# Phosphorus-31 Nuclear Magnetic Resonance Studies on $^{15}$N-Labelled $[Pt(S_2N_2)(PR_3)_2]$ ($PR_3$ = $PMe_3$, $PEt_3$, $PPh_3$, $PMe_2Ph$, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$), and Investigation into its Protonation†

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99% Nitrogen-15-enriched $(S_3N_2Cl)Cl$ and $S_4N_3Cl$ can be used to prepare enriched samples of $[Pt(S_2N_2)(PR_3)_2]$ (**1**; $PR_3$ = $PMe_3$, $PEt_3$, $PPh_3$, $PMe_2Ph$, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) in which both $^2J$ and $^4J(^{15}N-^{31}P)$ couplings are observed. Phosphorus-31 n.m.r. spectroscopy provides information on the degree of protonation of mixtures of (**1**) and $[Pt(S_2N_2H)(PR_3)_2]X$ (X = Cl, $BF_4$, or $PF_6$) and reveals the protonated Pt compounds to be stronger acids than their Pd analogues.

We have recently reported on the synthesis of compounds of the type $[M(S_2N_2)(PR_3)_2]$ (**1**)[1,2] and $[M(S_2N_2H)(PR_3)_2]X$ (**2**)[3–5] [M = Pt or Pd; L = phosphine or $\frac{1}{2}$(diphosphine); X = Cl, $BF_4$, or $PF_6$]. *X*-Ray crystallographic studies show that the $S_2N_2^{2-}$ and $S_2N_2H^-$ ligands are part of five-membered metallacycles with the proton situated on the nitrogen bound to the metal, Figure 1. The $S_2N_2H^-$ compounds are especially interesting since they show infinite stacking arrangements and to the best of our knowledge are the first examples of platinum stacking compounds containing phosphines.[5,6]

Conversion of (**1**) into (**2**) is achieved simply by addition of a dilute solution of HX (X = Cl or $BF_4$), $^{31}P$ n.m.r. being used to monitor the reaction since there is a significant change in the spectra of (**1**) upon protonation. In the case of the platinum compounds, protonation increases the ratio of the $^1J(^{195}Pt-^{31}P)$ coupling constants, *R* [$R = {}^1J$(P *trans* to N)/$^1J$(P *trans* to S)]. In (**1**) *R* is low ($\leqslant$1.07) whereas the protonated compounds invariably have *R* values $\geqslant$ 1.22.

Here we report on the $^{31}P$ n.m.r. spectra of $^{15}$N-labelled samples of (**1**), in which there is evidence for both $^2J$ and $^4J(^{15}N-^{31}P)$ couplings, together with an investigation into the relative acid strength of (**2**) and its dependence on the nature of the phosphine and metal.

## Experimental

All procedures, including $^{31}P$ n.m.r. measurements, were carried out under an inert atmosphere ($N_2$ or Ar). Tetrahydrofuran (thf) and hexane were distilled from sodium and $CH_2Cl_2$ from calcium hydride prior to use; $CDCl_3$ and $CD_2Cl_2$ were used as received.

$^{31}P-\{^1H\}$ N.m.r. spectra were obtained using either JEOL FX90Q or Bruker WM 250 spectrometers operating at 36.21 and 107.2 MHz respectively and are referred to external 85% $H_3PO_4$. Mass spectra were obtained using a VG2020 instrument.

99% Nitrogen-15-enriched $S_4{}^{15}N_3Cl$ (**3**) and $(S_2{}^{15}N_2Cl)Cl$ (**4**) were made by literature methods[7] from enriched $NH_4Cl$ (Amersham International). Tris(triphenylphosphine)platinum was made from $K_2PtCl_4$ (Johnson-Matthey) by standard methods[8] and the compounds $[PtCl_2(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] and $[PtCl_2(PEt_3)_2]$ by addition of stoicheiometric amounts of the phosphine to $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene).[9]

Compounds of the type $[M(S_2N_2)(PR_3)_2]$ (**1**) and $[M(S_2N_2H)(PR_3)_2]X$ (**2**) were made as described previously.[3]

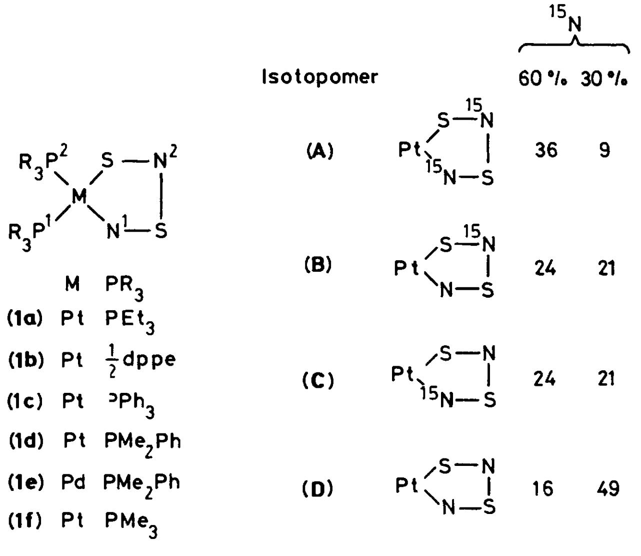

**Figure 1.** Structures of (**1**) and percentages of each isotopomer present in 60 and 30% $^{15}$N-enriched samples

In order to be certain of their purity they were used as crystals obtained by slow hexane diffusion into $CH_2Cl_2$ solutions.

*Preparation of* 99% $^{15}$*N-Enriched* $[Pt(S_2N_2)(PEt_3)_2]$.—A suspension of 99% $^{15}$N-enriched $S_4N_3Cl$ (21 mg, 0.1 mmol) in a solution of $[PtCl_2(PEt_3)_2]$ (50 mg, 0.1 mmol) in $CDCl_3$ (2 $cm^3$), in a 10-mm diameter n.m.r. tube, was treated with 2 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu). The $^{31}P$ n.m.r. spectrum of the resulting deep purple solution was measured and then the solution placed on a preparative t.l.c. plate and eluted with EtOH–$CH_2Cl_2$ (1:4). The yellow-brown band was taken off, eluted with $CH_2Cl_2$ and a pure sample of the product obtained by addition of hexane. Yield ≈ 10 mg. Mass spectrum: 525 ($M^+$), 478 ($M^+ - {}^{15}NS$).

99% Nitrogen-15-enriched $[Pt(S_2N_2)(dppe)]$ was made in the same manner although the product was only observed by $^{31}P$ n.m.r. and not isolated.

*Preparation of* 60% $^{15}$*N-Enriched* $[Pt(S_2N_2)(PPh_3)_2]$.—Solid 99% $^{15}$N-enriched $(S_3N_2Cl)Cl$ (30 mg, 0.15 mmol) was added to liquid ammonia (*ca.* 30 $cm^3$) at −70 °C giving an immediate dark red solution. The mixture was allowed to warm, with the $NH_3$ evaporating off under a blanket of nitrogen, leaving a dark coloured residue. This was extracted into thf (10 $cm^3$) and the resulting red solution added to a solution of

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

$[Pt(PPh_3)_3]$ (0.1 g, 1.0 mmol), in thf (10 cm$^3$) giving a dark green solution which was evaporated to dryness *in vacuo*. The residue was extracted into $CH_2Cl_2$ (5 cm$^3$) and a pale green-yellow solid precipitated by addition of hexane (50 cm$^3$). The $^{31}P$ n.m.r. spectrum of this crude product was measured in $CH_2Cl_2$–$CDCl_3$.

30% Nitrogen-15-enriched product was obtained in the same way using a 1:1 mixture of labelled and unlabelled $(S_3N_2Cl)Cl$ and the $^{31}P$ n.m.r. spectrum measured in $CD_2Cl_2$.

*Preparation of* 60% $^{15}N$-*enriched* $S_4N_4$.—The above reaction was repeated and the initial thf extract evaporated to dryness *in vacuo*. $S_4N_4$ was sublimed from the residue (80 °C, 0.003 mmHg) onto a liquid-nitrogen cooled cold-finger. Mass spectroscopy revealed that the product had a $^{15}N$ content of *ca.* 60%.

*Titration of* $[Pd(S_2N_2H)(PMe_2Ph)_2]BF_4$ *against* 1,8-*Diazabicyclo*[5.4.0]*undec*-7-*ene*.—The Pd compound (38 mg, 0.068 mmol) was dissolved in $CDCl_3$ (*ca.* 1.5 cm$^3$) in a 10-mm n.m.r. tube and the $^{31}P$ n.m.r. spectrum measured after successive additions of small aliquots of a solution of dbu (10 mg, 0.066 mmol) in $CDCl_3$ (0.5 cm$^3$).

## Results and Discussion

$^{15}N$-*Labelled Products*.—To study the effects of introducing $^{15}N$ into (**1**) we have developed new synthetic routes that use sulphur–nitrogen starting materials easily made in the 99% enriched form. The starting materials previously used, $S_4N_4H_4$ and $Na(S_3N_3)$, both involve multi-step preparations[10,11] that are potentially wasteful (and therefore expensive) when using 99% $^{15}N$-enriched reagents. $S_4{}^{15}N_3Cl$ (**3**) and $(S_3{}^{15}N_2Cl)Cl$ (**4**) can both be made in reasonable yield from $^{15}NH_4Cl$ and can be used to prepare enriched samples of (**1**).

We have obtained samples of 99% enriched $[Pt(S_2N_2)(PEt_3)_2]$ (**1a**) and $[Pt(S_2N_2)(dppe)]$ (**1b**) by treatment of $[PtCl_2(PR_3)_2]$ ($PR_3$ = $PEt_3$ or $\frac{1}{2}$dppe) with (**3**) in the presence of dbu, in an analogous fashion to the $S_4N_4H_4$ reactions. The reactions proceed quite cleanly by $^{31}P$ n.m.r. although the very dark colour of the final solutions indicates the presence of a variety of sulphur–nitrogen by-products. The presence of these impurities means that the reaction is not an efficient method for producing unlabelled compounds, compared to the very clean $S_4N_4H_4$ reaction.

The $^{31}P$ n.m.r. spectra of (**1a**) and (**1b**) both show four-line patterns for the resonance of P *trans* to sulphur ($P^1$) [Figure 2(*a*)]. Since $^{15}N$ nuclei have spin $\frac{1}{2}$ this splitting pattern suggests that only one of the nitrogens, probably $N^1$, is coupled to $P^1$ with $^2J(^{15}N–^{31}P)$ *ca.* 5 Hz.

The splitting patterns for $P^2$ in (**1a**) and (**1b**) consist of six and five lines respectively, indicating the presence of couplings from both nitrogens. Figure 2 shows how these patterns arise. There is a large coupling of 24 Hz, presumably from $N^1$, together with a smaller coupling, from $N^2$, of about 12 Hz. As Figure 2 shows, the difference in multiplicity in the patterns for (**1a**) and (**1b**) is due to the difference in the $^2J(^{31}P–^{31}P)$ coupling constants.

That $^{15}N$ in position $N^2$ couples to $P^2$ rather than $P^1$ suggests that this coupling is probably best described as a $^4J$ coupling *via* the $\pi$ density of the N=S=N region of the ligand.

Compound (**4**) dissolves in ammonia at −70 °C giving a deep red solution from which a dark solid can be obtained by evaporation of the $NH_3$ under a blanket of nitrogen. Extraction with thf gives a red solution which reacts with $[Pt(PPh_3)_3]$ to give $[Pt(S_2N_2)(PPh_3)_2]$ (**1c**). The $^{31}P$ n.m.r. spectrum of (**1c**) shows an even more complicated splitting pattern for $P^2$. Eleven lines are present including the lines found in unlabelled (**1c**), indicating that the degree of $^{15}N$ enrichment is significantly less than 99%. This means that the sample contains the four possible isotopomers shown in Figure 1 and on the basis of Figure 2 the splitting patterns expected for each singly labelled isotopomer can be deduced. By adding these to the patterns for both the unlabelled and fully labelled compounds the observed eleven-line spectrum is readily explained.

The above, unexpected, observations imply that during the reaction of (**4**) with $NH_3$ there is incorporation of N from the

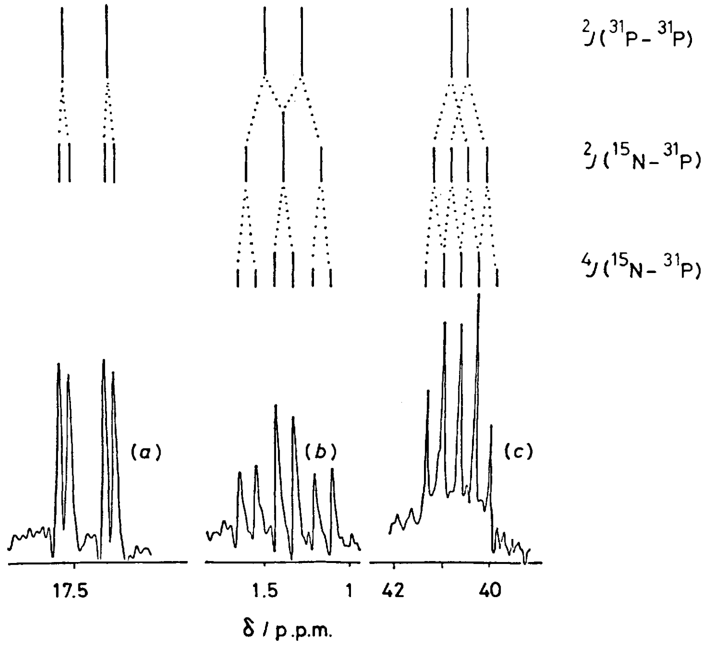

**Figure 2.** Origins of the observed splitting patterns for (*a*) $P^1$, (*b*) $P^2$ in 99% $^{15}N$-enriched $[Pt(S_2N_2)(PEt_3)_2]$ (**1a**); (*c*) $P^2$ in 99% $^{15}N$-enriched $[Pt(S_2N_2)(dppe)]$

ammonia into the final products. This can be confirmed by analysis of the initial thf extracts since upon evaporation they yield some $S_4N_4$, the $^{15}$N content of which can be determined by mass spectrometry. Analysis of the $S_4N_4$ sublimed from the residue of the reaction of (**4**) with ammonia reveals it to be *ca.* 60% $^{15}$N enriched. A similar degree of labelling in (**1c**) would give rise to the observed ratios of the lines although the poor resolution of this spectrum meant that precise integrations of the lines was impossible.

If a mixture of 6:1 unlabelled and fully labelled (**4**) is reacted with ammonia in the same way, the $S_4N_4$ obtained is 8.5% enriched [*i.e.* 1/7 of the enrichment obtained from fully labelled (**4**)] which is consistent with a complete intermixing of the nitrogens in the system. Thus by reacting solutions of the appropriate ratio of labelled and unlabelled (**4**) together, samples of (**1**) with a desired degree of $^{15}$N enrichment can be produced.

When a 1:1 mixture is used to produce 30% enriched (**1c**), the eleven-line splitting pattern for $P^2$ reflects the change in the ratios of the various isotopomers (Figure 3). Compared to the 60% enriched case there is more isotopomer (**D**) present and very much less (**A**), the latter being indicated by the small size of the outer two lines of the pattern.

One problem with the interpretation of the spectrum of 60% enriched (**1c**) is that it proves impossible to show unequivocably the presence of the splitting pattern due to isotopomer (**B**) since it is coincident with lines due to (**A**). As a result it cannot be shown whether the coupling from $N^2$ is real or virtual. This problem is resolved by the spectrum of the 30% enriched compound since in this case there is very little isotopomer (**A**) present and the splitting pattern due to (**B**) can be clearly distinguished. Thus the coupling from $^{15}$N at $N^2$ to $P^2$ is real and is independent of the nature of the nitrogen at $N^1$.

In conclusion, a $^{15}$N in position $N^1$ can couple to both $P^1$ and $P^2$, with coupling constants of 5 and 24 Hz respectively; a $^{15}$N at

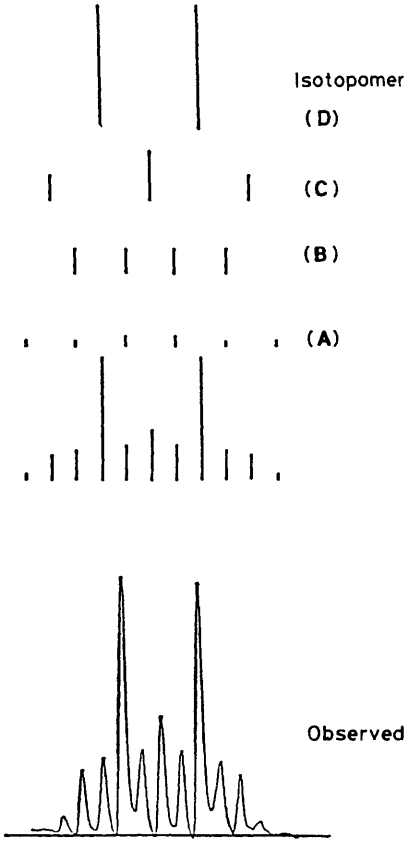

**Figure 3.** Origin of the splitting pattern for $P^2$ in 30% $^{15}$N-enriched $[Pt(S_2N_2)(PPh_3)_2]$ (**1c**)

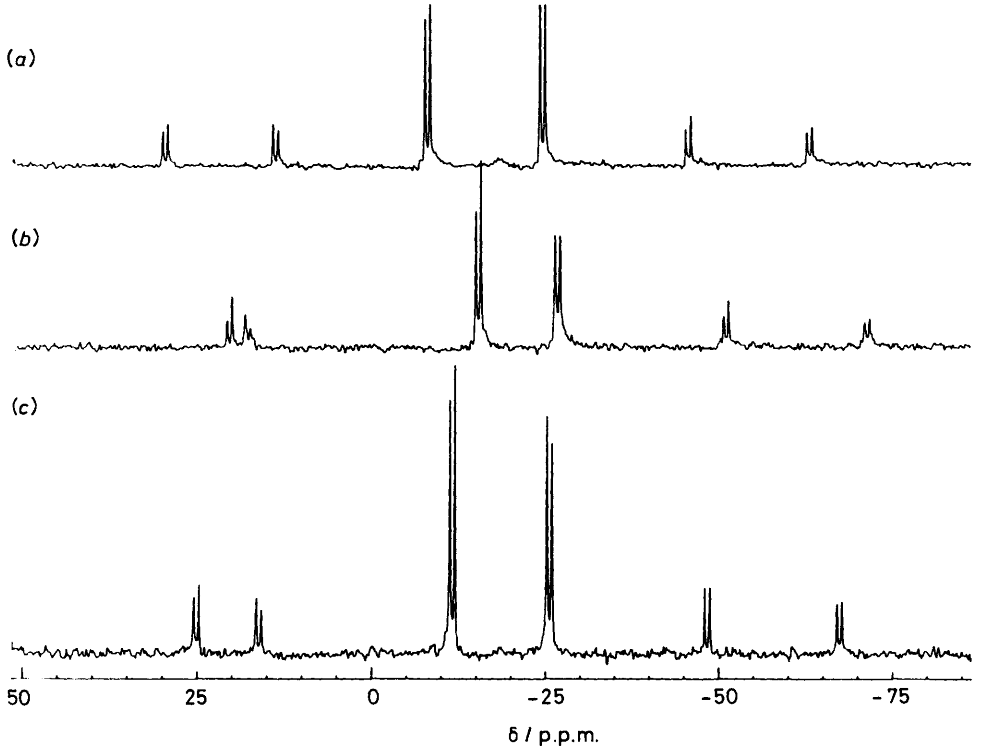

**Figure 4.** Typical $^{31}$P n.m.r. spectra of (*a*) compound (**1d**) and (*b*) compound (**2a**), together with (*c*) a mixture of the two

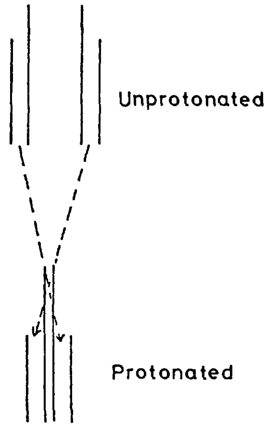

**Figure 5.** The cross over of the resonances of $P^1$ and $P^2$ during protonation of $[Pd(S_2N_2)(PMe_2Ph)_2]$

$N^2$ can only couple to $P^2$ and does so with a coupling constant of *ca.* 12 Hz.

*Protonation Reactions.*—As Figure 4 shows, if equimolar amounts of $[Pt(S_2N_2)(PMe_2Ph)_2]$ (**1d**) and $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ (**2a**) are mixed together the $^{31}P$ n.m.r. spectrum of the resulting solution consists of a simple AX pattern with chemical shifts and coupling constants that are averages of the values for the two constituents. Clearly the protons in the system are exchanging so rapidly that the spectrum actually seen is a time average of the two extremes: protonated and unprotonated.

The mixture in Figure 4 can be resolved into the component protonated and unprotonated compounds by crystallisation. Slow diffusion of hexane into this solution yields green crystals of (**2a**) and much smaller orange crystals of (**1d**). Attempts to resolve the two components in the mixture by cooling the solution to $-70$ °C failed; the intermediate spectrum is seen even at this temperature.

This averaging effect can be quantified by the *R* value of the spectrum. In the above case $R \approx 1.14$, the average of the *R* values of the protonated and unprotonated compounds. If an excess of protonated compound had been used then *R* would have been correspondingly higher and, similarly, *R* would have been lower had more unprotonated compound been present. If a solution of pure (**2a**) ($R = 1.24$) is titrated with a dilute solution of base, for example dbu, the *R* value is seen to drop as successive amounts are added. Thus the ratio *R* can act as a precise measurement of the degree of protonation of the system. The equilibrium present in these systems is represented by equation (1). In the case of (**2a**) and (**1d**), $K \approx 1$.

$$[Pt(S_2N_2)(PR_3)_2] + [Pt(S_2N_2H)(PR'_3)_2] \overset{K}{\rightleftharpoons} [Pt(S_2N_2H)(PR_3)_2] + [Pt(S_2N_2)(PR'_3)_2] \quad (1)$$

To measure the effect of different phosphines on this equilibrium we prepared samples of $[Pt(S_2N_2H)(PPh_3)_2]BF_4$ (**2b**) and $[Pt(S_2N_2)(PMe_3)_2]$ (**1f**) then measured the $^{31}P$ n.m.r. of the mixture. Both the *R* ratios were of intermediate values; 1.16 for $PPh_3$ and 1.15 for $PMe_3$, indicating an equilibrium as in equation (1).

Trimethylphosphine is more basic than triphenylphosphine. However, the position of the equilibrium in equation (1) indicates that the nature of the phosphine has little effect on the properties of the $S_2N_2^{2-}$ ligand.

This same conclusion can also be drawn from i.r. spectroscopy. For compounds of the type $[Pt(S_2N_2)(PR_3)_2]$ the main S–N stretches at *ca.* 1 045 and 680 $cm^{-1}$ vary only slightly as the phosphine is changed.[2] Also the *X*-ray structures for (**1**) with $PR_3 = PPh_3$, $PMe_3$, and $PMe_2Ph$ all show roughly similar S–N bond lengths, the only variations being in the Pt–P lengths.[1,2,6]

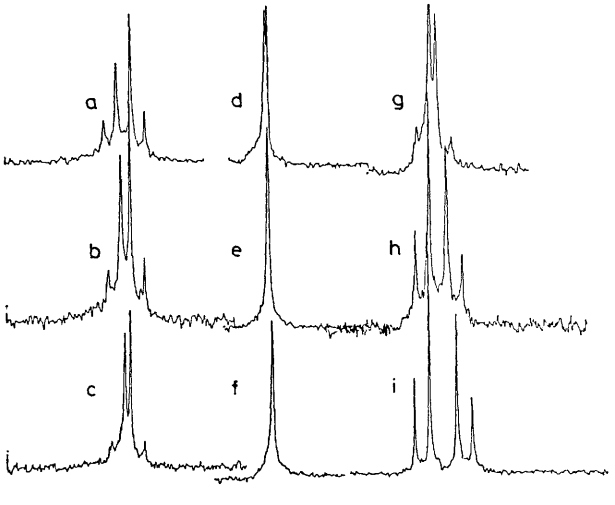

**Figure 6.** Phosphorus-31 n.m.r. spectra of the titration of $[Pd(S_2N_2H)(PMe_2Ph)_2]BF_4$ with dbu. (a) Contains no dbu; (i) completely deprotonated species

In contrast, the nature of the metal should have a much greater effect on the properties of the ligand. To investigate this we prepared samples of (**2a**) and $[Pd(S_2N_2)(PMe_2Ph)_2]$ (**1e**) and measured the $^{31}P$ n.m.r. spectrum of the mixture. The resulting spectrum shows the Pt to be almost completely deprotonated and the Pd fully protonated, *i.e.* the equilibrium in equation (2) is almost completely to the right.

$$(\mathbf{2a}) + (\mathbf{1e}) \rightleftharpoons (\mathbf{1d}) + [Pd(S_2N_2H)(PMe_2Ph)_2]BF_4 \quad (2)$$

The Pt compounds thus appear to be more acidic than their Pd counterparts, although the ease of protonation of the Pt compounds by, for example, acetic acid or $BF_3$ indicates that they are poor acids on a more general scale. When equimolar amounts of (**2a**) and (**1e**) are mixed the *R* value for the Pt spectrum is *ca.* 1.05. Since $R = 1.025$ for (**1d**) and 1.25 for (**2a**) this is equivalent to the Pt being *ca.* 10% protonated, and so the equilibrium constant for the system, $K \approx 80$.

One feature of the $^{31}P$ n.m.r. spectra of these Pd/Pt mixtures was that when exactly equimolar amounts were mixed the Pd part of the spectrum showed only a singlet instead of the AB spectrum expected for the protonated Pd compounds. This suggested that the change in the spectrum of the Pd compounds upon protonation was not, as we had initially thought, simply a case of the two phosphorus chemical shifts moving together to give an AB pattern; in fact the δ values of each phosphorus cross over, as in Figure 5. This means that if the compound is less than fully protonated the two δ values can coincide. In the case of the Pt/Pd mixtures the 10% of protons taken up by the Pt is enough to produce this coincidence of δ values and hence only a singlet is observed.

This effect is illustrated in Figure 6. Here a pure sample of $[Pd(S_2N_2H)(PMe_2Ph)_2]BF_4$ (**2c**) was titrated against a dilute solution of dbu. The initial AB pattern (a) starts to close up as the chemical shifts move together and when enough protons have been removed from the system the δ values coincide and a singlet is observed (e). As more dbu is added the δ values move apart again until, upon complete deprotonation, the final AX pattern is observed (i).

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