69. ^{15}N-NMR. and ^{31}P-NMR. Studies of Palladium and Platinum Complexes

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Summary

^{15}N-NMR. parameters for the complexes *trans*-$[MCl_2(^{15}NH_2(CH_2)_5CH_3)L]$ are reported; M = Pt, Pd, L = PBu^n_3, $PMePh_2$, $P(p\text{-}CH_3-C_6H_4)_3$, $AsBu^n_3$, $AsMePh_2$, $As(p\text{-}CH_3C_6H_4)_3$, $NH_2(CH_2)_5CH_3$ and (for Pt) C_2H_4. For both metals, the NMR. parameters depend on the *trans*-influence of the ligand L. The values $^1J(^{195}Pt, ^{15}N)$ vary from 138 to 336 Hz and can be shown to correlate with the values $^1J(^{195}Pt, ^{31}P)$ in the complexes *trans*-$[PtCl_2(PBu^n_3)L]$. There is a linear relation between the ^{15}N chemical shifts in the complexes of the two metals. The reactions of the complexes *sym-trans*-$[M_2Cl_4L_2]$, M = Pd, Pt, L = a tertiary phosphine or arsine, with neutral ligands are described. ^{195}Pt-, ^{31}P- and ^{13}C-NMR. data are reported.

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1. Introduction. - Despite the wealth of transition metal complexes containing nitrogen ligands, there are only a few reports containing ^{15}N-NMR. (I = 1/2) data for coordinated ligands. This stems primarily from the low natural abundance (0.36%) and sometimes unfavorable spin-lattice relaxation characteristics of this nucleus [1]. Further, signal nulling has been observed under conditions of broadband ^1H-decoupling when the nuclear *Overhauser* effect approaches minus one [2]. Of those complexes for which ^{15}N-measurements have been made, the iron derivatives have received the most attention [3] due to their biological relevance; however, there have been reports for platinum [4], rhodium [5], cadmium [6] and titanium [7] complexes. Several of the studies are concerned with the metal-nitrogen coupling [3-6]. Although $^1J(M, ^{15}N)$ is often relatively small, due to the small gyromagnetic ratios of the nuclei involved or the relatively small magnitudes of the expectation values $|\Psi(o)|^2$, or both, occasionally $^1J(M, ^{15}N)$ is sufficiently large to have a diagnostic value. This is especially true for ^{195}Pt (I = 1/2, natural abundance = 33.7%). The observed $^1J(^{195}Pt, ^{15}N)$ values in some ammonia complexes of platinum [4c] as well as in *o,o'*-dihydroxyazobenzene [4b] and dodecylamine complexes [4a] have been used as probes for structure and bonding. In contrast to ^{15}N, the measurement of ^{31}P- (I = 1/2, 100% natural abundance) NMR. spectra of

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metal complexes poses little or no technical difficulty. The subject of ^{31}P-NMR. in transition metal chemistry has been reviewed twice [8] [9] and, in particular, there exists an abundant literature on phosphine complexes of platinum.

As part of our study of the NMR. *trans* influence [10] in platinum chemistry, we have prepared and synthesized a series of hexyl amine complexes of platinum of the type *trans*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)L]$ enriched with >95% ^{15}N. These molecules were selected for their favorable nuclear magnetic resonance properties (the presence of protons on nitrogen is expected to result in both favorable nuclear *Overhauser* [2] and relaxation [1] characteristics) as well as their ease of preparation. Additionally, this set of molecules can be readily compared with analogous phosphine complexes of the type *trans*-$[PtCl_2(PBu^n_3)L]$ for which we have obtained ^1J(Pt, P) data *via* $^{31}P\{^1H\}$-NMR. spectroscopy. This is potentially an interesting comparison as the platinum phosphorus bond may contain both σ and π (d-d) character whereas the Pt, N interaction for our amines is essentially σ in nature. We report here our ^{15}N-, ^{31}P- and other NMR. data for these platinum(II) and analogous palladium(II) compounds.

2. Experimental. - NMR. spectra were measured on a *Bruker* HX-90E spectrometer operating in *Fourier* transform mode. ^{15}N, ^{195}Pt, ^{13}C and ^{31}P data were obtained at 9.12, 19.30, 22.63 and 36.43 MHz respectively on $CDCl_3$ solutions at ~30° under conditions of ^{1}H decoupling. Chemical shifts are considered accurate to ±0.1 ppm whereas coupling constants are accurate to ±1.5 Hz. The ^{15}N measurements were made on hexylamine complexes containing >95 atom % enriched ^{15}N. In some cases we were successful in obtaining data from samples containing ^{15}N in natural abundance and these agreed with those obtained from the enriched materials. When measured, we found nuclear *Overhauser* enhancements of about −4 which correspond to the theoretical maximum expected for ^{15}N, ^{1}H dipole-dipole relaxation [2].

Abbreviations: i.V. = in vacuo, RT. = room temperature.

The mixed complexes were generally synthesized *via* bridge splitting reactions involving the addition of two equivalents of $NH_2(CH_2)_5CH_3$ to one equivalent of *sym-trans*-$[M_2Cl_4L_2]$ in methylene chloride solution, L = a trisubstitued phosphine or arsine. The products gave satisfactory spectroscopic and microanalytical data *(Table 1)*. In some cases the *trans*-$[PdCl_2(NH_2(CH_2)_5CH_3)L]$ complexes were not stable over long periods of time and this will be discussed further in the next section. Typically this reaction was performed as follows:

Preparation of trans-*$[PtCl_2(NH_2(CH_2)_5CH_3)(PBu^n_3)]$.* A solution of 108 mg (1.068 mmol) hexylamine in 20 ml CH_2Cl_2 was added dropwise to a solution of 500 mg (0.534 mmol) *sym-trans*-$Pt_2Cl_4(PBu^n_3)_2$ in 20 ml CH_2Cl_2, at −20°. The resulting clear yellow solution was concentrated i.V. forming a yellow oil which was dissolved in 3 ml of ether and then filtered. Concentration of the ether solution followed by drying i.V. gave the product as a yellow oil. Yield: 586 mg (98%). The remaining derivatives were prepared as shown below:

Preparation of trans-*$[PdCl_2(NH_2(CH_2)_5CH_3)_2]$.* A solution of 390 mg (3.86 mmol) hexylamine in 20 ml CH_2Cl_2 was added to a solution of 500 mg (1.93 mmol) $PdCl_2(CH_3CN)_2$ in 80 ml CH_2Cl_2. The resulting pale yellow solution was concentrated i.V. and the residue treated with 20 ml of ether/petroleum ether (30-60°) 1:10 to give the product as yellow needles. Yield: 700 mg (95.5%).

Preparation of cis *and* trans-*$[PtCl_2(NH_2(CH_2)_5CH_3)_2]$.* 380 mg (3.76 mmol) $NH_2(CH_2)_5CH_3$ was added to a suspension of 500 mg (1.88 mmol) $PtCl_2$ in 50 ml CH_2Cl_2. The resulting suspension was then stirred at RT. for 72 hours. A yellow solution above a white precipitate remained. The solution was filtered and the precipitate washed with 30 ml 0.1M HCl to remove ionic compounds and then recrystallized from acetone to give *cis*-$[PtCl_2(NH_2(CH_2)_5CH_3)_2]$. Yield: 280 mg (32%). The yellow filtrate was extracted with 0.1M HCl and then dried over $MgSO_4$. Evaporation of the solvent followed by washing with ether and drying i.V. gave *trans*-$[PtCl_2(NH_2(CH_2)_5CH_3)_2]$. Yield: 260 mg (31%). The

Table 1. *Microanalytical Data for the Amine*[a]) *Complexes*

Compound	Elemental Analysis: % Found (% Calculated)				
	C	*H*	*N*	*Cl*	*Mol. Wt.*[b])
trans-$[PdCl_2(amine)_2]$	38.23 (37.96)	8.11 (7.96)	7.45 (7.37)	18.65 (18.68)	388 (380)
trans-$[PdCl_2(amine)(AsBu^n_3)]$[c])	41.08 (41.12)	7.88 (8.05)	2.29 (2.85)	14.18 (13.49)	515 (600)
trans-$[PdCl_2(amine)(P(p\text{-}CH_3C_6H_4)_3)_2]$	55.94 (55.64)	6.46 (6.23)	2.43 (2.40)	11.93 (12.17)	598 (583)
trans-$[PdCl_2(amine)(PMePh_2)]$	47.93 (47.67)	6.01 (5.90)	2.91 (2.92)	14.52 (14.81)	486 (479)
trans-$[PdCl_2(amine)(PBu^n_3)]$	44.85 (44.96)	8.81 (8.81)	2.82 (2.91)		491 (481)
trans-$[PdCl_2(amine)(PBu^n_3)]$[c])	44.91 (44.87)	8.72 (8.79)	3.11 (3.11)		
cis-$[PtCl_2(amine)_2]$	30.80 (30.77)	6.50 (6.46)	6.09 (5.98)	15.28 (15.14)	
trans-$[PtCl_2(amine)_2]$	31.42 (30.77)	6.36 (6.46)	6.06 (5.98)	15.64 (15.14)	531 (469)
cis-$[PtCl_2(amine)(C_2H_4)]$[c])	24.13 (24.25)	4.89 (4.83)	3.70 (3.79)	18.00 (17.89)	385 (396)
trans-$[PtCl_2(amine)(As(p\text{-}CH_3C_6H_4)_3)_2]$	44.96 (45.33)	5.19 (5.07)	2.06 (1.96)	10.64 (9.91)	703 (715)
trans-$[PtCl_2(amine)(AsMePh_2)]$	37.36 (37.33)	4.61 (4.62)	2.29 (2.29)	11.54 (11.60)	629 (611)
trans-$[PtCl_2(amine)(AsBu^n_3)]$	35.16 (35.24)	6.91 (6.90)	2.15 (2.28)	11.49 (11.56)	621 (613)
trans-$[PtCl_2(amine)(P(p\text{-}CH_3C_6H_4)_3)]$[c])	48.58 (48.22)	5.04 (5.40)	2.12 (2.23)	10.27 (10.54)	689 (673)
trans-$[PtCl_2(amine)(PMePh_2)]$[c])	40.05 (40.15)	5.03 (4.97)	2.63 (2.64)	12.23 (12.47)	582 (586)
trans-$[PtCl_2(amine)(PBu^n_3)]$[c])[d])	37.99 (37.90)	7.57 (7.42)	2.64 (2.63)	12.19 (12.43)	583 (571)
cis-$[PtCl_2(PBu^n_3)(DMSO)]$[e])	30.96 (30.78)	6.38 (6.09)		13.20 (12.98)	557 (546)

[a]) Amine = $NH_2(CH_2)_5CH_3$.

[b]) Measured in CH_2Cl_2.

[c]) Determined for the ^{15}N enriched material.

[d]) Phosphorus analysis: 5.26 (5.43).

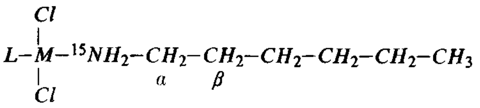
[e]) Phosphorus analysis: 5.84 (5.67).

trans derivative is quite soluble in most organic solvents, whereas the *cis* analogue is only sparingly soluble (*e.g.* ≈ 50 mg/100 ml of acetone).

Preparation of trans-*$[PtCl_2(C_2H_4)(^{15}NH_2(CH_2)_5CH_3)]$.* 79.3 mg (0.780 mmol) of $^{15}NH_2(CH_2)_5CH_3$ dissolved in 20 ml CH_2Cl_2 was added dropwise to a stirred solution of 300 mg (0.780 mmol) $K[PtCl_3(C_2H_4)]$ in 15 ml of methanol at −10°. Stirring was continued for 15 min then the combined solvents were removed *in vacuo*. The resulting material was treated with 5 ml of Et_2O, filtered and then concentrated to give the product in essentially quantitative yield as a yellow oil (which solidifies on cooling to icewater temperature).

Preparation of cis-*$[PtCl_2(C_2H_4)(NH_2(CH_2)_5CH_3)]$.* A solution of 210 mg (0.543 mmol) *trans*-$[PtCl_2(C_2H_4)(NH_2(CH_2)_5CH_3)]$ in 50 ml of pentane, under approximately 1 atm. of C_2H_4, was irradiated

Table 2. *NMR. Data*a) *for the Complexes*



$$L-\overset{Cl}{\underset{Cl}{M}}-{}^{15}NH_2-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-CH_2-CH_2-CH_2-CH_3$$

L	^1J(Pt,N)	δ^{15}N b)	δ^{195}Pt c)	δ d)	
				C_α	C_β
M = Pt					
PBu^n_3 e)	138.3	+ 0.7	−3.612	44.0 (n.o.)	31.5 (22.1)
$PMePh_2$ f)	155.9	− 0.4	−3.597	44.3 (12.5)	31.4 (21.3)
$P(p\text{-}CH_3C_6H_4)_3$ g)	158.8	− 0.2	−3.489	44.4 (n.o.)	31.5 (n.o.)
$AsBu^n_3$	183.8	− 4.8	−3.328	44.4 (n.o.)	31.4 (26.4)
$AsMePh_2$	208.8	− 6.8	−3.324	44.8 (12.1)	31.3 (29.4)
$As(p\text{-}CH_3C_6H_4)_3$	207.4	− 6.3	−3.322	45.0 (11.8)	31.3 (n.o.)
$^{15}NH_2(CH_2)_5CH_3$	286.8	−44.6	−2.130	46.6 (14.7)	31.1 (32.3)
C_2H_4	283.9	− 3.7	−3.006	45.9 (14.0)	31.0 (30.9)
Cl (*cis*-NH_2R) i)	336	-	−2.215		
Cl (*cis*-C_2H_4) j)	295.6	−32.9	−2.805		
M = Pd					
PBu^n_3		− 4.7		43.3	31.4
$PMePh_2$		− 5.9		43.5	31.3
$P(p\text{-}CH_3C_6H_4)_3$		− 5.9		43.5	31.3
$AsBu^n_3$		− 7.8		43.7	31.4
$AsMePh_2$		− 9.7		44.0	31.3
$As(p\text{-}CH_3C_6H_4)_3$		− 9.2			
$^{15}NH_2(CH_2)_5CH_3$		−33.2		45.2	31.3

a) Chemical shifts are considered to be ±0.1 ppm; coupling constants ±1.5 Hz. Data for $CDCl_3$ solutions.

b) Relative to aqueous $^{15}NH_4Cl$.

c) Relative to Na_2PtCl_6 (a negative sign indicates an upfield shift).

d) ^nJ(Pt,C) values in parenthesis.

e) ^1J(Pt,P) = 3377 Hz.

f) ^1J(Pt,P) = 3509 Hz.

g) ^1J(Pt,P) = 3575 Hz.

h) Disproportionates in solution.

i) The data are for *cis*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)_2]$ and were obtained on a DMSO-d_6 solution.

j) These data are for *cis*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)(C_2H_4)]$.

with UV. light for 1 h. An additional 10 ml pentane was added to the resulting pale yellow suspension, and this was stirred overnight. Filtration and drying i.V. was followed by recrystallization from acetone/ether to give the product. Yield: 153 mg (73%).

Preparation of $^{15}NH_2(CH_2)_5CH_3$. We have employed the following variation of the *Gabriel* synthesis: A suspension of 17.7 g (0.107 mol) hexylbromide *(Fluka, purum)*, 20.0 g (0.107 mol) potassium phthalimide (96.2 atom % ^{15}N, *Bio-Rad Laboratories*, Richmond, Calif.) and 55 ml DMF was heated for 5 h at 140°. The resulting suspension was poured onto 110 g of ice and allowed to stand for 12 h. Extraction with 6×20 ml CH_2Cl_2 was followed by washing with a) 1N KOH b) 0.5N HCl c) H_2O(NaCl) and then drying over $MgSO_4$. Treatment of the solution with active charcoal was then followed by filtration through *Celite* and concentration to give 20.8 g (83%) of ^{15}N-hexyl-phthalimide. The hexyl phthalimide was dissolved in 80 ml of abs. ethanol and then 6.2 g (0.105 mol) 85% hydrazine hydrate added at room temperature. Refluxing for 2 h was followed by cooling and the addition of 25 ml conc. chlorhydric acid. The resulting suspension was stirred for 2 h, 200 ml of H_2O were added, and the reaction mixture stirred for an additional 12 h. The suspension which remains was filtered twice and the solids washed with water. Removal of the solvent i.V. gave a yellow solid which was treated with 40% KOH-solution and then extracted into 100 ml of ether. Drying was followed by concentration and distillation (over KOH) to give 7.0 g (77%) of ^{15}N-hexylamine (b.p. 60°/50 Torr). The overall yield of ^{15}N-hexylamine from potassium phthalimide is 64%. The spectroscopic data (IR., ^{13}C- and ^{15}N-NMR.) are consistent with those expected for this molecule.

3. NMR. Results and Discussion.

- 3.1. *Coupling Constants.* In *Table 2* we show the various NMR. parameters for the platinum and palladium complexes of hexylamine. A typical $^{15}N\{^1H\}$-NMR. spectrum for these molecules is shown in *Figure 1.* The coupling of the nitrogen to phosphorus affords a doublet with a separation of ≈50 Hz, which is indicative of a *trans* orientation of these two atoms [11]. This main doublet is flanked by the ^{195}Pt satellites whose separation provides the value $^1J(^{195}Pt, ^{15}N)$.

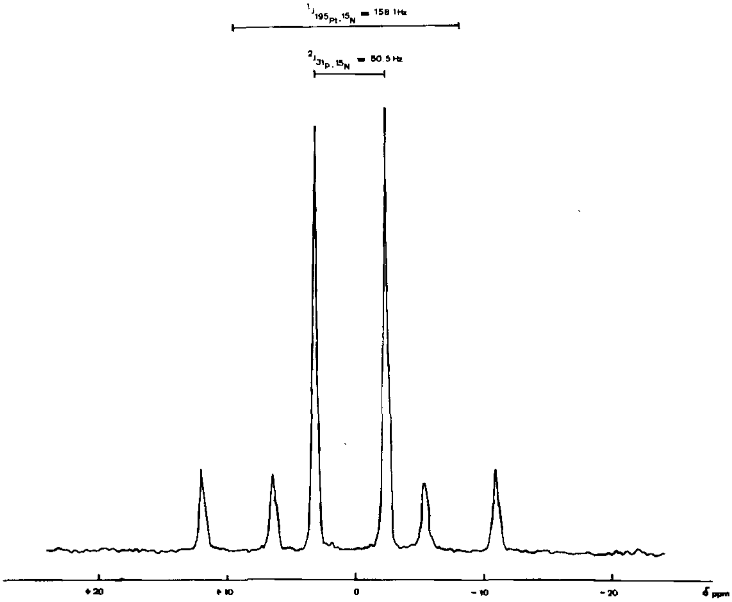
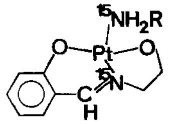


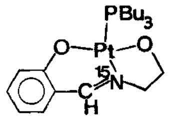
Fig. 1. *The* $^{15}N\{^1H\}$*-FT-NMR. spectrum of* trans-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)(P(p\text{-}CH_3C_6H_4)_3)]$ (100 mg/ml $CDCl_3$; 77000 10 μs pulses)

Table 2 shows an obvious dependence of ${}^1J({}^{195}\mathrm{Pt}, {}^{15}\mathrm{N})$ on the ligand *trans* to the nitrogen, with the smallest value, 138 Hz, observed for $\mathrm{L} = \mathrm{PBu}^n_3$ and the largest, 287 Hz, for $\mathrm{L} = {}^{15}\mathrm{NH_2(CH_2)_5CH_3}$. The total range increases to 336 Hz when the *cis*-dichloro complexes are included. Thus the total change in ${}^1J({}^{195}\mathrm{Pt}, {}^{15}\mathrm{N})$ can amount to more than a factor of two. The related phosphine complexes *trans*-$[\mathrm{PtCl_2(PBu^n_3)L}]$ *(Table 3)* do not show this change to the same extent, although the general trend is the same with smaller values of ${}^1J({}^{195}\mathrm{Pt}, {}^{31}\mathrm{P})$ for ligands with a large *trans*-influence. The relative *trans*-influence of these ligands, from our data, does not differ significantly from that reported for other systems [12]. In *Figure 2* we plot these two one-bond couplings against one another and obtain a straight line (r = 0.98). It is noteworthy that the complexes (1), which are not strictly related to our chloro complexes, show ${}^1J({}^{195}\mathrm{Pt}, {}^{15}\mathrm{N})$ and ${}^1J({}^{195}\mathrm{Pt}, {}^{31}\mathrm{P})$ values which correlate well with our data.



1a

resp.



1b

${}^1J({}^{195}\mathrm{Pt}, {}^{15}\mathrm{N}) = 319$ Hz
${}^1J({}^{195}\mathrm{Pt}, {}^{31}\mathrm{P}) = 3836$ Hz

The significance of this plot is best appreciated if one considers those factors which contribute to a one-bond coupling.

Eq. (1) shows the *Fermi* contact term, which is generally thought to govern changes in one-bond interactions.

$$ {}^1J(\mathrm{Pt,X}) \propto \gamma_{\mathrm{Pt}}\gamma_{\mathrm{X}} |\Psi_{\mathrm{Pt6s}}(\mathrm{o})|^2 |\Psi_{\mathrm{X_{ns}}}(\mathrm{o})|^2 \pi_{\mathrm{Pt,X}} \qquad (1)$$

$\pi_{\mathrm{Pt,X}}$ is the polarizability and is usually written as eq. (2). The coefficients, $\mathrm{C_s}$, are those of the valence s-atomic orbitals

$$ \pi_{\mathrm{Pt,X}} = \sum_{i}^{\mathrm{occ.}} \sum_{j}^{\mathrm{unocc.}} (\varepsilon_j - \varepsilon_i)^{-1} \mathrm{C_{isPt}} \mathrm{C_{jsPt}} \mathrm{C_{isX}} \mathrm{C_{jsX}} \qquad (2)$$

used in the linear combination to make up either an occupied or unoccupied molecular orbital (M.O.). The constants, γ, are the gyromagnetic ratios and the $|\Psi(\mathrm{o})|^2$ terms are the valence shell s-election densities for the platinum and X atoms. Eq. (1) is often simplified as shown in eq. (3) where the α^2-terms represent the percentage s-character in

$$ {}^1J(\mathrm{Pt,X}) \propto \gamma_{\mathrm{Pt}}\gamma_{\mathrm{X}} |\Psi_{\mathrm{Pt6s}}(\mathrm{o})|^2 |\Psi_{\mathrm{X_{ns}}}(\mathrm{o})|^2 \alpha^2_{\mathrm{Pt}}\alpha^2_{\mathrm{X}}/\Delta \mathrm{E} \qquad (3)$$

the orbitals used by platinum and X atoms to form the Pt-X bond, and ΔE is the mean triplet excitation energy approximation. For a related series of molecules the $|\Psi(\mathrm{o})|^2$ terms are not considered to vary significantly so that ${}^1J({}^{195}\mathrm{Pt,X})$ can be seen to depend on the polarizability, $\pi_{\mathrm{Pt,X}}$ (eq. (1)).

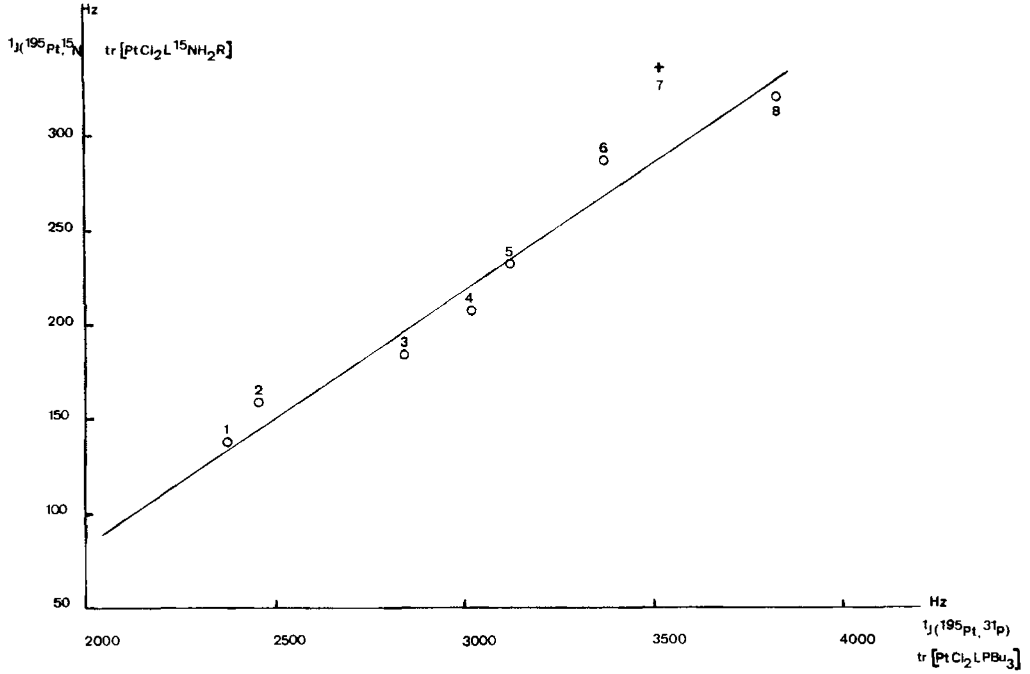


Fig. 2. *Plot of* $^1J(^{195}Pt,^{15}N)$ *against* $^1J(^{195}Pt,^{31}P)$. The value of $^1J(^{195}Pt,^{15}N)$ for point 5 (232 Hz) is for *trans*-[PtCl$_2$(^{15}NH$_3$)(DMSO)] [2c]. The value of $^1J(^{195}Pt,^{31}P)$ for point 3 (2846 Hz) is for *trans*-[PtCl$_2$(AsEt$_3$)(PBu$^n_3$)].

1: L = PBu$_3$; 2: L = P(*p*-CH$_3$C$_6$H$_4$)$_3$; 3: L = AsBu$_3$; 4: L = As(*p*-CH$_3$C$_6$H$_4$)$_3$; 5: L = (CH$_3$)$_2$SO; 6: L = ^{15}NH$_2$R, R = (CH$_2$)$_5$CH$_3$; 7: L = *cis*-PtCl$_2$(^{15}NH$_2$R)$_2$ resp. *cis*-PtCl$_2$(PBu$_3$)$_2$; 8: corresponds to **1a** and **1b**.

At this point further simplification, with confidence, becomes difficult. Making the ΔE approximation[2]) does lead to a useful simplification since the $^1J(^{15}N,H)$ couplings, which are known to be relatable to the a^2_N term [13], are all 71-74 Hz (sp^3 N-atom; $^{15}NH_4^+ = 73.2$ Hz, $PhNH_3^+ = 76.0$ [13]) in the complexes of both platinum and palladium. Thus, we conclude that the a^2_N term in $J(^{195}Pt,^{15}N)$ of eq. (3) (or the C_{isN} coefficient in eq.(2)) is not changing and that the a^2_{Pt} term controls the changes in $^1J(^{195}Pt,^{15}N)$. Since the two couplings, $^1J(^{195}Pt,^{15}N)$ and $^1J(^{195}Pt,^{31}P)$, are linearly related, it would seem that the a^2_{Pt} term also dominates changes in $^1J(^{195}Pt,^{31}P)$. This conclusion has been reached on the basis of other evidence [14]. As it is generally accepted that there is no metal-nitrogen π back-bonding in complexes of primary amines, our data suggest either a constant π contribution (where the constant may be zero) or one that is linearly related to the amount of π-bonding. Given the varying π-bonding capabilities of the phosphine, arsine, sulfur and nitrogen ligands, L, we would not expect a linear change in the dπ-dπ Pt-P interaction and therefore we favour the former explanation. We

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[2]) This is not a readily justifiable assumption, but it is commonly made. There is some experimental evidence for the dominance of the a^2 terms [8].

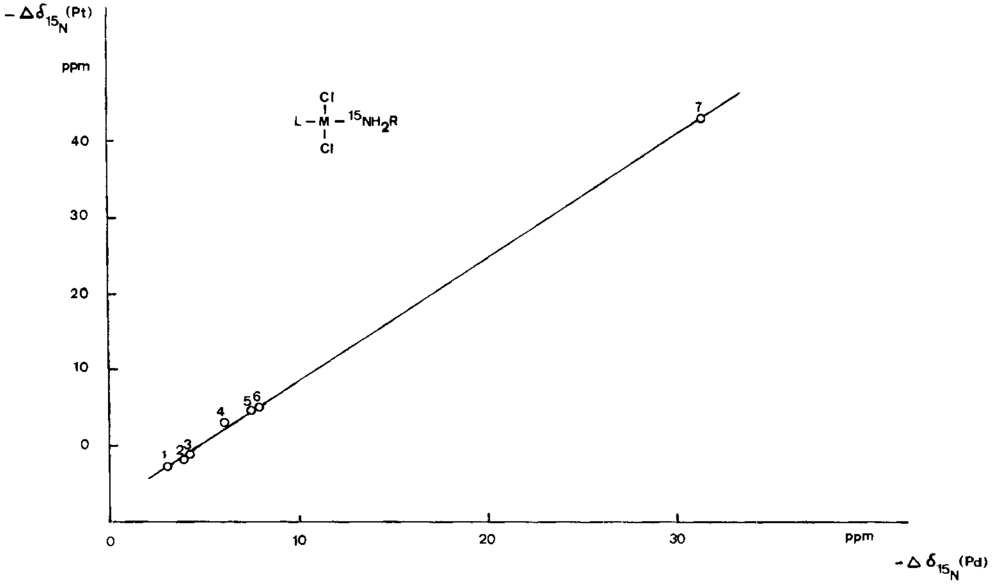


Fig. 3. *Plot of the coordination chemical shift, $\Delta\delta^{15}N$, for the platinum complexes against $\Delta\delta^{15}N$ for the palladium complexes*

1: L = PBu_3; 2: L = $PTol_3$; 3: L = PPh_2Me; 4: L = $AsBu_3$; 5: L = $AsTol_3$; 6: L = $AsPh_2Me$; 7: L = $^{15}NH_2R$, R = $(CH_2)_5CH_3$

conclude that, although there may be a dπ-dπ interaction in the phosphine complexes, this component does not vary much in our series of molecules.

3.2. *Chemical Shifts.* In *Table 2* we give the ^{15}N chemical shifts for our $[MCl_2(^{15}NH_2(CH_2)_5CH_3)L]$ complexes of platinum and palladium. For the compounds of both metals the ^{15}N chemical shift varies as a function of L over a range of approximately 40 ppm. A plot of the nitrogen coordination chemical shift, $\Delta\delta^{15}N_{Pt}$, against $\Delta\delta^{15}N_{Pd}$ *(Fig. 3)* is linear thus suggesting that the same factors are affecting the changes in these parameters. This dependence of the nitrogen chemical shift on the *trans* ligand, L, may provide a useful structural probe for palladium complexes of nitrogen ligands since metal-ligand coupling constants are not observed.

The ^{195}Pt chemical shifts *(Table 2)* are also sensitive to the nature of the ligand L and cover a range of about 1500 ppm. This type of chemical shift change, for heavy metals in general, and for ^{195}Pt in particular, is not unusual. The total range of chemical shifts for platinum(II) is about 5,000 ppm [15] with softer ligands such as arsine, phosphine, cyanide and iodide producing large high field shifts relative to the harder Cl^-, Br^-, nitrogen and oxygen ligands. In any case it is noteworthy that changing a single ligand can induce a very pronounced change in the metal chemical shift. A plot of the $\Delta\delta^{15}N$ values against the $\delta^{195}Pt$ data is shown in *Figure 4.* A correlation is certainly observable, although there are deviations. It would seem that there are several ways of monitoring the comparative influence of

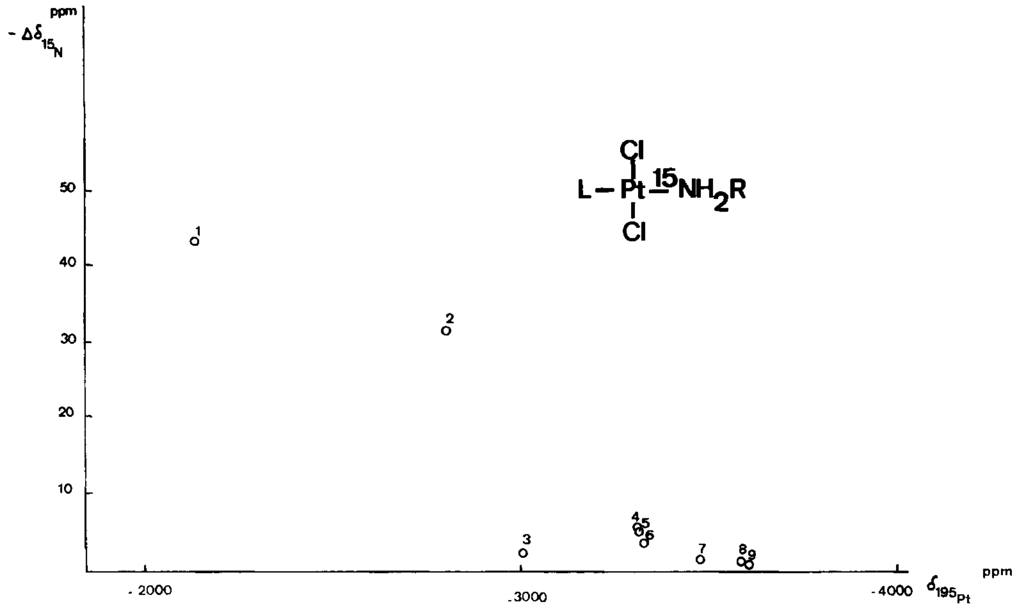


Fig. 4. *Plot of the coordination chemical shift, $\Delta\delta^{15}N$ against $\delta^{195}Pt$ for the complexes* trans-*[$PtCl_2(^{15}NH_2(CH_2)_5CH_3)L$]*

1: L = $^{15}NH_2R$, R = $(CH_2)_5CH_3$; 2: L = *cis*-C_2H_4 Komplex; 3: L = C_2H_4; 4: L = $AsTol_3$; 5: L = $AsPh_2Me$; 6: L = $AsBu_3$; 7: L = $PTol_3$; 8: L = PPh_2Me; 9: L = PBu_3

the ligand L on NMR. chemical shifts and that these correlate roughly linearly with one another.

The complexity of the paramagnetic screening contribution, which is thought to be responsible for changes in the chemical shifts of nuclei other than hydrogen, prevents a detailed analysis of our ^{15}N- and ^{195}Pt-shift data. However, an empirical understanding of the effects of various ligands on chemical shifts should add to the chemist's armament of structural methods.

Table 3. ^{31}*P-NMR. Data*[a]) *for the Complexes trans*-[$PtCl_2L(PBu^n_3)$]

L	$^1J(Pt,P)$	$\delta^{31}P$
$NH_2(CH_2)_5CH_3$	3375	3.0 (9.9)
$(CH_3)_2SO$	3121 (3412[b]))	3.2 (−3.2)
As(*p*-$CH_3C_6H_4)_3$	3022 (3359[b]))	1.3 (0.3)
$AsEt_3$	2846 (3466[b]))	5.5 (−2.6)
P(*p*-$CH_3C_6H_4)_3$	2457 (3822[c]), 3389[d]))	4.4 (0.9)
PBu^n_3	2377 (3519[b])[e]))	

[a]) Coupling constants in Hz, chemical shifts are relative to H_3PO_4.
[b]) $^1J(Pt,P)$ values for the corresponding *cis* isomers.
[c]) *cis* isomer, P(*p*-$CH_3C_6H_4)_3$ *trans* to Cl.
[d]) *cis* isomer PBu^n_3, *trans* to Cl.
[e]) *G. Balimann*, PhD thesis, ETH Zürich 1977.

4. Bridge Splitting Reactions. - Throughout this study we have extensively utilized the reaction shown in eq. (4).

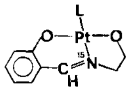
$$sym\text{-}trans\text{-}[Pt_2Cl_4L_2] + 2\,A \longrightarrow 2\,[PtCl_2LA] \qquad (4)$$

L = a trialkyl or triaryl arsine or phosphine; A = $NH_2(CH_2)_5CH_3$ or an L type ligand

The monomeric complex which results may have either *cis* or *trans* geometry and, according to a recent report [16], might disproportionate. Although we have observed disproportionation only for $[PdCl_2(NH_2(CH_2)_5CH_3)(arsine)]$ derivatives, we have found that both geometric isomers often exist in solution with the *trans* forming first and isomerizing quickly, slowly, or scarcely, depending upon the nature of L. Thus, although we have been successful in determining NMR. and microanalytical data (as a purity check) for our complexes, we have not always isolated both isomeric forms. A typical example is the case for L = PBu^n_3, A = $(CH_3)_2SO$, (DMSO). Addition of slightly less than two equivalents of DMSO dissolved in $CDCl_3$ to a $CDCl_3$ solution of the dimer affords, approximately 5 min after mixing, a single product to which we assign the structure *trans*-$[PtCl_2(DMSO)(PBu^n_3)]$, $^1J(Pt,P) = 3121$ Hz, $\delta^{31}P = 3.0$ ppm, $^3J(Pt,CH_3) = 12.1$ Hz, $\delta CH_3 = 3.15$ ppm.

This complex slowly isomerizes (93% complete after 24 h) when left in solution at room temperature to *cis*-$[PtCl_2(DMSO)(PBu^n_3)]$, $^1J(Pt,P) = 3412$ Hz, $\delta^{31}P = 9.9$ ppm, $^3J(Pt,CH_3) = 22.9$ Hz, $\delta CH_3 = 3.55$ ppm. These NMR. data are fully consistent with the *trans* and *cis* isomers, respectively, with the coupling constants showing the expected dependence upon the nature of the *trans* ligand. The magnitude of the $^3J(Pt,CH_3)$ values are consistent with DMSO coordination *via* sulfur [17]. Confirmation of the geometric orientation of the ligands in complexes containing the ^{15}N ligand and a phosphine derivative followed from the observed

Table 4. *$^2J(^{31}P,^{15}N)$ Values in Some Complexes*

$MCl_2(^{15}NH_2(CH_2)_5CH_3)L$					
L	$^2J(^{31}P,^{15}N)$ [Hz]	L	$^2J(^{31}P,^{15}N)$ [Hz]	L	$^2J(^{31}P,^{15}N)$ [Hz]
M = Pt		M = Pd			
PBu^n_3	47	PBu^n_3	50	PBu^n_3 d)	50
$PMePh_2$	52	$PMePh_2$	54	$P(p\text{-}CH_3C_6H_4)_3$ d)	53
$P(p\text{-}CH_3C_6H_4)_3$	50	$P(p\text{-}CH_3C_6H_4)_3$	54	$P(OEt)_3$ d)	76
		$Pt(^{15}NO_2)_2(PBu^n_3)_2$ a)			
		cis	61 b), 3 c)		
		trans	3		
		$Pt(^{15}NCS)_2(P(OPh)_3)_2$ e)			
		cis	95 b), 7 c)		

a) *R. W. Kunz & P. S. Pregosin*, unpublished results.
b) P *trans* to ^{15}N.
c) P *cis* to ^{15}N.
d) *H. Motschi & P. S. Pregosin*, unpublished results.
e) See [11].

$^2J(^{31}P, ^{15}N)$ values which are often 50-70 Hz when the atoms are *trans* to one another and 10 Hz or less when they are in a *cis* orientation (see *Table 4*). Similar isomerization reactions occur for A = $AsEt_3$, $As(p\text{-}CH_3C_6H_4)_3$ and $P(p\text{-}CH_3C_6H_4)_3$, L = PBu_3^n and one-bond platinum-phosphorus coupling constants and ^{31}P chemical shifts for both the *cis* and *trans* isomers may be found in *Table 3*.

In summation, we have used multinuclear NMR. methods to increase our understanding of the structure and bonding in some square planar complexes of platinum and palladium. In particular ^{15}N-NMR. methods have been used to help evaluate the relative contribution of phosphine-metal $d\pi$-$d\pi$ bonding in simple phosphine complexes of platinum(II). A variety of NMR. techniques have been used to monitor the isomerization of the complexes *trans*-MCl_2LA to their *cis* counterparts.

Further studies relating our ^{15}N-data for the hexylamine system with similar measurements for sp^2 nitrogen derivatives are currently in progress.

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