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Nitrogen-15 and Platinum-195 Nuclear Magnetic Resonance Spectroscopy of Platinum Complexes.
Schiff's Base Complexes of the Tridentate Ligand Formed from Ethanolamine-^{15}N and Salicylaldehyde

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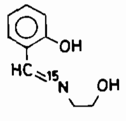
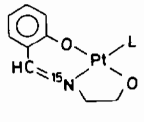
Platinum complexes of the type [Pt(1)L], (1) = the dianion of the Schiff's base formed from ethanolamine-^{15}N and salicylaldehyde, have been synthesized and studied using ^{15}N and ^{195}Pt NMR methods. The values $^1J(^{195}Pt, ^{15}N)$ and $\delta^{15}N$ are strongly dependent upon the trans influence *of the remaining ligand. There is a linear correlation between $^1J(^{195}Pt, ^{15}N)$ and this same coupling in the complexes* trans-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)L]$. *This correlation is interpreted in terms of changes in the σ-bond strength of the platinum–nitrogen bond.*

Introduction

Nuclear Magnetic Resonance (NMR) methods involving the ^{31}P and ^{13}C nuclei are now recognized as valuable aids for determining structures in metal complexes [1]. There is still, however, relatively little reported concerning the ^{15}N NMR characteristics of coordinated nitrogen ligands. We have shown that this method can be of value in determining the site of complexation in some azobenzene [2] and thiocyanate complexes of platinum [3]. Further, in the complexes *trans*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)L]$ we have recently reported a marked effect of the *trans-influence* of L on the values $^1J(^{195}Pt, ^{15}N)$ [4]. In view of the extensive chemistry involving sp^2 hybridized nitrogen ligands we have synthesized the nitrogen-15 enriched tridentate Schiff's base, (1)*, as well as a series of platinum complexes of type (2) and report here the ^{15}N and ^{195}Pt NMR properties of these molecules.



(1)



(2)

Experimental

With the exception of the DMSO compound the complexes gave satisfactory microanalytical data (see Table I).

The DMSO complex proved difficult to free of small traces of excess DMSO (as shown by ^{1}H NMR spectroscopy) and was characterized spectroscopically (^{1}H, ^{13}C, ^{15}N, ^{195}Pt NMR and I.R.) and by its solution molecular weight.

Synthesis

^{15}N-ethanolamine

^{15}N enriched ethanolamine was prepared by the following modification of the Gabriel synthesis: A suspension of β-bromoethanol (7.42 g; 59.4 mmol; Merck 98%) and potassium phthalimide (10.0 g; 54.0 mmol, 99 atom% ^{15}N, Stohler Isotope Chem.) was heated in 35 ml DMF at 140 °C for 4 h. The resulting suspension was filtered and the solid washed with 2 X 50 ml methylene chloride. The combined filtrates were concentrated and then dried under vacuum to afford a yellow oil which slowly crystallized. After stirring with 200 ml of water for several hours the solid was filtered and washed with pentane to afford 8.89 g (86.1% yield), of the alkylated phthalimide, m.p. = 120 °C. The ^{1}H and ^{13}C {^{1}H} spectra were consistent with N-β hydroxyphthalimide. 85% Hydrazine (2.13 g, 42.5 mmol) was then added to a solution of the crude product (8.00 g; 41.6 mmol) in 200 ml absolute ethanol and the reaction mixture heated under reflux for 6 h. Cooling to room temperature was followed by the addition of 20 ml of conc. HCl and stirring for 12 h. The resulting white suspension was filtered and washed with *ca.* 250 ml water. Slow concentration

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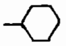
*The symbol (1) in the complexes will henceforth be used to denote the dianionic form of the ligand.

TABLE I. Microanalytical and Molecular Weight Data[a] for the complexes [Pt(1)L].

L	%C	%H	%N	Mol. Weight
PBu$_3$[b]	45.22	6.62	2.37	540
	(44.95)	(6.47)	(2.50)	(560)
P(p-CH$_3$C$_6$H$_4$)$_3$[c]	54.49	4.67	2.27	692
	(54.30)	(4.56)	(2.26)	(664)
P(OEt)$_3$[c,d]	34.31	4.74	2.88	535
	(34.29)	(4.60)	(2.85)	(525)
AsBu$_3$	41.42	5.87	2.25	607
	(41.72)	(6.00)	(2.32)	(605)
As(p-CH$_3$C$_6$H$_4$)$_3$	51.53	4.45	1.97	681
	(50.92)	(4.27)	(2.12)	(708)
C≡N 	39.97	4.50	6,11	504
	(41.11)	(4.31)	(5.99)	(467)
DMSO[e]	29.86	3.44	3.10	453
	(27.46)	(2.77)	(3.20)	(437)
Pyridine	38.49	3.29	6.31	453
	(38.45)	(3.23)	(6.40)	(437)
^{15}NH$_2$(CH$_2$)$_5$CH$_3$	38.51	5.12	6.20	
	(39.13)	(5.25)	(6.30)	
Piperidine	38.00	4.51	6.40	484
	(37.92)	(4.66)	(6.31)	(443)

[a]Calculated values in parenthesis. [b]P 5.79 (5.53). [c]N-15 labelled. [d]P 5.92 (5.90). [e]S 7.17 (7.33).

on a rotary evaporator precipitated additional phthaldiimide. After several concentration–filtration steps, the remaining filtrate (15 ml) was taken to dryness, washed with 5 ml of conc. HCl and then dried *in vacuo*. Washing with 20 ml of absolute hot ethanol was followed by removal of the insoluble hydrazine hydrochloride by filtration. Addition of 40 ml methylene chloride and further concentration gave 3.37 g ethanolamine hydrochloride-^{15}N (83% yield), m.p. = 80 °C, lit. = 82–83 °C. The crude hydrochloride (3.20 g; 32.5 mmol) was first melted and placed under nitrogen in a glove bag. After treatment with finely powdered potassium hydroxide (5.50 g; 97.5 mmol) the reaction mixture was then removed from the nitrogen atmosphere and fractionally distilled (10 torr) to give 1.70 g of β-hydroxyethanolamine-^{15}N (84.5% yield). The compound gave a satisfactory ^{1}H NMR spectrum.

Synthesis of (1)

The Schiff's base was prepared by the condensation of one equivalent of ^{15}NCH$_2$CH$_2$OH with salicylaldehyde as follows: A solution of β-hydroxyethanolamine-^{15}N (1.64 g; 26.5 mmol) in 10 ml of benzene was added to a benzene solution of salicylaldehyde (3.23 g; 26.5 mmol) and the resulting mixture heated under reflux for 30 minutes. Distillation of the solvent gave a yellow oil, which contained quantities of the starting materials. Washing with 250 ml of pentane gave 2.89 g of product (65.7% yield) as an oil. The nitrogen-15 containing Schiff's base was diluted to 100 ml with methylene chloride and aliquots taken as needed for the synthesis of the platinum complexes.

Preparation of the Complexes

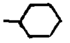
K$_2$PtCl$_4$ (361 mg; 0.870 mmol) was warmed in 5 ml of DMSO and then treated with solid potassium carbonate (355 mg; 3.00 mmol). 5 ml of the methylene chloride solution containing the nitrogen-15 ligand (145 mg; 0.870 mmol) was concentrated, redissolved in 5 ml of DMSO and then added to the above suspension. Heating at 140 °C for 0.75 h affords a brown-red suspension which was treated in various ways depending upon the ligand, L.

a) for L = PBu$_3^n$, P(p-CH$_3$C$_6$H$_4$)$_3$, P(OEt), AsBu$_3^n$, As(p-CH$_3$C$_6$H$_4$)$_3$, C≡N–C$_6$H$_{11}$, SbPh$_3$.

The suspension was cooled to 100 °C and flushed with nitrogen. A stoichiometric quantity of the ligand L was added, without solvent, and the reaction stirred for 0.25 h. The DMSO was then removed *in vacuo* at 60 °C and the residue extracted several times with methylene chloride until a colourless extract was obtained (for L = PBu$_3^n$, AsBu$_3^n$, P(OEt)$_3$, pentane is a better solvent). Filtration through celite-active charcoal was followed by concentration to afford product.

L	*Yield*
PBu$_3^n$	449 mg; 91.9%, yellow oil
P(p-CH$_3$C$_6$H$_4$)$_3$	465 mg; 80.6%, yellow crystals, from Aceton/Water

TABLE II. ^{15}N[a] and ^{195}Pt[b] NMR Data for the Complexes {Pt(1)L}.

L	$^1J(Pt, ^{15}N)$	$\delta ^{15}N$	$\delta ^{195}Pt$
PBu^n_3	294.1	210.1	−2,510
$P(OEt)_3$	303.0	206.6	−2,647
$P(p\text{-}CH_3C_6H_4)_3$	323.6	206.4	−2,511
$AsBu^n_3$	366.2	200.1	−2,207
C≡N –	397.1	191.0	−2,364
$As(p\text{-}CH_3C_6H_4)_3$	413.3	196.1[c]	−2,233
	416.2	195.0[d]	
DMSO	431.0 (broad)	185.6[c]	−2,463
	422.1	185.2[d]	
$SbPh_3$	not observed	195.1	not observed
Piperidine	464.7	173.2	−1,630
$^{15}NH_2(CH_2)_5CH_3$[e]	478.0	173.8	−1,532
Pyridine	494.2	170.1	−1,598

[a] ^{15}N chemical shifts are in ppm relative to an external acidified saturated solution of $^{15}NH_4Cl$, and are considered to be ±0.2 ppm. Coupling constants are in Hz. [b] ^{195}Pt chemical shifts are in ppm relative to an external aqueous solution of Na_2PtCl_6 and are considered to be accurate to ±1 ppm. [c] in $CDCl_3$. [d] in DMSO-d_6 at 30 °C. [e] $^1J(^{195}Pt, ^{15}N)$ for the hexylamine = 316 Hz; $^2J(^{15}N, ^{15}N)$ = 4.4 Hz. $\delta ^{15}N$ for the hexylamine nitrogen = −33.9 ppm.

$P(OEt)_3$	287 mg; 62.9%, yellow crystals, from Pentane
$AsBu^n_3$	449 mg; 85.1%, yellow oil
$As(p\text{-}CH_3C_6H_4)_3$	370 mg; 59.9%, yellow crystals, from Ether/Hexane
$C{\equiv}N\text{-}C_6H_{11}$	276 mg; 67.7%, yellow crystals, from Ether/Pentane
$SbPh_3$	320 mg; 51.6%, yellow crystals, from Ether/Pentane

b) for L = piperidine, $^{15}NH_2(CH_2)_5CH_3$, pyridine.

The suspension was concentrated and the residue treated with a tenfold excess of L (L = piperidine and pyridine) at 80–100 °C for 0.25 h. For L = $^{15}NH_2(CH_2)_5CH_3$, an equivalent amount of the ligand in approximately 10 ml of toluene was used. Cooling was followed by extraction with methylene chloride and concentration to afford products.

L	
piperidine	275 mg; 71.2%, yellow crystals from Ether/Pet. Ether
$NH_2(CH_2)_5CH_3$	280 mg 69.7%, yellow crystals from Ether/Pet. Ether
pyridine	254 mg; 66.6%, yellow crystals from Ether/Pet. Ether

c) For L = DMSO

The suspension was cooled to 60 °C and all of the solvent removed. After drying at room temperature for 12 h *in vacuo* the residue was extracted several times with ether until the extract appeared colorless. The ether solution was then filtered through celite active-charcoal and concentrated to afford 320 mg of product (84% yield).

NMR Measurements

The NMR measurements were made using a Bruker HX-90 spectrometer operating at 9.12 and 19.34 MHz for ^{15}N and ^{195}Pt, respectively. The samples were contained in 10 mm tubes and, unless otherwise specified, were measured as $CDCl_3$ solutions. The ^{195}Pt NMR measurements presented no problems. 50° pulse angles and 0.2 sec acquisition times were routinely employed. However, initial attempts at obtaining ^{15}N signals for the complexes at room temperature were unsuccessful. The potential difficulties involved in ^{15}N NMR spectroscopy have been discussed by Hawkes *et al.* [5] and will not be reviewed here. We circumvented these problems and obtained signals by lowering the sample temperature and thus increasing the contribution of the dipole–dipole relaxation mechanism. Associated with this mechanism is the possibility of a large negative nuclear Overhauser effect, NOE, and indeed for complex (2) with L = $PTol_3$ we find an NOE of 2.92 for a $CDCl_3$ solution at 235 K. An alternative successful approach, involved using room temperature solutions of DMSO-d_6 since this solvent is considerably more viscous than $CDCl_3$. For (2) with L = DMSO we find only a slight variation in $^1J(^{195}Pt, ^{15}N)$, 431 Hz in $CDCl_3$ and 422 Hz in DMSO-d_6 and essentially no change in $\delta ^{15}N$; however, in view of possible complexation of the DMSO we preferred the low temperature approach. Typically, 35° pulse angles and 0.7 sec acquisition times were employed.

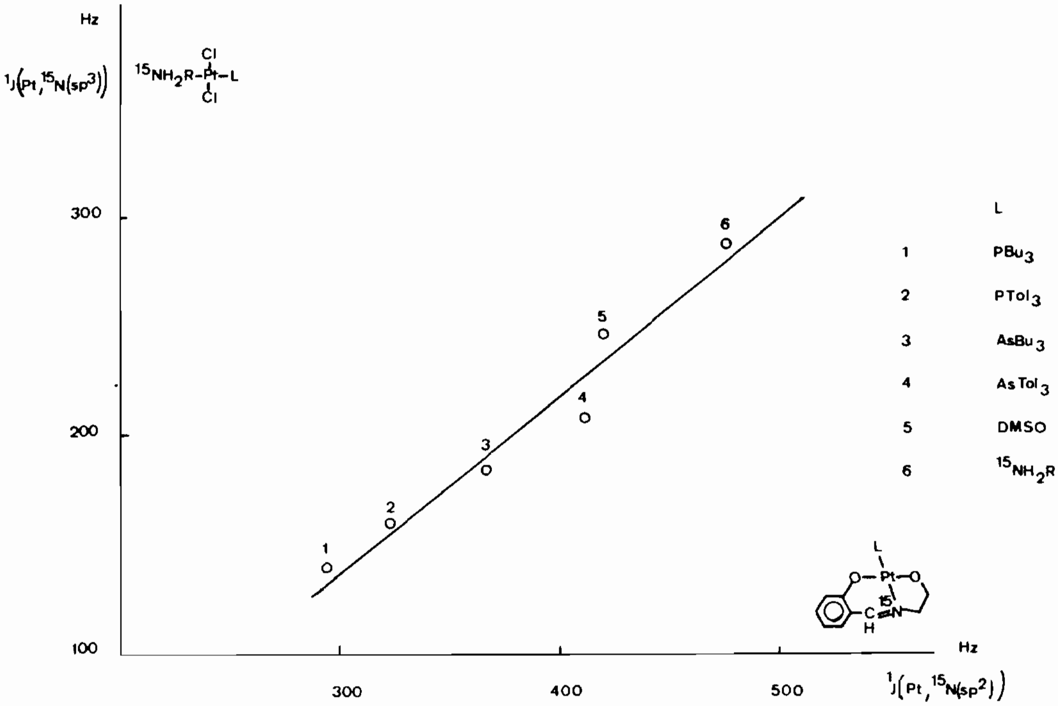


Fig. 1. Plot of $^1J(^{195}Pt, ^{15}N)$ for the complexes *trans*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)L]$ *vs.* $^1J(^{195}Pt, ^{15}N)$ for the complexes [Pt(1)L].

Results and Discussion

Nitrogen-15–Platinum-195 Coupling Constants

The values $^1J(^{195}Pt, ^{15}N)$ for the complexes (2) are shown in Table II and may be seen to range from 294 to 494 Hz. These values are considerably larger than those found for the *trans*-$[(PtCl_2(^{15}N(CH_2)_5CH_3)L]$ complexes (138 Hz to 336 Hz) with similar L ligands [4]. As expected, the one-bond coupling constant shows a dependence on the *trans influence* of the L group with $^1J(^{195}Pt, ^{15}N)$ increasing in the order PR_3 < AsR_3 < DMSO < aliphatic amine < pyridine. In this series the cyclohexyl isonitrile ligand shows a *trans influence* similar to that of the AsR_3 ligands.

In view of the possibility of d_π–p_π back donation to the Schiff's base, it is of interest to compare these one-bond coupling constant data with those for the $^{15}NH_2(CH_2)_5CH_3$ complexes cited above, for the same L ligand. These values are plotted against one another in Fig. 1, and, although there are only six points, the two one-bond couplings are linearly related ($r = 0.98$). It would seem therefore, that either a) the Schiff's base does not compete sufficiently for metal d-electron density to affect changes in possible d_π–d_π back-bonding to L or b) the NMR measurements are not sensitive enough to detect these relative large, but absolutely small, back-bonding changes (compared to the σ effect) or c) the platinum–ligand bonding is primarily σ in nature for both L and the Schiff's base in these complexes. In any case, the changes in $^1J(^{195}Pt, ^{15}N)$ for both series are consistent with an explanation involving changes in the platinum–nitrogen σ-bonding. The σ-bonding argument has also been advanced previously to explain $^1J(^{195}Pt, ^{31}P)$ [6–8] and $^1J(^{195}Pt, ^{13}C)$ [9] data.

Before leaving this subject it should be pointed out that a knowledge of $^1J(^{195}Pt, ^{15}N)$ can have a diagnostic value. The presence of sulfur bound coordinated DMSO* is supported by the observation of a one-bond coupling constant which is too small for an oxygen ligand *trans* to ^{15}N, since oxygen ligands have a very low NMR *trans* influence [7, 10, 11].

Nitrogen-15 Chemical Shifts

Table II shows that $\delta^{15}N$ is also sensitive to the nature of the ligand L, with the total range of shifts encompassing 40 ppm. A plot of $\delta^{15}N$ against $^1J(^{195}Pt, ^{15}N)$ is given in Fig. 2 and shows that there is a common factor affecting these two parameters ($r = 0.97$). We [2, 12] and others [13] have shown that, for sp^2 nitrogen ligands, coordination or protonation of the nitrogen lone-pair results in a large upfield shift of the nitrogen-15 resonance. This

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* ^1H NMR spectroscopy and I.R. measurements support S-bonding.

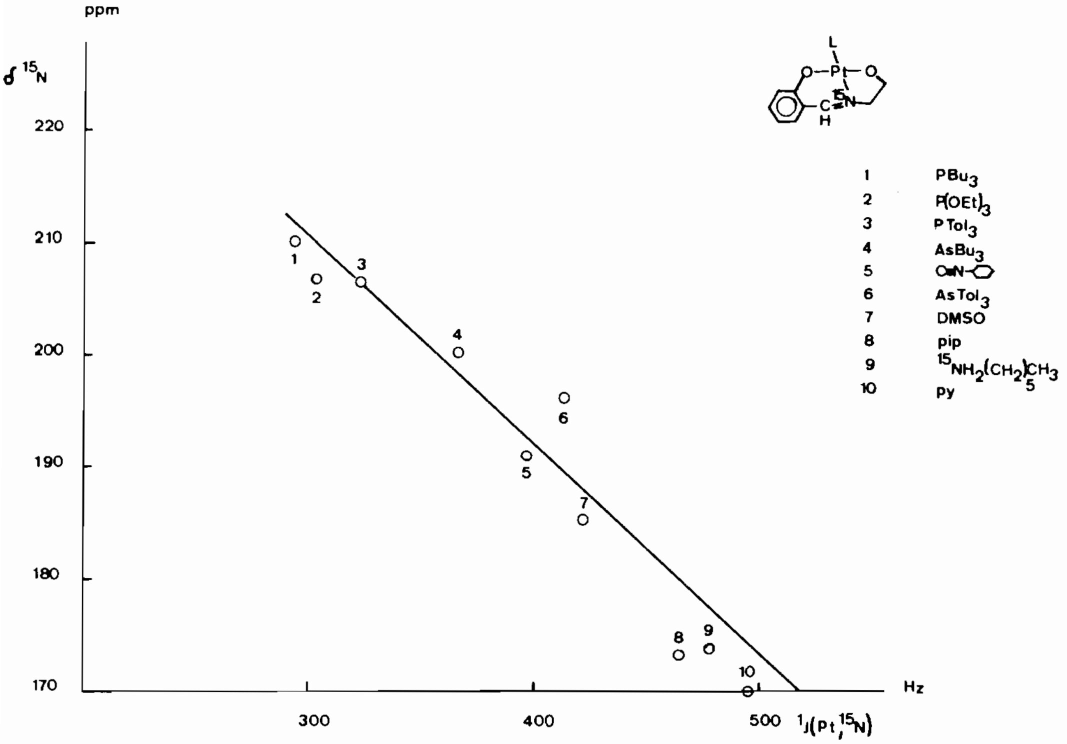

Fig. 2. Plot of $\delta\,^{15}N$ *vs.* $^1J(^{195}Pt, ^{15}N)$ in the complexes [Pt(1)L].

is thought to be related to an increase in the n → π* transition resulting from nitrogen coordination and thus a decrease in the ΔE term in the paramagnetic screening expression [13, 14]. If we take the one-bond coupling constants as a qualitative measure of the changes in bond strength, we see from Fig. 2 that the ^{15}N resonance moves upfield as the platinum–nitrogen bond strength increases. Indeed, using the figure to extrapolate $\delta\,^{15}N$ to a 'zero' one-bond coupling, one finds a chemical shift of 270 ppm in moderate agreement with that of the free ligand, δ = 264. This suggests that the nitrogen chemical shift parameter will prove useful in the study of the interaction of nitrogen ligands with non NMR active metals.

Platinum-195 Chemical Shifts

In Table II we also show the ^{195}Pt chemical shifts for the complexes. These data are referred to Na_2PtCl_6, a low field reference, and can be seen to range over more than 1,000 ppm. This is not unusual as the total range of platinum(II) chemical shifts is known to exceed 5,000 ppm [15, 16]. The displacement of the values $\delta\,^{195}Pt$ to higher field in the order PR_3 > :C≡NC_6H_{11} > AsR_3 > nitrogen ligand has been observed previously for a variety of platinum complexes and has been related, in part, to changes in the energies of d–d transitions [15]. Given a compilation [15] relating the effects of different ligands on $\delta\,^{195}Pt$ it is interesting to ask how (1) affects the position of the platinum signal. This will involve replacing 'three ligands' by two oxygen and one nitrogen ligand. Substituting the tridentate ligand (1) for three chloride ligands (*e.g.* $[PtCl_3(PBu_3)]^-$ → $[Pt(1)(PBu_3)]$*) results in a low field shift in $\delta\,^{195}Pt$ of 1014 ppm ($\delta\,[PtCl_3(PBu_3)]^-$ = –3524, δ $[Pt(1)(PBu_3)]$ = –2510). This is reasonable in that it is known that substitution of one chloride for water in $PtCl_4^{2-}$ (solvolysis of $PtCl_4^{2-}$ in aqueous solution) results in a large downfield shift of approximately 425 ppm [17]. Substitution of trimethylamine for chloride ($[PtCl_4^{2-}]$ → $[PtCl_3(NMe_3)]^-$*) affords a moderate upfield shift 90 ppm, so that a net large deshielding effect, relative to three chloride ligands, is reasonable. The knowledge that coordinated oxygen ligands produce relatively low field platinum shifts provides further evidence supporting S-bonding for [Pt(1)DMSO], whose platinum resonance, –2463 ppm, appears at relatively high field in between the signals for $[Pt(1)(C\equiv NC_6H_{11})]$ and $[Pt(1)(PBu_3)]$.

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* ^1H NMR spectroscopy and I.R. measurements support S-bonding.

*The data for $[PtCl_3PBu_3)]^-$ and $[PtCl_3(NMe_3)]^-$ were converted from reference 15 using Na_2PtCl_6 at 4533 ppm.

Phosphorus-31 NMR

There are three complexes of the form [Pt(1)-(PR$_3$)], R = Bu^n, p-CH$_3$C$_6$H$_4$ and OEt, which are of interest in that the phosphorus-31 couples to both the metal and the enriched nitrogen. The three values ^{1}J(^{195}Pt, ^{31}P), 3885, 4013 and 6139 Hz, respectively, for R = Bu^n, p-CH$_3$C$_6$H$_4$ and OEt are not unusual; however, the values ^{2}J(^{31}P, ^{15}N) are worthy of note. We have observed [4] that this two-bond coupling depends markedly on the geometric orientation of the two atoms with values greater than 50 Hz for ^{2}J(^{31}P, ^{15}N)$_{trans}$ and less than 10 Hz for ^{2}J(^{31}P, ^{15}N)$_{cis}$. Our observed values for the complexes [Pt(1)(PR$_3$)], 50.0, 51.5 and 76.5 Hz for R = Bu, p-CH$_3$C$_6$H$_4$, OEt are in agreement with our previous findings and support the proposed molecular structures for these molecules.

Acknowledgments

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