110. A Comparative Study of Platinum Di(*t*-butyl)($^{15}N_2$)diimine[1]) and *trans*-[$PtCl_2$(N-Ligand)PBu_3)] Complexes by ^{195}Pt-, ^{31}P- and ^{15}N-NMR.

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Summary

^{195}Pt-, ^{31}P- and ^{15}N-NMR. data are presented for [$PtCl_2$(*t*-Bu^{15}N=CH−CH=^{15}N(*t*-Bu)) (η^2-styrene)] (**1**), *trans*-[{$PtCl_2(PBu_3)$}$_2$(*t*-Bu^{15}N=CH−CH=^{15}N(*t*-Bu))] (**2**), *trans*-[$PtCl_2$(*t*-Bu^{15}N=CH−CH=^{15}N(*t*-Bu)) (PBu_3)] (**3**) and various complexes of the type *trans*-[$PtCl_2$(N-ligand)(PBu_3)]. In solution the gross structural features of **1** and **2** are shown to be in agreement with those found in the solid state; namely, **1** contains five-coordinate Pt and **2** is dinuclear. In **3** Pt is four-coordinate with only one N-atom of the diimine ligand being coordinated at − 50° in CD_2Cl_2. The NMR. data for **2** and **3** are compared with those of *trans*-[$PtCl_2$(N-ligand)(PBu_3)] (N-ligand = pyridine, 2,6-dimethylpyridine, (^{15}N)-hexylamine, (^{15}N)-*t*-butylamine and (^{15}N)-aniline) and are discussed in terms of the donor and acceptor properties of the N-ligands.

Introduction. - The study of a metal-ligand interaction is facilitated when both the metal and ligating atoms are observable by NMR. methods. For the Pt, N-bond this is possible *via* the measurement of ^{195}Pt- and ^{14}N(^{15}N-)-NMR. spectra. However, for both N-isotopes there are difficulties to be overcome in the measurement of their NMR. spectra; for ^{14}N ($I = 1$) the resonances are often broad due to the electric quadrupole moment and for ^{15}N ($I = \frac{1}{2}$) the low natural abundance (~0.4%) excludes easy measurement on relatively dilute solutions. Fortunately, the availability of reasonably inexpensive ^{15}N-enriched materials permits the synthesis of ligands which possess more favourable NMR. characteristics, thereby enabling the study of nitrogen in metal complexes. Direct measurement of ^{195}Pt-NMR. ($I = \frac{1}{2}$, 34% natural abundance) presents problems only when the metal is directly bound to ligand atoms having relatively large electric quadrupole moments, *e.g.* ^{14}N [1]; consequently the use of ^{15}N-enriched ligands conveniently circumvents this problem.

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1) *t*-Bu-^{15}N=CH−CH=^{15}N-*t*-Bu(3,6-$^{15}N_2$)-2,2,7,7-tetramethyl-3,6-diaza-3,5-octadiene (95% ^{15}N-enriched).

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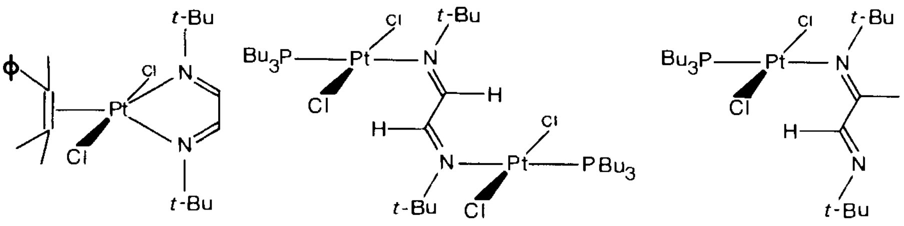

1 **2** **3**

Figure. *Three coordination modes of the* t*-Bu-dim ligand in platinum(II) complexes:* σ,σ-N,N'*-chelating* (**1**). σ-N-,σ-N'*-bridging* (**2**) *and* σ-N*-monodentate* (**3**) (styrene is coordinated either *via* its *re* or *si* face, in **1** the *re*-coordination is shown).

In our previous work on the coordination of α-diimines, R–N=CH–CH=N–R (R-dim), to Rh^{I}, Pd^{II} and Pt^{II} [2-5], we observed that this potentially chelating nitrogen ligand may function in either of three modes: *a)* σ-*N*-monodentate, *b)* σ-*N*, σ-*N'*-bridging, or *c)* σ,σ-*N*,*N'*-chelating with the remaining ligands strongly influencing the observed mode of α-diimine bonding. In the chemistry of Pt^{II} we have identified all three possibilities; representative examples being shown above.

The solid state molecular geometries of [PtCl$_2$(*t*-Bu-dim)(η^2-styrene)] (**1**) [4] and *trans*-[{PtCl$_2$(PBu$_3$)}$_2$(*t*-Bu-dim)] (**2**) [3] were determined by X-ray analysis. ^{31}P-, ^{13}C- and ^{1}H-NMR. studies revealed that the main structural features of these compounds are retained in solution [4] [5]. Both **1** and **3** show temperature-dependent NMR. spectra. For **1** this behaviour can be accounted for by olefin-rotation with retention of the σ,σ-*N*,*N'*-chelate bonded R-dim ligand on the NMR. time scale, evidence coming from ^{195}Pt,^{13}C- and ^{195}Pt,^{1}H spin-spin coupling-constants for the C- and H-atoms in both the olefin and R-dim-moieties. In *trans*-[PtCl$_2$(*t*-Bu-dim)(PBu$_3$)] (**3**) the fluxional process, which is fast on the ^{1}H-NMR. timescale (60 MHz) at about 120°, involves an intramolecular head-to-tail rearrangement of the *t*-Bu-dim ligand that proceeds *via* a five-coordinate transition state [2].

In order to improve our knowledge in this field of chemistry and specifically to probe the Pt,N-bond directly, we have prepared **1**, **2** and **3** containing ^{15}N-enriched *t*-Bu-diimine and studied their ^{195}Pt-, ^{15}N- and, where applicable, ^{31}P-NMR. spectra. This approach should provide a more comprehensive picture of the changes within the platinum coordination sphere and supply further insight into the dynamic processes occurring in solution. In addition, for comparative purposes, we have prepared some model complexes of the type *trans*-[PtCl$_2$(nitrogen ligand)(PBu$_3$)] and report herein their relevant NMR. data.

Experimental Part. - Starting complexes, K[PtCl$_3$(η^2-styrene)] and [{PtCl$_2$(PBu$_3$)}$_2$], were prepared by published methods [4] [6]. ^{15}NH$_4$Cl(95%-enriched) was purchased from *Merck, Sharp* and *Dohme.* All platinum di(*t*-butyl)glyoxaldiimine complexes were synthesized under N$_2$ and identified as the pure compounds by spectral comparison with non-enriched analogue [2-4] *trans*-[PtCl$_2$(N-ligand)(PBu$_3$)] complexes were synthesized according to literature procedures for closely related species [7] and identified by NMR. spectroscopy; the hexylamine [7a] and pyridine [7b] derivatives have been reported earlier. Solvents were dried and distilled before use.

NMR. spectra were measured using a *Bruker* WM-250 spectrometer operating at 53.77, 101.27 and 25.34 MHz for ^{195}Pt, ^{31}P and ^{15}N respectively. The samples were measured as solutions in rotating 10 mm tubes. Chemical shifts are relative to external Na_2PtCl_6 (aq.), H_3PO_4 and NH_4Cl for ^{195}Pt, ^{31}P and ^{15}N, respectively, with a positive sign indicating a shift to lower field (higher frequency). The uncertainty in chemical shifts is ±0.5 ppm for ^{195}Pt, and ±0.1 ppm for ^{31}P and ^{15}N. Coupling constants are given in Hz. The details of our ^{195}Pt- and ^{31}P-NMR. measurements have been reported previously [7–9]. The ^{15}N-NMR. spectra for the diimine complexes were recorded using a 40° pulse angle with a 0.8 s acquisition time and gated ^{1}H-decoupling (NOE-suppression).

Preparation of t-$Bu^{15}N{=}CH{-}CH{=}^{15}N$-t-$Bu$. – a) *(^{15}N)-Trichloramine*($^{15}NCl_3$). A solution of $^{15}NCl_3$ in CH_2Cl_2 was prepared from the reaction of $Ca(OCl)_2$ [4.05 g (18 mmol) suspended in CH_2Cl_2/H_2O 1:1] with $^{15}NH_4Cl$ [0.98 g (18 mmol) in aq. HCl-solution] at ~0° in a modification of a method described elsewhere [10a].

b) *Preparation of (^{15}N)-Butylammonium chloride*(t-$Bu^{15}NH_3Cl$) was prepared from the reaction of a fresh solution of $^{15}NCl_3$ in CH_2Cl_2 *(vide supra)* with $AlCl_3$ (4.81 g, 36 mmol) and *t*-BuCl (2.97 g, 36 mmol) at −10°, using a work-up suitable for water soluble amines, in a manner similar to that described in the literature [10b] and recrystallised from water/diethyl ether/ethanol.

c) *Preparation of* t-Bu-$^{15}N{=}CH{-}CH{=}^{15}N$-t-$Bu$(($^{15}N_2$)-t-*Bu-dim*). A solution of *t*-$Bu^{15}NH_2$, obtained from *t*-$Bu^{15}NH_3Cl$ (1 equiv.) dissolved in 5 ml water and made basic with 50% aq. NaOH-solution, was slowly added to a stirred mixture of glyoxal (30% aq. solution, 0.75 equiv.) and 15 ml pentane. After stirring for 10 min, the pentane and water layers were separated, washed with 5 ml water and 5 ml pentane respectively, and the combined pentane fractions dried over Na_2SO_4. Evaporation of this solution afforded crude ($^{15}N_2$)-*t*-Bu-dim which was purified by sublimation (30°, 3 Torr). With non-enriched materials yields varied from 30–55% (based on NH_4Cl for a 18 mmol scale reaction). – ^{1}H-NMR. (60 MHz, $CDCl_3$, 34°); 1.30 ($^{3}J(^{15}N,^{1}H) = 1.9$, $C(CH_3)_3$); 7.93 ($^{2}J(^{15}N,^{1}H) = 2.4$, $^{3}J(^{15}N,^{1}H) = 1.2$ Hz, HC=N).

Preparation of [$PtCl_2$(($^{15}N_2$)-t-*Bu-dim*)(η^2-*styrene*)]. ($^{15}N_2$)-*t*-Bu-dim (85 mg, 0.5 mmol) was added to a stirred solution of K[$PtCl_3(\eta^2$-styrene)] (213 mg, 0.48 mmol) in acetone (1 ml) and after 5 min the mixture was filtered to remove KCl. Concentration of the filtrate and addition of 2 ml hexane afforded yellow microcrystalline [$PtCl_2$(($^{15}N_2$)-*t*-Bu-dim)(η^2-styrene)] which was collected by filtration after standing for 2 h at −30°. The crystals were washed with hexane (3× 1 ml) and dried i.V. at RT. – ^{1}H-NMR. (90 MHz, $CDCl_3$, 34°): 1.60 ($^{3}J(^{15}N,^{1}H) = 2.3$, $C(CH_3)_3$); 8.69 ($^{2}J(^{15}N,^{1}H) = 2$, $^{3}J(^{15}N,^{1}H) = 2$, $^{3}J(^{195}Pt,^{1}H) = 40$, HC=N). – At 50°: 1.54 and 1.70 ($^{3}J(^{15}N,^{1}H) = 2.0$ and 2.3 respectively $C(CH_3)_3$); 8.7 (*m* flanked by platinum satellites, HC=N). – ^{13}C-NMR. (20 MHz, $CDCl_3$, 34°): 30.2 ($C(CH_3)_3$); 64.0 ($^{2}J(^{15}N,^{13}C) = 25$, $C(CH_3)_3$); 157 ($^{1}J(^{15}N,^{13}C) = 12$, $^{3}J(^{15}N,^{13}C) = 3.5$ Hz, C=N).

[$PtCl_2$(($^{15}N_2$)-t-*Bu-dim*)] obtained as the decomposition product of **1** by styrene release. – ^{1}H-NMR. (90 MHz, $CDCl_3$, 34°): 1.79 ($^{3}J(^{15}N,^{1}H) = 2.3$, $C(CH_3)_3$); 8.80 ($^{2}J(^{15}N,^{1}H) = 2.1$, $^{3}J(^{195}Pt,^{1}H) = 90$ Hz, HC=N).

[{$PtCl_2(PBu_3)$}$_2$(($^{15}N_2$)-t-*Bu-dim*)]. *t*-Bu-dim-$^{15}N_2$ (102 mg, 0.6 mmol) was added to a stirred suspension of [{$PtCl_2(PBu_3)$}$_2$] (468 mg, 0.5 mmol) in methanol (2 ml). Stirring for 1 h is accompanied by formation of a yellow precipitate; after adding hexane (1 ml) and setting the mixture aside at −30° for several days the crystals were filtered off, washed with hexane and dried i.V. at RT.

In situ *preparation of* [$PtCl_2(PBu_3)$(($^{15}N_2$)-t-*Bu-dim*)] *for NMR. studies.* *t*-Bu-dim-$^{15}N_2$ (1.2 equiv.) was added to a solution of [{$PtCl_2(PBu_3)$}$_2$(($^{15}N_2$)-*t*-Bu-dim)] (1 equiv.) in CD_2Cl_2 (3 ml). The resulting solution was a mixture of excess diimine ligand and [$PtCl_2(PBu_3)$(($^{15}N_2$)-*t*-Bu-dim)].

Results and Discussion. – In our experience we have found *t*-Bu-dim to bestow favourable stability characteristics on our complexes and we therefore required the ^{15}N-labelled ligand for the present spectroscopic study. Consequently we have optimized the reported synthesis of *t*-butylamine from NH_4Cl in such a way as to make this suitable for a small scale preparation [10] (see experimental part).

Comparison of the IR. spectra of compounds **1** and **2** containing labelled and non-labelled *t*-Bu-dim confirmed the earlier assignment of the ν(CN)-vibrations in these complexes [3] [4] (see *Table 1*).

Table 1. *IR. spectra*[a]) *of* t-*Bu-dim and* $(^{15}N_2)$-t-*Bu-dim and complexes* **1** and **2**

	$\nu(C{=}^{14}N)$	$\nu(C{=}^{15}N)$
t-Bu-dim	1631	1607
trans-$[\{PtCl_2(PBu_3)\}_2$(*t*-Bu-dim)]	1607	1574
$[PtCl_2$(*t*-Bu-dim)(η^2-styrene)]	1603	1581

[a]) KBr pellets, cm^{-1}.

To our knowledge there is only one other report of the use of ^{15}N-enriched *a*-diimines in organometallic chemistry, *i.e.* in $[Mo(CO)_4(CH_3{}^{15}N{=}CH{-}CH{=}^{15}NCH_3)]$ [11]. However, this *in situ* synthesis of $(^{15}N_2)$-Me-dim, by our co-workers, is not of general applicability.

a) *NMR. properties of* $(^{15}N_2)$-t-*Bu-dim Pt(II) complexes.*

$[PtCl_2$(t-Bu-$^{15}N{=}CH{-}CH{=}^{15}N$-t-Bu)($\eta^2$-styrene)] (**1**). The NMR. data for $[PtCl_2((^{15}N_2)$-*t*-Bu-dim) (η^2-styrene)] are collected in *Table 2.* The low-temperature spectra (CD_2Cl_2, −80°) reveal unambiguously that rotation of the styrene around the platinum-olefin bond axis is slow on the NMR. time scale. In particular there are two non-equivalent ^{15}N-signals (317.7 and 303.0 ppm) both flanked by ^{195}Pt-satellites whose separations suggest one bond Pt, N-interactions. This is in agreement with the expected asymmetry in the molecule. From previous ^1H- and ^{13}C-NMR. data [4], as well as from the solid state

Table 2. *NMR. Data*[a]) *for complexes* **1**, **2**, **3** *and* trans-*$[PtCl_2$(N-ligand)(PBu_3)]*

Complex	$\delta(^{195}Pt)$	$\delta(^{31}P)$	$\delta(^{15}N)$	$^1J(^{195}Pt,^{31}P)$	$^1J(^{195}Pt,^{15}N)$
1[b])	−1979		–		156
1[b])[c])	−1996		317.7 303.0		135 178
2[d])	−3412	−7.7	296.0	3442	211
3[e])	−3415	−9.0	370.0 283.5	3372	217
trans-$[PtCl_2$(N-ligand)$(PBu_3)]$					
Pyridine	−3505	−8.2		3338	
2,6-Dimethylpyridine	−3451	−9.8		3434	
(^{15}N)-Hexylamine[f])	−3612	−6.9	0.7	3377	138
t-Butylamine	−3534	−7.7	30.9[g])	3397	159[g])
(^{15}N)-Aniline	−3601	−4.5	10.8	3533	103
trans-$[PtCl_2(DMSO)(PBu_3)]$[f])		3.2		3121	
trans-$[PtCl_2(AsEt_3)(PBu_3)]$[f])		5.5		2846	
trans-$[PtCl_2(PBu_3)_2]$[d])		4.4		2377	

[a]) Chemical shifts are in ppm, coupling constants in Hz. Data are for $CDCl_3$ solutions unless otherwise specified. See experimental part for details.

[b]) In acetone-d_6.

[c]) At −80°; $^3J(^{15}N,^{15}N) = 5$ Hz.

[d]) In CD_2Cl_2. This molecule is dinuclear, see [3]. $^3J(^{15}N,^{15}N) = 2.4$ Hz, $\delta(^{15}N)$ free ligand = 355.3.

[e]) In CD_2Cl_2 at −50°. One N-atom of the chelate is uncoordinated.

[f]) Data from [7].

[g]) ^{15}N-data from mixture with **3**.

X-ray structure of **1** (a trigonal bipyramid with axial Cl-atoms), one anticipates the two N-atoms, the metal and the two olefinic atoms to lie in the same plane [4] [5].

The observation of markedly different $^1J(^{195}Pt, ^{15}N)$ values (178 and 135 Hz) is in line with the results of *Powell & Cooper*, who found correlations between $^1J(^{195}Pt, C)$ values and the differing (Pt, C)-bond lengths in platinum-styrene complexes [12]. There is a coupling of 5 Hz between the two N-atoms (*cf.* data for **3**), though, given that there are two coupling pathways $^2J(^{15}N\text{-}Pt\text{-}^{15}N)$ and $^3J(^{15}N{=}CH{-}CH{=}^{15}N)$, it is difficult to attribute meaning to this number.

The ^{195}Pt-NMR. spectrum at −80° is consistent with the ^{15}N-NMR. results and consists of a four-line pattern, a consequence of the splitting from the non-equivalent ^{15}N-atoms. The ^{195}Pt-chemical shift (−1996 ppm) is noteworthy, being distinctly different from those observed in four-coordinate *trans*-$[PtCl_2(L)(\eta^2\text{-olefin})]$ (L = N-donor ligand) complexes for which $\delta(^{195}Pt) = -2850$ to −3050 ppm [1] [7-9] (see *Table 3*). At 32° the four-line pattern at −1979 ppm (slightly shifted due to the large temperature-dependence of $\delta(^{195}Pt)$) now appears as a pseudo triplet [13]. The spacings within this triplet (165 Hz) are the average of the two separate one-bond (Pt, N)-couplings observed at −80°, thus confirming that both N-atoms are coordinated to the metal at 32°. Similar conclusions have already been drawn, based on ^{1}H- and ^{13}C-NMR. measurements [4]. Taken together, the various NMR. data are compatible only with a five-coordinate structure for complex **1** in which olefin-rotation gives rise to the temperature-dependent features.

[{PtCl₂(PBu)}₂(t-Bu-¹⁵N=CH−CH=¹⁵N-t-Bu)] (**2**). The structure of **2**, shown diagrammatically above, has been solved by X-ray diffraction methods [3]. Among the most relevant features of this structure is the s-*trans*-geometry of the diimine ligand bridging the two *trans*-$[PtCl_2(PBu_3)]$ units, the (P−Pt−N=C−C=N−Pt−P)-skeleton being virtually planar.

The ^{195}Pt-, ^{31}P- and ^{15}N-NMR. spectra of ^{15}N-enriched **2** are in agreement with the basic structural features, each nucleus giving rise to a single resonance pattern with corresponding first order spin-spin couplings (see *Table 2*). Both the ^{31}P- and ^{15}N-NMR. spectra show a 50 Hz two-bond P, N coupling constant, a value which denotes a *trans*-geometric orientation for these two spins. The ^{195}Pt-chemical shift at −3412 ppm is fully compatible with a complex of type *trans*-$[PtCl_2LL']$ in which L and L′ are phosphine (arsine) and N-donor ligands, respectively (see *Table 2*).

trans-*[PtCl₂(t-Bu-¹⁵N=CH−CH=¹⁵N-t-Bu)(PBu₃)]* (**3**). Previous studies have shown that analytically pure platinum-R-dim complexes $[PtCl_2(R\text{-dim})(PR_3)]$ and $[PtCl_2(R\text{-dim})(AsR_3)]$ can be obtained as solids when both triaryl-phosphines or arsines are used. However, for the tributylphosphine analogues $[PtCl_2(R\text{-dim})(PBu_3)]$, *in situ* reaction of the complex $[\{PtCl_2(PBu_3)\}_2(R\text{-dim})]$ with an equivalent of free R-dim was found to be the best method. Unlike the dinuclear complex, monomeric $[PtCl_2((^{15}N_2)\text{-}t\text{-Bu-dim})(PBu_3)]$ (**3**) exhibits temperature-dependent NMR.-behaviour.

The ^{15}N-NMR. spectrum at −50° shows two widely separated groups of signals centred at 283.5 and 370 ppm with the latter being only slightly shifted from the position of free $(^{15}N_2)$-*t*-Bu-dim (355.3 ppm). The higher-field resonance is accompanied by ^{195}Pt-satellites ($^1J(^{195}Pt, ^{15}N) = 217$ Hz) and the signals are further split by coupling to ^{31}P (^{2}J(^{31}P, ^{15}N) = 51 Hz). Both ^{15}N-resonances show a further small splitting of 2.4 Hz which we assign to ^{3}J($^{15}N{=}CH{-}CH{=}^{15}N$). A high-field shift on coordination is in agreement with the literature for other sp^2 hybridized N-ligands [8]. The ^{195}Pt-resonance at −50° is a four-line pattern centred at −3415 ppm (only 3 ppm away from δ(^{195}Pt) for the four-coordinate dinuclear complex **2**) and consists of a doublet, stemming from coupling to the P-atom of PBu_3, further split by a single ^{15}N-spin. The ^{31}P-NMR. spectrum echoes the ^{195}Pt- and ^{15}N-NMR. results and together these data allow us to confirm that structure of **3**, previously suggested from ^{1}H- and ^{13}C-NMR. measurements.

The NMR. spectra for **3** at room temperature are somewhat different. Neither δ(^{195}Pt) nor δ(^{31}P) has changed appreciably, however the doublets now appear as pseudo triplets. Closer inspection of the spectra shows that the centre resonance of the triplet is considerably broader then the outside lines, which is somewhat reminiscent of the X-part of an *ABX* spectrum.

These pseudo triplets probably result from the two originally inequivalent ^{15}N-donor-atoms equilibrating by an exchange process having an intermediate rate at this temperature. A probable mechanism, which is consistent with the data, is a process in which the *t*-Bu-dim ligand is undergoing an intramolecular exchange during which the uncoordinated end of the chelate attacks the metal to afford a five-coordinate transition state (or intermediate) which is probably not present in significant concentrations. Although it is not possible to be precise concerning the exchange mechanism, the similarity of δ(^{195}Pt)-values at −50° and RT. is noteworthy, since δ(^{195}Pt) for the five-coordinate complex (**1**) is rather different than that for a four-coordinate complex. Because of the wide separation of the δ(^{15}N) in the slow-exchange limit (2162 Hz) the coalescence temperature will be high and therefore an intermediate exchange rate is expected at RT. (compare fast exchange limit in the ^{1}H-NMR., 60 MHz, at 120° [2]).

b) *Comparative spectroscopy of* trans-*[$PtCl_2$(N-donor)(PBu_3)] complexes with* **1**, **2** *and* **3**. In view of the versatility of the diimine ligand we considered it useful to compare its NMR. spectroscopic properties with those of some potentially similar ligands. To this end we have prepared several complexes of the type *trans*-[$PtCl_2$

Table 3. *^{195}Pt-NMR. Chemical Shift Data*

L_1 in $[PtCl_3L_1]^-$	δ(^{195}Pt)[a]	L_2 in *trans*-$[PtCl_2(C_2H_4)L_2]$		*trans*-[$PtCl_2$(N-ligand)PBu_3]	
			δ(^{195}Pt)[b]	N-ligand	δ(^{195}Pt)
PMe_3	−3500	$MeNH_2$	−3040	*t*-Bu-$^{15}N{=}CH{-}CH{=}^{15}N$-*t*-Bu	−3415
PEt_3	−3540	*i*-$PrNH_2$	−3008	Hexylamine	−3612
PPr_3	−3520	PhCH(*t*-Bu)NH_2	−2990	*t*-Butylamine	−3534
PPh_3	−3513	Pyridine	−2979	Pyridine	−3505
PF_3	−3626	2,6-Dimethylpyridine	−2877	2,6-Dimethylpyridine	−3451
		t-Bu-$^{15}N{=}CHCH{=}^{15}N$-*t*-Bu	−1979[c]		

[a] Data from [14]. Converted using 4533 ppm as the chemical shift of Na_2PtCl_6 relative to the given TMS reference.

[b] Data from [15].

[c] Five-coordinate complex **1**, acetone-d_6.

(N-ligand)(PBu_3)] and measured their ^{195}Pt-, ^{31}P-, and in one case ^{15}N-NMR. spectra.

Chemical shifts. In *Table 3* we show ^{195}Pt-NMR. chemical shift data for our diimine compounds as well as for the model complexes which contain the nitrogen ligands ^{15}N-substituted pyridine, 2,6-dimethylpyridine, hexylamine, *t*-butylamine and aniline. As may be seen the Pt-chemical shifts cover a 200 ppm range from -3412 to -3612 ppm (relative to Na_2PtCl_6) with the diimine complexes falling at the low-field end of this range.

The question as to whether this is a significant change may be answered after considering the following arguments:

a) changing a ligand atom can affect δ (^{195}Pt) by more than 1,000 ppm. Pt-chemical shifts for the anions $[PtCl_3(NMe_3)]^-$, $[PtCl_3(PMe_3)]^-$ and $[PtCl_3(AsMe_3)]^-$ are: -1715, -3500 and -3173 ppm, respectively [14]. Consequently, our variations in δ (^{195}Pt) are only moderate in magnitude;

b) changing the substituents on a donor-atom can affect δ (^{195}Pt) by slightly more than 100 ppm. Some examples are shown in *Table 3;*

c) there is a steric effect on δ (^{195}Pt) [1] [15]. Bulky substituents induce a low-field shift whose magnitude can be 50–100 ppm, *i.e.* δ (^{195}Pt) for (**2**) = -3412. For (**2**) with R = *i*-Pr instead of *t*-Bu, δ (^{195}Pt) = -3472.

With point *c* in mind, we see from the *Tables 2* and *3* that the differences in δ (^{195}Pt) (54 ppm between the chemical shifts the pyridine and 2.6-dimethylpyridine complexes and 78 ppm between those of the hexylamine and *t*-butylamine complexes) are in reasonable agreement with the literature. Moreover, it seems acceptable that the pyridine complex should be to low-field of the hexylamine compound as a similar effect is found in the C_2H_4 complexes (see *Table 3*). Interestingly, our diimine complexes show resonances which are 36 and 39 ppm to lower-field of the 2,6-dimethylpyridine derivative. Although this is a small difference, it confirms that the sp^2-N-donors have lower-field Pt-chemical shifts than the sp^3-analogs. Ideally, the remaining chemical shift data for ^{31}P and ^{15}N should provide additional information concerned with how these differences originate.

Unfortunately, our ^{15}N-chemical shift data are insufficient (although the ^{15}N-coordination chemical shift has received some attention [7a] [8] [16]) and our ^{31}P-NMR.-results show no obvious trends; consequently we turn to coupling constants.

Coupling Constants. The one-bond coupling constants ^1J (^{195}Pt, ^{31}P), for the PBu_3 complexes are shown in *Table 2* and may be seen to vary from 3338 Hz to 3533 Hz. If one excludes the (^{15}N)-aniline complex, the total range is reduced from 195 Hz to 102 Hz. Considering that this coupling constant is known to be sensitive to the nature of the *trans*-ligand [17] [18] - we show some values in *Table 2* which cover the range 2377 to 3533 Hz - these changes are rather small.

The magnitude of ^1J (^{195}Pt, ^{31}P) for all of our compounds is not unusual and suggests that the *trans*-influence of our N-ligands is similar to $N{=}C{=}S^-$ [19] [20], but slightly larger than Cl^- [7a] [18]. In short, there seems nothing special about these values.

Some ^1J (^{195}Pt, ^{15}N) values are also shown in *Table 2,* with the values varying from 103 to 217 Hz. Theory [21] [22] predicts that a one-bond coupling involving an

sp^3-N-atom will be smaller by ~25% than that for the analogous sp^2-N-atom, *e.g.* $^1J(^{15}N, ^1H)$ for $^{15}NH_4^+$ is 73.2 Hz, yet for the quinolinium ion is 96.0 Hz [23]. *Al-Najjar et al.* [24] have found $^1J(^{195}Pt, ^{15}N)$ values of 409 Hz and 299 for the complexes *trans*-[$PtCl_2(\eta^2$-$C_2H_4)$(N-ligand)] with (^{15}N)-pyridine and (^{15}N)-dimethylamine, respectively, thereby qualitatively supporting this expectation. Given our value of 159 Hz for *trans*-[$PtCl_2(^{15}NH_2$-*t*-Bu)(PBu_3)]³) and that of 171 Hz reported for *trans*-[$PtCl_2(^{15}NHMe_2)(PPh_3)$] [24], we might expect an sp^2-N-ligand *trans* to a tertiary phosphine to show a $^1J(^{195}Pt, ^{15}N)$ value near 210 Hz. Our observed $^1J(^{195}Pt, ^{15}N)$ coupling constants of 211 and 217 Hz for *trans*-[{$PtCl_2(PBu_3)$}$_2$(*t*-Bu-dim-$^{15}N_2$)] (**2**) and *trans*-[$PtCl_2(^{15}N_2)$-*t*-Bu-dim)(PBu_3)] (**3**), respectively, therefore, seem quite normal. Consequently, neither $^1J(^{195}Pt, ^{15}N)$ nor $^1J(^{195}Pt, ^{31}P)$ markedly distinguishes between the diimine ligand and aliphatic amine.

Conclusions. - The results of our studies on various Pt(II) complexes containing monodentate- and bidentate-N-donor ligands may be briefly outlined as follows: i) the low temperature ^{195}Pt- and ^{15}N-NMR. data of [$PtCl_2$(*t*-Bu-dim)(η^2-styrene)] (**1**) provide conclusive proof, together with previous ^{13}C- and ^{1}H-NMR. data, that this compound in solution is five-coordinate with σ,σ-*N,N'* chelate-bonded *t*-Bu-dim. At room temperature when olefin-rotation is known to take place, retention of ^{15}N-coupling to the Pt-centre is evidence that the *t*-Bu-dim ligand does not dissociate to generate a four-coordinate intermediate; ii) the solution-NMR. data for *trans*-[$PtCl_2$(*t*-Bu-dim)PBu_3)] (**3**) at −50° indicate that the Pt is four-coordinate with a σ-*N* monodentate-bonded *t*-Bu-dim positioned *trans* to the P-donor-atom. At higher temperature a fluxional process takes place which begins to equilibrate both N-donor-atoms of the *t*-Bu-dim ligand on the NMR. timescale. This behaviour has been interpreted in terms of a head to tail rearrangement which presumably involves a five-coordinate transition state; iii) The σ-*N*-,σ-*N'*-bridging mode of the *t*-Bu-dim ligand in [{$PtCl_2(PBu_3)$}$_2$(*t*-Bu-dim)] (**2**) is retained in solution at RT. No fluxional behaviour was observed and the NMR. parameters are consistent with the known solid state features; iv) Both chemical shift and coupling constant data suggest that the donor properties of the *t*-Bu-diimine ligand are similar to those of other N-ligands. There is some indication that the metal chemical shift recognizes sp^2-N-atoms differently than the sp^3-analogues but the data are not readily quantitatively interpreted. For seven complexes, in which a variety of N-ligands are *trans* to PBu_3, the value of $^1J(^{195}Pt, ^{31}P)$ does not vary greatly ($3413 \pm 3\%$), thus indicating that these N-ligands have a similar *trans*-influence. Since there is little π-back-bonding from Pt(II) to aliphatic tertiary phosphines [7a] [18] the data also imply that the *trans*-N-donor-atom does not significantly alter the σ-component of the (Pt, P)-bond.

Clearly, in all of this work the use of multinuclear ^{195}Pt-, ^{31}P- and ^{15}N-NMR., in conjunction with ^{15}N-labelling of the *t*-Bu-dim ligand, can provide a direct approach to the elucidation of the bonding modes (including fluxionality) of the α-diimine ligand in platinum (II) complexes.

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³) We chose this value to compare with our diimine as the complex also contains a *t*-butyl group.

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