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# Coupling Constants in *cis*-Phosphine Platinum Complexes Containing Chalcogen-Nitride Anions

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## ABSTRACT

*The $^{31}P$ NMR spectra of complexes of the type $Pt(SeSN_2)(PR_3)_2$ and $Pt(Se_2N_2)(PR_3)_2$ display* trans *$^2J\{^{77}Se-^{31}P\}$ couplings of ca. 30–80 Hz, with no corresponding* cis *coupling; in contrast $Pt(TeSN_2)(PMe_2Ph)_2$ has both* trans *and* cis *$^2J\{^{125}Te-^{31}P\}$ couplings of 146 Hz and 103 Hz respectively. The $^{31}P$ spectra of the complexes $Pt(S_2{}^{15}N_2)(PMe_2Ph)_2$ and $[Pt(S_2{}^{15}N_2)Cl(PMe_2Ph)]^-$ show both $^2J$- and $^4J\{^{15}N-^{31}P\}$ couplings, which alter substantially upon protonation of the $S_2N_2{}^{2-}$ ligand. The $^{15}N$ NMR spectra of $Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$ and $Pt(S_3{}^{15}N)Cl(PMe_2Ph)$ show the presence of both $^{31}P-^{15}N$ and $^{195}Pt-^{15}N$ couplings but no significant $^{15}N-^{15}N$ interactions.*

## INTRODUCTION

We have recently reported on the preparation of a number of complexes of the type $Pt(S_2N_2)(PR_3)_2$, $[Pt(S_2N_2H)(PR_3)_2]^+$, and $Pt(S_2N_2H)Cl(PR_3)$ [1–3], which contain the bidentate $S_2N_2{}^{2-}/S_2N_2H^-$ ligands. Although we have found $^{14}N$ NMR spectroscopy to be a useful means of investigating the chemistry of these systems [4], $^{31}P$ NMR is also a very convenient method. The $^{31}P-^{31}P$ and $^{195}Pt-^{31}P$ couplings observed in such spectra provide useful information about metal oxidation state, etc. and further information can be obtained by the use of $^{15}N$ (spin $\frac{1}{2}$) labeling. Previous work has shown that both $^{15}N$ atoms in the $S_2N_2{}^{2-}$ ligand can couple to the phosphine groups [5]; here we report on the substantial effect protonation of the ligand has upon these couplings. We also present the $^{15}N$ NMR spectra of the labeled species $Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$ and $Pt(S_3{}^{15}N)Cl(PMe_2Ph)$, which, in addition to the $^{31}P-^{15}N$ couplings, also reveal $^{195}Pt-^{15}N$ and $^1H-^{15}N$ interactions.

We have recently prepared analogous complexes of the $SeSN_2{}^{2-}$, $Se_2N_2{}^{2-}$, and $TeSN_2{}^{2-}$ ligands, together with their protonated counterparts [6–9]. The elements Se and Te both have spin $\frac{1}{2}$ nuclei of low natural abundance (ca. 7%) and are thus potentially useful in structural studies. Although the solubilities of the new compounds make $^{77}Se$ and $^{125}Te$ measurements difficult, $^{31}P$ measurements are again useful. Here we report the magnitudes of the $^2J\{^{77}Se-^{31}P\}$ and $\{^{125}Te-^{31}P\}$ couplings present in the $^{31}P$ NMR spectra of these complexes. To our knowledge the latter constitute the first reported examples of $^2J\{^{125}Te-^{31}P\}$ couplings directed through a transition metal.

## EXPERIMENTAL

All procedures were carried out under an inert atmosphere (Ar). Solvents were dried and distilled before use: $CH_2Cl_2$ from $CaH_2$, THF from Na/benzophenone, and $CDCl_3$ over 4Å molecular sieves. $^{31}P-\{^1H\}$ NMR spectra were obtained on Jeol FX-90Q and Bruker WM250 spectrometers operating at 36.21 MHz and 101.4 MHz respectively and are referenced to external 85% $H_3PO_4$; $^{15}N-\{^1H\}$ spectra were recorded on a Bruker AM500 spectrometer operating at 50.68 MHz and are referred to $NH_3$.

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The compounds $Pt(SeSN_2)(PEt_3)_2$, $Pt(Se_2N_2)dppe$ (dppe = 1.2-bis(diphenylphosphino)ethane), and $Pt(Se_2N_2)(PPh_3)_2$, together with their protonated analogues (as $BF_4^-$ salts) and the tellurium substituted complex $Pt(TeSN_2)(PMe_2Ph)_2$, were made by the literature methods [6–9], as were $^{15}N$ labeled $S_4N_4$ and $[S_4N_3]Cl$ [10]. $Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$ and $Pt(S_3{}^{15}N)Cl(PMe_2Ph)$ were prepared by photolysis of a mixture of $PtCl_2(PMe_2Ph)_2$ and $S_4{}^{15}N_4$ in $CH_2Cl_2$ [11].

### $[Pt(S_2{}^{15}N_2H)(PMe_2Ph)_2]BF_4$ (**1b**)

A mixture of $PtCl_2(PMe_2Ph)_2$ (108 mg, 0.2 mmol) and $S_4{}^{15}N_4$ (40 mg, 0.22 mmol) in $CH_2Cl_2$ (20 mL) was treated with excess DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) (ca. 15 drops) giving a red color that darkened with time. After stirring for 1 hour more DBU (6 drops) was added and the resulting solution stirred for a further 2 hours. At this point the $CH_2Cl_2$ was removed in vacuo and the resulting solid stirred with water (70 mL) for 40 min. to give a brown powder. After filtration, the solid was dried then extracted into $CH_2Cl_2$ (10 mL) and reprecipitated as a yellowish solid by addition of hexane (100 mL). After filtration this solid was suspended in THF (10 mL) and treated with $BF_3.Et_2O$, which was added dropwise until the solid had completely dissolved, giving a brown/orange solution. After removal of half of the THF in vacuo $Et_2O$ was added (50 mL) to give a yellow solid and oil; further stirring resulted in solidification of the oil, which was filtered and washed with a small volume of cold THF. The residue was extracted into $CH_2Cl_2$ and crystallized by slow hexane diffusion yielding well-formed crystals of the product, which were coated in a dark by-product oil. The oil was washed off with cold $CHCl_3$ and the product recrystallized from $CH_2Cl_2$/hexane. The final well-formed green crystals had a satisfactory CHN analysis.

### *Preparation of Partially $^{15}N$ Labeled $Pt(SeSN_2)(PMe_2Ph)_2$*

$[S_4{}^{15}N_3]Cl$ (0.040 g, 0.19 mmol) and $SeCl_4$ (0.20 g, 0.91 mmol) were added as solids to liquid ammonia (15 mL) at −78°C, and the resultant slurry was stirred for 0.5 hr. Solid $PtCl_2(PMe_2Ph)_2$ (81 mg, 0.15 mmol) was added and the mixture was stirred for a further 1 hr at −78°C. The reaction was allowed to warm to room temperature (ca 0.5 hr) with the ammonia being blown off by a stream of nitrogen. Extraction with $CDCl_3$ (10 mL) afforded a red solution that was filered through celite to obtain the $^{31}P$ $\{^1H\}$ NMR spectrum of the partially labeled (ca. 33% $^{15}N$) $Pt(SeSN_2)(PMe_2Ph)_2$.

## *RESULTS AND DISCUSSION*

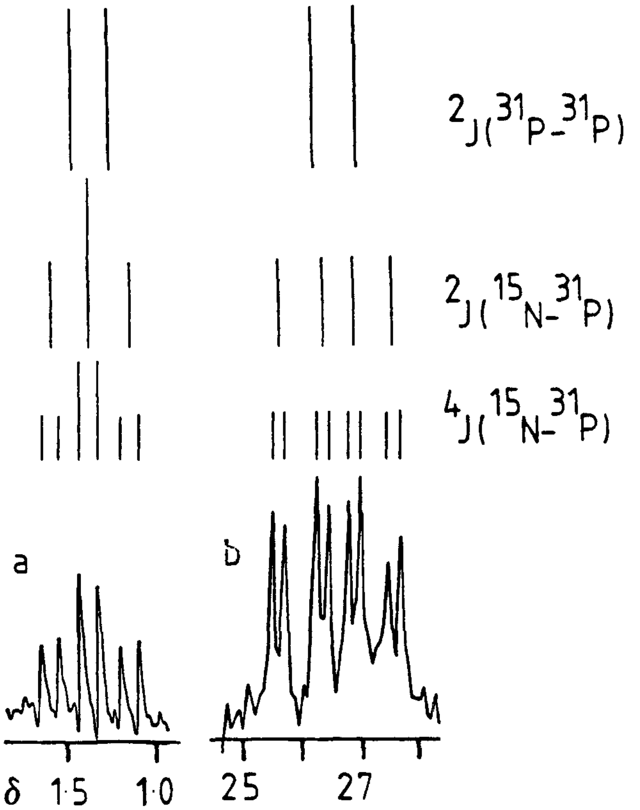

**FIGURE 1** The $^{31}P$ NMR spectra of (a) $Pt(S_2{}^{15}N_2)(PEt_3)_2$ and (b) $[Pt(S_2{}^{15}N_2H)(PMe_2Ph)_2][BF_4]$. Note that (a) was recorded at an operating frequency of 101.4 MHz compared to 36.21 MHz for (b).

We have previously shown that the $^{31}P$ NMR spectrum of $Pt(S_2{}^{15}N_2)(PEt_3)_2$ contains splitting patterns due to $^{15}N-^{31}P$ couplings (Figure 1a) [5]. In contrast to the phosphorus *trans* to sulfur, which shows only a weak coupling (ca. 5 Hz) to just the metal-bound nitrogen, the other phosphorus couples to both nitrogens in the ligand with $^2J\{^{15}N-^{31}P\} = 24$ Hz and $^4J\{^{15}N-^{31}P\} = 12$ Hz (NOTE: The latter coupling may be formally described as a $^3J$ interaction; however, as previous results suggested that the mode of coupling was via the N═S═N fragment of the ring, we assigned it as $^4J$ and for the sake of consistency we continue that practice here). We have now been able to prepare pure samples of the related protonated species, $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$, by reaction of $S_4{}^{15}N_4$ with $PtCl_2(PMe_2Ph)_2$ and DBU followed by treatment with $BF_3$ (the change in phosphine group was necessary to facilitate purification by crystallization; impurities present prevent crystallization of the $PEt_3$ analogue). The $^{31}P$ NMR spectrum of the resulting product contains an eight line pattern that is quite different in appearance to that of the unprotonated species (Fig. 1b). This difference is brought about by an increase in the $^2J$ coupling from 24 Hz to 45 Hz together with a decrease in the $^4J$ from 12 Hz to 7 Hz. This change is also seen when $Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$, prepared by reaction of

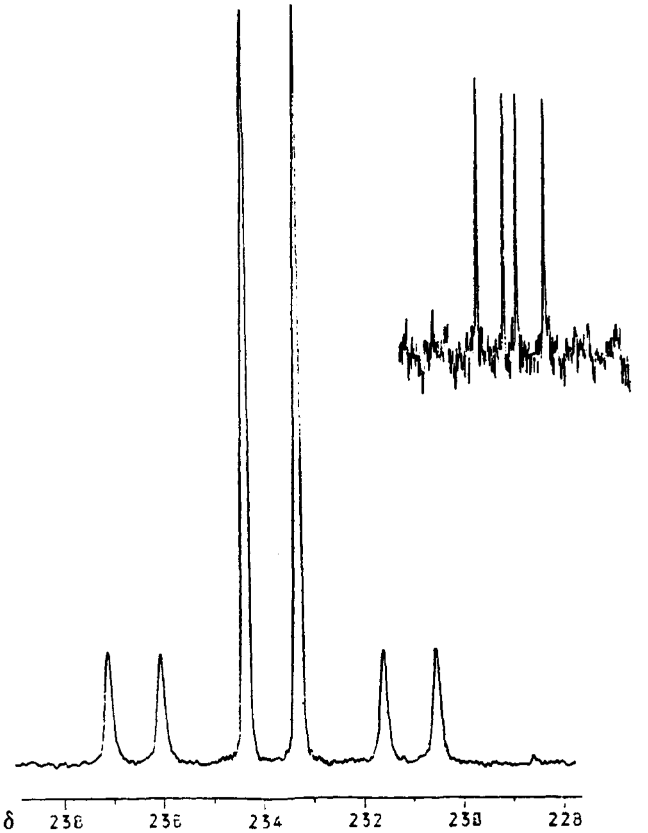

FIGURE 2 The $^{15}N$–{$^{1}H$} NMR splitting pattern of the metal-bound nitrogen in fully $^{15}N$ labeled $Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$; inset—the proton coupled spectrum, showing the presence of $^{1}H$–$^{15}N$ coupling (80 Hz).

$S_4{}^{15}N_4$ with $PtCl_2(PMe_2Ph)_2$ at high temperature, is deprotonated with DBU [3]. In this case the couplings of 54 Hz and 7 Hz change to 32 Hz and 12 Hz upon deprotonation. Thus it would appear to be a general rule that protonation of the $S_2{}^{15}N_2{}^{2-}$ ligand results in a substantial increase of ca. 70–90% in the magnitude of the $^{2}J$ coupling from the metal-bound nitrogen (to the phosphorus *trans*) together with a lowering of the $^{4}J$ coupling from the far nitrogen by around 40%. In the case of $Pt(S_2N_2)(PEt_3)_2$ protonation lowers the $^{2}J$ coupling from $^{15}N$ to the P *trans* to sulfur from 5 Hz to 3 Hz. These effects are a consequence of the change in the character of the Pt—N bond. Upon protonation the Pt–N–S angle changes from 117.3(6)° to 121.4(4)°; that is, the nitrogen in the $S_2N_2H^-$ ligand is more closely trigonal (and $sp^2$ hybridized) than in the nonprotonated case. It should be noted that although the two spectra in Figure 1 were obtained from complexes of different phosphines, this does not affect the results as the magnitude of the $^{2}J\{^{31}P–^{31}P\}$ coupling constant is the same in each case.

We have also investigated the couplings present in this type of system through observation of the $^{15}N$ NMR spectra of the complexes $Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$ (**1**) and $Pt(S_3{}^{15}N)Cl(PMe_2Ph)$ (**2**), mixtures of which can be prepared by reaction of $S_4{}^{15}N_4$ with $PtCl_2(PMe_2Ph)_2$ either at high temperatures [3] or, more safely, at RT under UV photolysis [11]. The mixtures of (**1**) and (**2**) may be purified by elution on a bio-beads gel-permeation column, although they cannot be separated from each other except by Preparative Thin Layer Chromatography on silica, a medium to which they are actually quite sensitive. Thus all measurements were performed upon the mixture, and hence the $^{15}N$–{$^{1}H$} NMR spectrum contains signals due to three nitrogens, at δ 234, 323, and 450. Each nitrogen signal is further split into six lines, of relative intensity 1:1:4:4:1:1, which correspond to couplings to the phosphorus and to the platinum. Figure 2 shows the splitting pattern that contains the largest couplings (δ 234), and this can be positively assigned to the metal bound (protonated) nitrogen in (**1**) by reference to the $^{1}H$ coupled spectrum (Fig. 2 inset), which clearly shows a $^{1}J\{^{1}H–^{31}P\}$ coupling of 80 Hz. This assignment is supported by the large $^{195}Pt–^{15}N$ coupling (280 Hz) and a $^{31}P–^{15}N$ coupling (54 Hz) identical to that previously observed by $^{31}P$ NMR [3]. The latter parameter also allows the two other peaks in the spectrum to be assigned; the resonance at δ 323 ($^{4}J\{^{31}P–^{15}N\}$ 8 Hz, $^{2}J\{^{195}Pt–^{15}N\}$ 25 Hz) can be assigned to the far nitrogen in (**1**), whereas the remaining peak at δ 450 ($^{4}J$ 11 Hz, $^{2}J$ 40 Hz) is due to the lone nitrogen in (**2**). Note that again, to be consistent we have referred to the $^{31}P–^{15}N$ coupling in (**2**) as $^{4}J$ although it may more formally regarded as $^{3}J$. The assignment of the resonances in (**1**) is in accord with $^{14}N$ NMR results obtained for $Ni(S_2N_2H)_2$ (δ $^{14}N$ 217 and 347) [12] and related $S_2N_2H^-$ complexes [4]. An interesting and somewhat surprising feature of the spectrum of (**1**) is the lack of any significant $^{15}N–^{15}N$ couplings; if they are present they must be smaller than 5 Hz in magnitude.

The $^{2}J\{^{77}Se–^{31}P\}$ and $\{^{125}Te–^{31}P\}$ coupling constants obtained in this work are shown in Table 1. The couplings can be assigned to *cis* and *trans* by reference to the chemical shift positions of the phosphine resonances and the observed magnitude of the $^{1}J\{^{195}Pt–^{31}P\}$ coupling constants [1, 6]. The $^{2}J\{^{77}Se–^{31}P\}$ coupling constants are in the range of 30–82 Hz for the *trans* phosphine, the exact value being dependent upon the nature of the ligand and the degree of protonation. Comparison of the spectra of the $SeSN_2{}^{2-}$ and $Se_2N_2{}^{2-}$ species reveals that introduction of the second selenium into the system tends to increase the value of the $^{2}J\{^{77}Se–^{31}P\}$ coupling constant by ≈100%. This effect is difficult to rationalize and highlights the complicated nature of geminal couplings of this type. The observed magnitude of the $^{2}J\{^{77}Se–^{31}P\}$ coupling constants equates to those already found in the literature. For example, in complexes of the type $Pt(Se_2CN—R)PPh_3Cl$ the *trans* and *cis* $^{2}J\{^{77}Se–^{31}P\}$ couplings

**TABLE 1** $^{2}J$ $^{27}$Se–$^{31}$P and $^{125}$Te–$^{31}$P Coupling Constants (Hz)

| | $^{2}J$trans | $^{2}J$cis$^{a}$ |
|---|---|---|
| $Pt(SeSN_2)(PEt_3)_2$ | 35 | 0 |
| $[Pt(SeSN_2H)(PEt_3)_2]BF_4$ | 30 | 0 |
| $Pt(Se_2N_2)(dppe)$ | 80 | 0 |
| $[Pt(Se_2N_2H(dppe)]BF_4$ | 82 | 0 |
| $Pt(Se_2N_2)(PPh_3)_2$ | 60 | 0 |
| $[Pt(Se_2N_2H)(PPh_3)_2]BF_4$ | 62 | 0 |
| $Pt(TeSN_2)(PMe_2Ph)_2$ | 146 | 103 |

$^{a}J$ = 0 means that the coupling was not resolved within the line halfwidth of 3–4 Hz.

**TABLE 2** $^{15}$N NMR Parameters for $Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)$ (**1**) and $Pt(S_3{}^{15}N)Cl(PMe_2Ph)$ (**2**). N(1) (metal bound) and N(2) are in (**1**) whilst N(3) is in (**2**). Coupling Constants in Hz

| | $\delta$ | $^{31}P$–$^{15}N$ | $^{195}Pt$–$^{15}N$ | $^{1}H$–$^{15}N$ |
|---|---|---|---|---|
| N1 | 234 | 54 | 280 | 80 |
| N2 | 323 | 8 | 25 | — |
| N3 | 450 | 11 | 40 | — |

are 100 Hz and ca. 0–10 Hz respectively [13]; in the main group compounds $PPh_3NSeCl_3$ (87 Hz) and $[(PPh_3N)_2SeCl]^+$ (28 Hz) [14] as well as the heterocycle $(PPh_2N)_2CH_2SeCl_2$ [15] (49 Hz) $^{2}J\{^{77}Se–^{31}P\}$ couplings have also been observed.

The small magnitudes of the previously reported *cis* $^{2}J\{^{77}Se–^{31}P\}$ coupling constants probably explain why no definable *cis* selenium satellites could be resolved in the spectra of (*2*)–(*4*), except for the presence of a slight broadening of the appropriate $^{31}$P resonance. Certainly, if such couplings do exist they must be less than 5 Hz in size.

Reaction of a mixture of $[S_4N_3]Cl$, $SeCl_4$, and $PtCl_2(PMe_2Ph)_2$ in liquid ammonia produces $Pt(SeSN_2)(PMe_2Ph)_2$, which can be prepared with ca. 33% $^{15}$N enrichment if $[S_4{}^{15}N_3]Cl$ is used. The isotopomer patterns observed in the $^{31}$P NMR of the latter product show $^{2}J\{^{15}N–^{31}P\}$ and $^{4}J\{^{15}N–^{31}P\}$ couplings of 24 Hz and 12 Hz respectively, for the phosphorus *trans* to nitrogen, and a $^{2}J\{^{15}N–^{31}P\}$ of 6 Hz for the phosphorus *trans* to selenium. Interestingly, these coupling constants are virtually identical to those observed in analogous $S_2N_2{}^{2-}$ species, suggesting that the nature of the metal-bound chalcogen is not important in determining the magnitudes of $^{15}$N couplings. This result mirrors the effect of the chalcogen atoms upon the basicity of the metal-bound nitrogen; previous work has shown that while there is little difference in basicity between the $S_2N_2{}^{2-}$ and $SSeN_2{}^{2-}$ complexes, introduction of the second selenium greatly increases the affinity of the ligand for protons. This may well suggest that $^{15}$N–$^{31}$P couplings would be changed by the introduction of a second selenium; however, we have as yet no route to labeled $Se_2N_2{}^{2-}$ complexes.

The $^{31}$P NMR spectrum of the tellurium-substituted derivative $Pt(TeSN_2)(PMe_2Ph)_2$ shows the presence of both *trans* and *cis* $^{2}J\{^{125}Te–^{31}P\}$ couplings, of 146 Hz and 103 Hz respectively. The increase in the magnitude of the *trans* coupling relative to that observed in the selenium complexes is consistent with the higher gyromagnetic ratio of the tellurium nucleus (−8.5 for Te compared to 5.1 for Se [16]). In contrast, however, the fact that the magnitude of the *cis* $^{2}J\{^{125}Te–^{31}P\}$ coupling constant is approximately 70% that of the *trans* is somewhat unexpected and is clearly at odds with results for the selenium complexes (in which no *cis* couplings were observed) and square-planar platinum complexes in general (in which the *cis* coupling is often only some 10% the magnitude of the *trans* [16]). As yet we can offer no explanation for this anomalously large coupling, especially since, to the best of our knowledge, these results constitute the first examples of $^{2}J\{^{125}Te–^{31}P\}$ coupling constants in metal complexes. Such a coupling has been observed in a main group compound; $(PPh_2N)_2CH_2TeCl_2$ shows a $^{2}J\{^{125}Te–^{31}P\}$ coupling of 132 Hz [15].

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