Preparation and Properties of $[M(S_2N_2H)Cl(L)]$ (M = Pt, L = PMe_2Ph or C_2H_4; M = Pd, L = PMe_2Ph), $[Pt(S_3N)Cl(PMe_2Ph)]$, and Corresponding ^{15}N-Enriched Complexes†

Jennifer M. Jolliffe, Paul F. Kelly, and J. Derek Woollins *
Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY

Reaction of $[PPh_4][MCl_3(PMe_2Ph)]$ (M = Pt or Pd) with $[Sn(S_2N_2)Me_2]_2$ leads to $[M(S_2N_2H)Cl(PMe_2Ph)]$; similarly $K[PtCl_3(C_2H_4)]$ reacts to give $[Pt(S_2N_2H)Cl(C_2H_4)]$. The complex $[Pt(S_2N_2H)Cl(PMe_2Ph)]$ (**1a**) is also formed in the reaction of S_4N_4 with $[PtCl_2(PMe_2Ph)_2]$ at 160 °C, together with $[Pt(S_3N)Cl(PMe_2Ph)]$ (**2**); $S_4{}^{15}N_4$ reacts to give ^{15}N-enriched (**1a**) and (**2**), the ^{31}P n.m.r. spectra of which show the presence of both ^2J- and ^4J-(^{15}N–^{31}P) couplings.

In a recent paper we reported the reaction of $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ with bromine which results in the platinum(IV) dibromo species $[Pt(S_2N_2H)Br_2(PMe_2Ph)_2]BF_4$.[1] The latter decomposes *via* reductive elimination to give $[Pt(S_2N_2H)Br(PMe_2Ph)]$, isolated in yields of $\leqslant 20\%$. Although the reaction can be extended to include complexes of trialkylphosphines, such as trimethylphosphine *etc*., the low yield means that the reaction is not an efficient route to the platinum(II) complexes. The fact that the complexes are potentially useful in the preparation of new species *via* reaction at the halogen only serves to highlight the inefficiency of the above method.

Here we describe the preparation of the chloro analogues $[M(S_2N_2H)Cl(PMe_2Ph)]$ [M = Pt(**1a**) or Pd(**1b**)] by reaction of $[MCl_3(PMe_2Ph)]^-$ with $[Sn(S_2N_2)Me_2]_2$, which has the great advantage of being both quick and efficient, with the product being isolated in yields $\geqslant 60\%$. Furthermore, we have evidence to suggest that the equivalent reaction with Zeise's salt produces an analogous ethylene complex.

We have also investigated the reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with S_4N_4 at 160 °C; this leads to a mixture of complexes including (**1a**) together with $[Pt(S_3N)Cl(PMe_2Ph)]$ (**2**), which can be separated by chromatography. This reaction enables ^{15}N-labelled samples of these complexes to be prepared, the ^{31}P n.m.r. spectra of which reveal the presence of ^{15}N–^{31}P couplings.

Experimental

General reaction conditions and procedures were as described previously.[1] The complexes $[\{MCl_2(PMe_2Ph)\}_2]$ (M = Pt or Pd) were prepared by reaction of $[MCl_2(PMe_2Ph)_2]$ with MCl_2 in xylene at *ca*. 160 °C;[2] $[PPh_4][MCl_3(PMe_2Ph)]$ was prepared *in situ* by reaction of the dimers with 2 equivalents of $[PPh_4]Cl$.[3]

Synthesis of $[M(S_2N_2H)Cl(PMe_2Ph)]$.—A mixture of $[\{PtCl_2(PMe_2Ph)\}_2]$ (0.103 g, 0.13 mmol) and $[PPh_4]Cl$ (0.096 g, 0.26 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and, after stirring for 15 min, was treated with solid $[Sn(S_2N_2)Me_2]_2$ (0.063 g, 0.13 mmol). The resulting solution was stirred for 30 min during which time the colour darkened from light yellow to orange. The volume of the solution was then reduced to *ca*. 2 cm^3 *in vacuo* and the resulting sample placed on a Bio-bead gel-permeation column (2 × 25 cm) and eluted with CH_2Cl_2. Two orange bands separated, the slower moving of which was collected and reduced in volume to 5 cm^3 and treated with hexane (30 cm^3). Evaporation of the CH_2Cl_2 *in vacuo* yielded $[Pt(S_2N_2H)Cl(PMe_2Ph)]$ (**1a**) as well formed yellow microcrystals (81 mg, 68%) (Found: C, 21.9; H, 2.4; N, 5.8. $C_8H_{12}ClN_2PPtS_2$ requires C, 20.8; H, 2.4; N, 6.1%). The ^{31}P n.m.r. spectrum shows a singlet at $\delta = -21.0$ p.p.m., $^1J(^{195}Pt$–$^{31}P)$ 3 408 Hz ($CDCl_3$); *m/z* 462 (M^+), 425 $\{[Pt(S_2N_2)(PMe_2Ph)]^+\}$, and 379 $\{[Pt(SN)(PMe_2Ph)]^+\}$.

The complex $[Pd(S_2N_2H)Cl(PMe_2Ph)]$ (**1b**) was prepared in an analogous fashion by reaction of $[Sn(S_2N_2)Me_2]_2$ (50 mg, 0.1 mmol) with a mixture of $[PPh_4]Cl$ (77 mg, 0.21 mmol) and $[\{PdCl_2(PMe_2Ph)\}_2]$ (65 mg, 0.1 mmol), followed by purification on a Bio-beads column. The final product was isolated in similar yield to (**1a**), although it was less pure due to poorer separation on the column; an analytically pure crystalline sample was prepared by slow diffusion of hexane into a solution of this product (Found: C, 25.6; H, 3.1; N, 7.2. $C_8H_{12}ClN_2PPdS_2$ requires C, 25.8; H, 3.2; N, 7.5%). The ^{31}P n.m.r. spectrum shows a singlet at $\delta = 2.3$ p.p.m. ($CDCl_3$); *m/z* 374 (M^+), 336 $\{[Pd(S_2N_2)(PMe_2Ph)]^+\}$, and 290 $\{[Pd(SN)(PMe_2Ph)]^+\}$.

Reaction of $[PtCl_2(PMe_2Ph)_2]$ *with* S_4N_4.—A mixture of $[PtCl_2(PMe_2Ph)_2]$ (0.2 g, 0.37 mmol) and S_4N_4 (140 mg, 0.76 mmol) was suspended in xylene (15 cm^3) and heated to 150 °C, with vigorous stirring, by means of a pre-heated silicone oil-bath. The mixture gradually darkened in colour; after 5 min it was visibly red, after 10 min (with the temperature now at 160 °C) it was a dark red colour with only a small amount of the platinum starting material still undissolved. After 20 min at a maximum temperature of 170 °C the mixture consisted of a dark purple solution with an oily precipitate. At this point heating was stopped and the xylene removed *in vacuo*. The residue was dissolved in a small volume of CH_2Cl_2 and placed on a Bio-beads gel-permeation column. Elution with CH_2Cl_2 revealed a dark red band in between two fainter bands, a faster moving green band and a band consisting of two poorly separated green and orange fractions. The main red band was collected, concentrated, then placed on a silica preparative thin-layer chromatography (p.t.l.c.) plate and eluted with CH_2Cl_2. This gave rise to two intensely coloured bands, yellow (R_f *ca*. 0.4) and purple (R_f *ca*. 0.8) in colour. Both were collected and washed from the silica with CH_2Cl_2–MeOH. The yellow complex was shown to be (**1a**) by ^{31}P n.m.r. spectroscopy; the purple species was recrystallised from boiling light petroleum (b.p. 60—80 °C) giving well formed purple-red needles. The ^{31}P n.m.r. spectrum of this complex [$\delta = -11.1$ p.p.m., ^1J-(^{195}Pt–^{31}P) 3 055 Hz] was identical to that of $[Pt(S_3N)Cl-$

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† *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

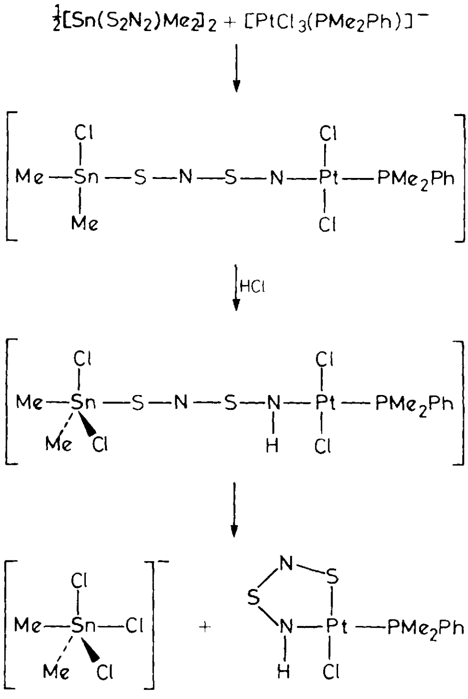


Figure 1. Proposed mechanism of the reaction between $[Sn(S_2N_2)Me_2]_2$ and $[PtCl_3(PMe_2Ph)]^-$

$(PMe_2Ph)]$ {previously prepared from $[PtCl_2(PMe_2Ph)_2]$ and $Hg(S_7N)Ph$} and this was confirmed by microanalysis (Found: C, 20.4; H, 1.8; N, 3.0. $C_8H_{11}ClNPPtS_3$ requires C, 20.1; H, 2.3; N, 2.9%) and mass spectroscopy (actually performed upon a ^{15}N-labelled sample see Discussion); *m/z* 480 (M^+), 397 {$[PtS_2(PMe_2Ph)]^+$}. Yields: (**1a**) 22 (13), (**2**) 15 mg (9%).

Results and Discussion

The preparation of complexes of the type $[Pt(S_2N_2)(PR_3)_2]$, from *cis*-$[PtCl_2(PR_3)_2]$, can be achieved by a number of methods,[4,5] the most effective of which is reaction with $S_4N_4H_4$ in the presence of the base dbu (1,8-diazabicyclo[5.4.0]undec-7-ene).[6] However, although the complexes are readily prepared, further reactions are somewhat limited. Protonation, to give complexes of $S_2N_2H^-$, is easily achieved and the resulting species are of interest since they provide the first examples of phosphine-containing one-dimensional stacking arrays.[7] Unfortunately, more diverse reactions are limited by the inert nature of the two phosphine groups. Of greater potential use are complexes of the type $[Pt(S_2N_2H)X(PR_3)]$ (X = Br or I, R = alkyl) which are the ultimate products of the reaction of $[Pt(S_2N_2H)(PR_3)_2]$ with X_2. These complexes have the great advantage of the presence of the reactive halogen atom, although this advantage is offset by the poor yield of product when prepared in the above manner.

In attempts to find more useful routes to these complexes we have investigated the reaction of $[PPh_4][PtCl_3(PMe_2Ph)]$ (and the palladium analogue), prepared *in situ* from $[\{MCl_2(PMe_2Ph)\}_2]$ and $[PPh_4]Cl$, with $[Sn(S_2N_2)Me_2]_2$. The reaction proceeds, with abstraction of a proton from HCl present in the solvent (CH_2Cl_2), to give $[Pt(S_2N_2H)Cl(PMe_2Ph)]$ (**1a**) in good yield [equation (1)]. The similarity of the chemical shift of the phosphorus in (**1a**) (δ −21.0 p.p.m.) to that observed for $[Pt(S_2N_2H)Br(PMe_2Ph)]$ (δ −23.5 p.p.m.)[1] suggests that they are in identical environments. Since the latter complex has been shown by *X*-ray crystallography to have the phosphine group *trans* to nitrogen, then the same can be assumed to be true for (**1a**). This is confirmed by the fact that the product obtained when (**1a**) is stirred with KBr for a few days has identical ^{31}P n.m.r. parameters to the aforementioned bromo complex.

$$[PPh_4][PtCl_3(PMe_2Ph)] + \tfrac{1}{2}[Sn(S_2N_2)Me_2]_2 \xrightarrow{HCl} [Pt(S_2N_2H)Cl(PMe_2Ph)] + [PPh_4][SnCl_3Me_2] \quad (1)$$

The formulation of the tin-containing by-product of the reaction is tentative and is based on the fact that the initial products in the reaction of the tin reagent with $[PtCl_2(PR_3)_2]$ are of the type $[Pt(S_2N_2H)(PR_3)_2][SnCl_3Me_2]$. Presumably this by-product is present in the faster moving of the two orange bands observed during elution of the crude reaction products on Bio-beads; the ^{31}P n.m.r. spectrum of this band shows the presence of $[PPh_4]^+$ (δ 23.3 p.p.m.), but attempts to isolate the compound yield only oils. Interestingly, in the palladium case, the colour of the fastest running band is more intense than in the platinum case. This suggests that in both cases this band may well be due to something more complex than a simple salt of $[SnCl_3Me_2]^-$, although we have yet to ascertain its true nature.

The ^{31}P n.m.r. spectrum of the palladium compound (**1b**) consists of a singlet at δ = 2.3 p.p.m.; comparison of this value with the chemical shift of $[Pd(S_2N_2H)Br(PMe_2Ph)]$ (δ 0.4 p.p.m.)[8] reveals that replacing the bromine by chlorine results in an increase of some 1.9 p.p.m. in the chemical shift of the phosphorus. This compares favourably with the change observed in the analogous platinum species and there is a direct relationship between the electronegativity of X and the chemical shift of the phosphorus, with greater electronegativity resulting in higher δ values.

In reactions involving $[Sn(S_2N_2)Me_2]_2$ it is reasonable to assume that the point of attack (*i.e.* the weakest bound chlorine) in $[MCl_3(PMe_2Ph)]^-$ will be the chlorine *trans* to the phosphine. Thus, the reaction must proceed *via* formation of a Pt–N bond, followed by protonation of the metal-bound nitrogen by HCl present in the CH_2Cl_2. N.m.r. studies show that neutral $S_2N_2^{2-}$ complexes are not themselves protonated by CH_2Cl_2. The final stage of the reaction is the formation of the third tin–chlorine bond, and the platinum metallacycle (Figure 1).

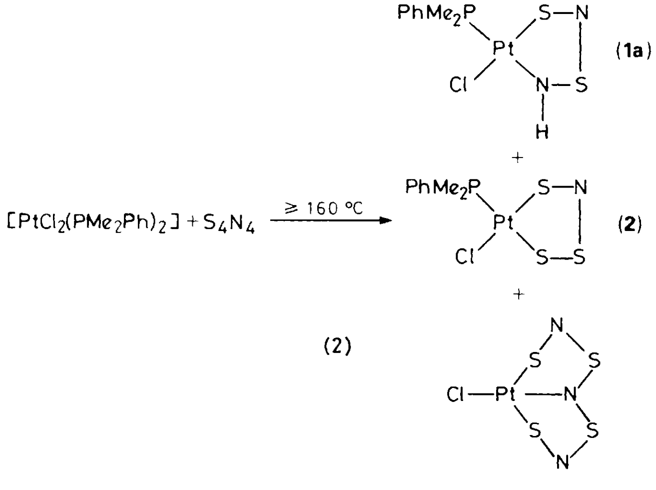
Once isolated complex (**1a**) can be deprotonated by bases such as dbu or $[NBu^t_4]OH$ (but not NEt_3), resulting in a colour change from bright yellow to pale green [^{31}P n.m.r.: δ −19.4 p.p.m., $^1J(^{195}Pt-^{31}P)$ 3 015 Hz]. We have yet to isolate any of these salts, mainly due to their great affinity for protons (thus when CH_2Cl_2 is added, the solution reverts to the yellow colour of the protonated species). Attempts at chlorine abstraction from the deprotonated species, using $Ag[BF_4]$, gave a red insoluble solid which has similar properties to the known dimeric complex $[\{Pt(S_2N_2)(PPh_3)\}_2]$.[9]

An interesting property of (**1a**) is the fact that it can be sublimed without decomposition in high vacuum. Thus if a sample is heated at 180 °C, under a vacuum of *ca.* 0.005 mmHg, a ring of well formed bright yellow crystals soon appears above the area of applied heat; ^{31}P n.m.r. spectroscopy reveals these to be pure (**1a**).

In an attempt to extend the application of equation (1) to systems containing ligands other than phosphines we have investigated the reaction of $[Sn(S_2N_2)Me_2]_2$ with Zeise's salt, $K[PtCl_3(C_2H_4)]$. Reaction of the two compounds in CH_2Cl_2–tetrahydrofuran leads to a dark solution from which a lighter coloured product can be extracted with diethyl ether. Elution of a CH_2Cl_2 solution of this product on Bio-beads separates a fast moving yellow band from a slower purple species. The mass spectrum of the yellow fraction clearly shows the presence of the ethylene complex, $[Pt(S_2N_2H)Cl(C_2H_4)]$ (**1c**) [*m/z* 352 (M^+), 324 {$[Pt(S_2N_2H)Cl]^+$}, 287 {$[Pt(S_2N_2)]^+$}, and 241

{[Pt(SN)]$^+$}] together with a higher-molecular-weight impurity. The presence of this impurity is also confirmed by the poor microanalysis. Thus it would appear that (**1c**) is unstable in solution, a conclusion further supported by the poor yields of this complex (typically substantially less than 10%).

Although we have found a number of synthetic uses for complexes of the type [$PtCl_2(PR_3)_2$] in the preparation of metal sulphur–nitrogen species, we have previously assumed them to be inert to S_4N_4. However, if a 2:1 mixture of S_4N_4 and [$PtCl_2(PMe_2Ph)_2$] is heated to *ca.* 160 °C in xylene the colour of the solution gradually darkens from yellow through to cherry red and finally deep purple-red. The ^{31}P n.m.r. spectrum of the resulting mixture shows the presence of a number of species, including two singlets, with ^{195}Pt satellites, at -11.1 [$^1J(^{195}Pt-^{31}P)$ 3 055] and -21.2 p.p.m. [$^1J(^{195}Pt-^{31}P)$ 3 390 Hz]. Clearly the latter corresponds to (**1a**) prepared above, a fact further confirmed by t.l.c. which shows its presence as an intense yellow band R_f *ca.* 0.4 (CH_2Cl_2). The other complex can be identified by comparison with results obtained previously from the reaction of [$PtCl_2(PMe_2Ph)_2$] with the mercury reagent Hg(S_7N)Ph.[10] This reaction leads to the intensely red-purple complex [Pt(S_3N)Cl(PMe_2Ph)] (**2**), which has identical ^{31}P n.m.r. parameters to the species formed above. The structure of (**2**) can be inferred from the *X*-ray structure of the PEt_3 analogue, which we have previously obtained[11] and which shows the ligand to adopt the conformation shown in equation (2). Also seen in the ^{31}P n.m.r. spectrum of the crude products are a number of peaks without ^{195}Pt satellites, the most intense of which are at δ 42.3 and 24.4 p.p.m.



(2)

Compounds (**1a**) and (**2**) can be separated from the other products on a Bio-beads gel-permeation column; they can then be separated from each other by p.t.l.c. If a solution of (**2**) is evaporated to dryness *in vacuo* the result is an amorphous red oil. This can be crystallised by extraction into boiling light petroleum followed by overnight cooling at -15 °C. The microanalysis of these crystals confirms their formulation. The final yields of both complexes are low; this is evident from the ^{31}P n.m.r. spectrum of the crude products wherein the ratio of the combined non-platinum-containing products to (**1a**) and (**2**) is around 4:1. We have yet to ascertain the nature of these products; the compounds at δ 42.3 and 24.4 p.p.m. are contained in the green band which moves ahead of (**1a**) and (**2**) on Bio-beads. The yields of the platinum complexes are further reduced by the need for the two-stage (*i.e.* Bio-beads then silica) chromatographic separation, especially since both complexes begin to decompose if they are left on silica for more than a few minutes.

The formation of complexes of $S_2N_2H^-$ and S_3N^- is not surprising since it has been known for many years that S_4N_4 reacts with $PtCl_2$ in boiling methanol to give [$Pt(S_2N_2H)_2$], [$Pt(S_3N)_2$], *etc.* However, what is interesting about the reaction is the high temperature required; no reaction is apparent before at least 140—145 °C, and full reaction only seems to take place at still higher temperatures. It may be that this is the temperature at which the phosphine groups become labile enough to react, a feature which is also noted in the reaction of [$PtCl_2(PMe_2Ph)_2$] with $PtCl_2$ to give [{$PtCl_2(PMe_2Ph)$}$_2$]. This would also explain why no bis(phosphine) products are observed.

Another possibility is that at these high temperatures S_4N_4 itself starts to decompose to more reactive species. To investigate this possibility we heated a mixture of S_4N_4 and fully ^{15}N-labelled $S_4{}^{15}N_4$ in xylene. At a number of temperatures a sample of the solution was removed and evaporated to dryness; the residue was then extracted into CH_2Cl_2 from which S_4N_4 was crystallised, by slow evaporation, and its ^{15}N content determined by mass spectrometry. After 30 min at 100—110 °C the resulting S_4N_4 sample proved to be a simple mixture of S_4N_4 and $S_4{}^{15}N_4$, with only a slight degree of intermixing. However, a sample taken from the solution after heating to 140—150 °C for a similar time proved to consist of 50% labelled S_4N_4, with all the $^{14}N/^{15}N$ atoms intermixed. Thus at this temperature S_4N_4 must undergo some kind of rearrangement, possibly *via* species such as S_2N_2 or NS$^\bullet$ although we have not been able to observe these by ^{14}N n.m.r. spectroscopy. The suggestion that S_4N_4 decomposes at these temperatures is further supported by the presence of a red impurity, possibly S_4N_2, in the CH_2Cl_2 extract; samples taken from the solution after heating to 190 °C are very dark red. In this case pure S_4N_4 can be extracted from this red mixture by allowing it to stand under N_2 for a few days followed by washing with diethyl ether. Again, mass spectroscopy reveals this S_4N_4 to be fully intermixed 50% ^{15}N labelled.

We have yet to ascertain which of the above features is most important in these reactions; the fact that at the temperatures in question the phosphine groups on the starting material become labilised, or that S_4N_4 is rearranging. It is noteworthy, however, that if the reaction is performed on a 1:1 molar ratio then 50% of the [$PtCl_2(PMe_2Ph)_2$] remains unreacted, indicating that 2 mol of S_4N_4 per platinum are definitely required for full reaction. Interestingly, when the crude products of the 1:1 reaction are eluted on the Bio-beads column a slow-moving purple band, not apparent in the 2:1 reaction, is observed. If this is collected and the CH_2Cl_2 solution allowed to stand overnight then dark microcrystals are deposited in moderate yield. The mass spectrum of these crystals indicates that they are the known complex [Pt(S_4N_3)Cl], which has previously been prepared by reaction of [$Pt(PhCN)_2Cl_2$] with S_4N_4.[12]

If $S_4{}^{15}N_4$ is heated with [$PtCl_2(PMe_2Ph)_2$], and the products isolated as described above, then 100% ^{15}N-labelled (**1a**) and (**2**) can be isolated. The ^{31}P n.m.r. spectra of these complexes both show more lines than their unlabelled counterparts,[13] due to splitting by the ^{15}N ($I = \frac{1}{2}$) present (Figure 2). In the simplest case, that of (**2**), which contains only one ^{15}N atom, the spectrum consists of a doublet (with ^{195}Pt satellites) with a $^{15}N-^{31}P$ coupling constant of *ca.* 11 Hz. For labelled (**1a**) a quartet is observed, indicating splittings from both ^{15}N atoms present, with couplings of 54 and 7 Hz. It is reasonable to assume that the larger of the two is due the metal-bound nitrogen.

If labelled (**1a**) is treated with dbu to give a salt of [$Pt(S_2{}^{15}N_2)Cl(PMe_2Ph)$]$^-$ then there is a considerable change in the $^{15}N-^{31}P$ coupling constants which now become 32 and 12 Hz. Thus the effect of protonation is to increase the coupling from the metal-bound nitrogen, while decreasing the coupling from the other.

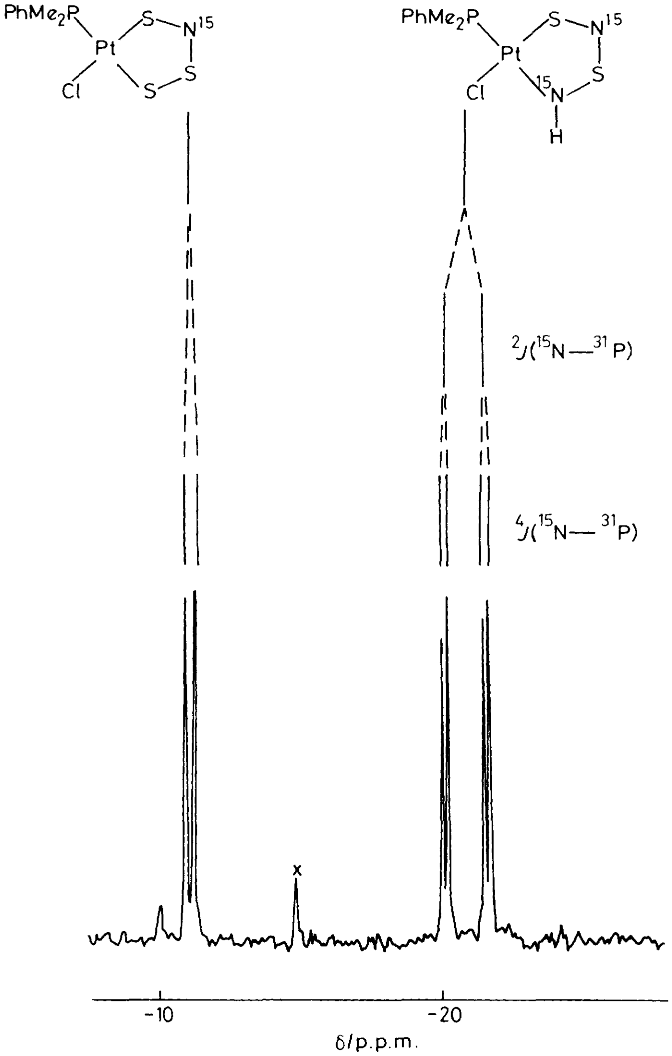


Figure 2. The observed ^{31}P-{^{1}H} n.m.r. splitting patterns and their origins for ^{15}N-labelled [Pt(S_2N_2H)Cl(PMe_2Ph)] (**1a**) and [Pt(S_3N)Cl(PMe_2Ph)] (**2**). X is due to residual [$PtCl_2(PMe_2Ph)_2$]

The preparation of the ^{15}N-labelled complexes also helps in the analysis of complicated areas of the i.r. spectra of these species, for example the region between 300 and 400 cm^{-1} for (**1a**). There are four main bands in this area (Table); comparison with other systems such as [$Pt(S_2N_2H)_2$] and [$PtCl_2(PMe_2Ph)_2$] suggests these should be due to δ(N–S), ν(Pt–S), and ν(Pt–Cl), together with a stretch due to the phosphine ligand. Comparison of the spectrum of (**1a**) with that of the iodine analogue, [Pt(S_2N_2H)I(PMe_2Ph)], reveals that the band at 313 cm^{-1}, absent in the latter, can be assigned to ν(Pt–Cl). Similarly, comparison of this area of the spectrum of (**1a**) with that of its ^{15}N-labelled counterpart reveals that the only band which is significantly shifted is at 341 cm^{-1}, the effect of introducing ^{15}N into the system being to lower the frequency of the band by some 10 cm^{-1}. Thus this band can be positively assigned to δ(N–S). This leaves one of the remaining two to be assigned to ν(Pt–S), most likely that at 357 cm^{-1}.

Table. Observed low-frequency vibrations (*a*) and mid-i.r. vibrations (cm^{-1}) (*b*) for complexes (**1**), (**2**) and corresponding ^{15}N complexes

(*a*)

[Pt(S_2N_2H)I(PMe_2Ph)]	368m, 355w, 340s
[Pt(S_2N_2H)Br(PMe_2Ph)]	379m, 360w, 345s
[Pt(S_2N_2H)Cl(PMe_2Ph)]	377m, 357w, 341s, 313s
[Pt($S_2{}^{15}N_2H$)Cl(PMe_2Ph)]	376m, 357w, 331s, 314s

(*b*)

	ν(N–H)	δ(N–H)	ν(N–S)	ν(N–S)
[Pt(S_2N_2H)Cl(PMe_2Ph)]	3 180(br)	1 165m	1 039s	695*
[Pt($S_2{}^{15}N_2H$)Cl(PMe_2Ph)]	3 166(br)	1 155w	1 016s	683vs
[Pd(S_2N_2H)Cl(PMe_2Ph)]	3 274m	1 262w	1 054m	689*
[Pt(S_3N)Cl(PMe_2Ph)]	—	—	972m	706vs
[Pt($S_3{}^{15}N$)Cl(PMe_2Ph)]	—	—	949m	692vs

* Strength of the band enhanced by phosphine vibration present at the same frequency.

In a previous study, the band at 345 cm^{-1} in the i.r. spectrum of [$Pt(S_2N_2)(PEt_3)_2$] was assigned to ν(Pt–S).[14] This frequency is significantly lower than of complex (**1a**) reflecting the change in the ligand *trans* to sulphur. In (**1a**) the sulphur is *trans* to chlorine, which has a relatively weak *trans* influence, and so the Pt–S bond is correspondingly stronger (*i.e.* higher frequency) than in the bis-(phosphine) complexes, wherein the sulphur is *trans* to the phosphine group. This effect is confirmed by comparison of Pt–S bond lengths, for example 2.222(3) in [Pt(S_2N_2H)Br(PMe_2Ph)] compared with 2.288(5) Å in [$Pt(S_2N_2)(PPh_3)_2$].

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