2 836	2 665	22	1.06
$[Pt(S_2N_2)(PBu^n_3)_2]$[b]	−7.7	9.0	2 854	2 672	22	1.07
$[Pt(S_2N_2)(dppe)]$	41.1	43.7	2 784	2 756	12	1.01
$[Pd(S_2N_2)(dppe)]$	48.8	55.4			29	
$[Ni(S_2N_2)(dppe)]$[b]	47.6	55.4			51	

[a] $CDCl_3$ solutions; reference 85% H_3PO_4. [b] Compound not isolated; formulation is tentative.

The ^{31}P n.m.r. spectra (Table 5) consist of AX doublets with ^{2}J couplings that are appropriate to M^{II} complexes. In the case of the platinum complexes, satellites due to ^{1}J couplings with

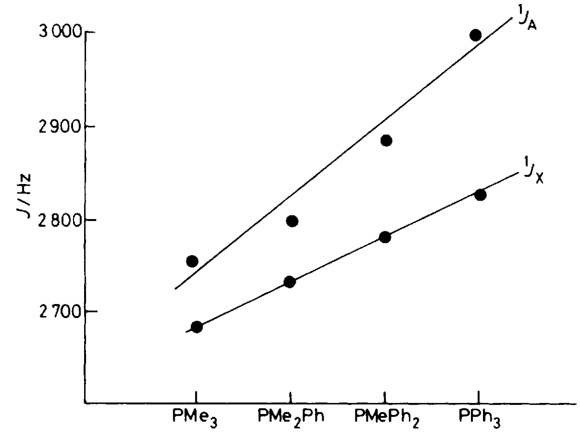

Figure 3. Variation of ^{31}P–^{195}Pt coupling constant in [Pt(S$_2$N$_2$)(PR$_3$)$_2$] complexes

^{195}Pt are also apparent (Figure 2). The two ^1J values, which are in the usual range for Pt^{II}, are quite different with the larger value being assigned to the phosphorus *trans* to nitrogen on the basis of the Pt–P bond distances[3] in [Pt(S$_2$N$_2$)(PPh$_3$)$_2$], the shorter distance being associated with the larger coupling constant. In the trimethylphosphine complex (see below) the Pt–P bond distances are not crystallographically distinguishable and this is in accord with the two ^1J values being very similar. On replacing methyl by phenyl groups in the phosphine there is an increase in the magnitude of ^1J (Figure 3), as has been noted for other complexes.[25,26] It is surprising to note that the change in ^1J for the phosphorus *trans* to sulphur appears to be closer to linear than for the phosphorus *trans* to nitrogen and there is no ready explanation for this effect.

The assignment of the individual phosphorus resonances is further supported by comparison of chemical shifts with similar compounds. Thus, *cis*-[Pt(PPh$_3$)$_2$(SSCH$_2$S)] and *cis*-[Pt(PPh$_3$)$_2${S$_2$(CH$_2$)$_3$}] have δ 21.5 and 23.6 p.p.m. respectively,[27] which compares well with δ 23.6 p.p.m. for the phosphorus *trans* to sulphur in [Pt(S$_2$N$_2$)(PPh$_3$)$_2$], whilst the resonance for phosphorus *trans* to nitrogen in this latter complex (δ 11.4 p.p.m.) is very similar to that observed in [Pt(N=S=NSiMe$_3$)$_2$(PPh$_3$)$_2$] (δ 11.8 p.p.m.). We have not yet been able to isolate a pure sample of the nickel complex but comparison of the reported[27] chemical shift (δ 55.6 p.p.m.) in [Ni(dppe){S$_2$(CH$_2$)$_3$}] with the shift observed here (δ 55.4 p.p.m.) supports our formulation.

The chemical shifts of the complexes show a fairly constant co-ordination shift compared to the free phosphine and the starting chloro complexes. Thus, δ_A (P *trans* to nitrogen) and δ_X (P *trans* to sulphur) are shifted by *ca.* +21 and *ca.* +38 p.p.m. relative to the free phosphine and by *ca.* −8 and *ca.* +7 p.p.m. relative to the *cis*-[PtCl$_2$(PR$_3$)$_2$] complexes respectively.

The crystal structure of [Pt(S$_2$N$_2$)(PMe$_3$)$_2$] (Figure 1, Tables 1 and 2) reveals the geometry expected from the spectroscopic data. The Pt–P distances are crystallographically indistinguishable; in comparison to [Pt(S$_2$N$_2$)(PPh$_3$)$_2$] the Pt–P distance *trans* to sulphur is shorter for the trimethylphosphine complex [2.317(4) *versus* 2.268(5) Å], with the other Pt–P distances being similar to each other [PPh$_3$, 2.263(4); PMe$_3$, 2.261(6) Å]. The sulphur–nitrogen ligand contains one short, one medium, and one long S–N distances, as is the case in previously reported examples.[2,3,7–10]

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