218. The *trans*-Influence in Platinum(II) Complexes. ^{1}H- and ^{13}C-NMR. and X-Ray Structural Studies of Tridentate *Schiff*'s Base Complexes of Platinum(II)

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Summary

^{1}H- and ^{13}C-NMR. data are reported for the complexes [Pt(**1**)L] and [Pt(**2**)L]; **1** = $OC_6H_4CH=NCH_2CH_2O$, **2** = $OC_6H_4CH=NC_6H_4O$; L = PR_3, AsR_3, C≡N(cyclohexyl), DMSO, pyridine, secondary amine. The molecular structures of [Pt(**2**)($NHEt_2$)] (I) and [Pt(**2**)(PPh_3)] (II) have been determined by X-ray analysis. Relevant bond distances for I: Pt-N(amine) = 2.076 Å, Pt-N(imine) = 2.017 Å, Pt-O = 1.992 Å and 2.002 Å; for II: Pt-P = 2.248 Å, Pt-N = 2.064 Å, Pt-O = 1.964 and 2.005 Å. Both the solid and solution state data are interpreted in terms of differences in the *trans* influence of the ligand L. The question of metal-ligand d-p π back bonding to the imine is discussed.

1. Introduction. – The concept of the *trans* influence in platinum chemistry has been the subject of many reports [1] [2]. As this idea involves a ground state phenomenon, several spectroscopic methods have been employed in its study, with IR., NMR. and X-ray methods appearing most frequently. Despite the extensive literature there is still some disagreement as to the relative importance of σ- and π-bonding in the weakening (or strengthening) of the M-L bond in the moiety *trans*-'L-M-(variable *trans* ligand)'. Reasonably enough, these σ- and π-components are thought to be dependent upon the metal (M) and its formal oxidation state, as well as the type of donor atom (L)[1].

We have recently reported ^{15}NMR.-data for the complexes: a) *trans*-[$PtCl_2$($^{15}NH_2(CH_2)_5CH_3$)L], L = PBu^n_3, $PMePh_2$, $P(pCH_3C_6H_4)_3$, $AsBu^n_3$, $AsMePh_2$, $As(pCH_3C_6H_4)_3$, $^{15}NH_2(CH_2)_5CH_3$, C_2H_4 [3] and b) [Pt(**1**)L], L = PBu^n_3, $P(pCH_3C_6H_4)_3$, $P(OEt)_3$, $AsBu^n_3$, $As(pCH_3C_6H_4)_3$, cyclohexyl isocyanide, dimethyl

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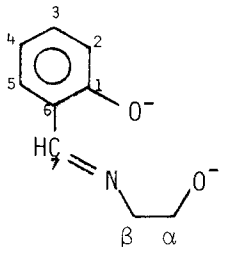

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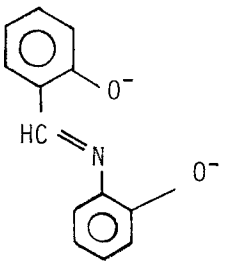

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sulfoxide, pyridine and $NH_2(CH_2)_5CH_3$ [4] and have shown that both the ^{15}N-chemical shifts and the values $^1J(^{195}Pt, ^{15}N)$ are sensitive to the *trans* influence of the ligand, L. Interestingly, these two series of complexes are related in that a plot of $^1J(^{195}Pt, ^{15}N_{sp^3})$ *vs.* $^1J(^{195}Pt, ^{15}N_{sp^2})$ is linear [4].

One possible conclusion to be drawn from the more than 200 Hz difference [4] in the values $^1J(^{195}Pt, ^{15}N)$ within each set is that the Pt-N bond lengths vary significantly as a function of L, due to the different nature of the metal orbitals used in these bonds.

To further our understanding of the *trans* influence, and to investigate the validity of using solution NMR. data to predict qualitative differences in Pt-N bond lengths we have carried out ^1H- and ^{13}C-NMR. studies on the complexes [Pt(**1**)L] and [Pt(**2**)L] and report here these results and those of X-ray structural studies for two members of the latter series.

2. Experimental. – a) *Synthesis.* – The syntheses of the complexes [Pt(**1**)L] have been reported previously [4]. The complexes [Pt(**2**)L], were prepared using a similar method and a typical synthesis is shown below.

*Preparation of [Pt(**2**)L].* A solution of K_2PtCl_4 (830 mg, 2.00 mmol) in 20 ml of dimethyl sulfoxide at 100° was treated with *N*-(*o,o'*-dihydroxybenzylidene)aniline (426 mg, 2.00 mmol) and Na_2CO_3 (0.50 g, 4.72 mmol), and then heated to 140° for 15 min. Cooling to 100° was followed by the addition of 2.4 mmol of L. After 15 min at this temperature the reaction mixture was cooled to RT. (= room temperature) and treated with 20 ml of water. The powder which precipitated was filtered off and washed with water until the filtrate was colourless. The crude product was dissolved in ethyl/acetate and the solution treated with active charcoal. Filtration through *Celite,* concentration on a RV. (= rotary evaporator) and recrystallization from chloroform gave the products in 40–70% yields.

All of the complexes gave satisfactory IR., ^1H- and ^{13}C-NMR. spectra. The microanalytical data for the new complexes are shown in *Table 1.*

b) Physical Measurements. – IR. spectra were measured as KBr pellets on a *Beckman* IR 4250 spectrophotometer. NMR. spectra were measured in $CDCl_3$ using a *Bruker* HX-90 spectrometer operating in *Fourier* transform mode. Chemical shifts (ppm) are ±0.01 (for ^1H) and ±0.1 (for ^{13}C). Coupling constants (Hz) are ±0.4 (for ^1H) and ±1.5 (for ^{13}C). The ^1H-NMR. spectrum of [Pt(**2**)($NHEt_2$)] was measured at both 90 and 360 MHz.

Crystal Data. Red-orange crystals of [Pt(**2**)(Et_2NH)] (I) and orange crystals of [Pt(**2**)(Ph_3P)] (II), were obtained by slow evaporation of CCl_4 and toluene solutions, respectively. A summary of crystal data is given in *Table 2.*

Intensity Measurements. Intensities were measured with an automatic diffractometer *Syntex* $P2_1$ using graphite-monochromated Mo*Kα* radiation ($\theta_{max} = 28°$, ω-scan range = 0.9°). Data were processed as described previously [5], with p = 0.006 (I) and 0.008 (II) as calculated from the variance of the standard reflections [6], and corrected for *Lorentz,* polarization and shape anisotropy effects; 2084 (I) and 2494 (II) independent reflections with $I > 3\sigma(I)$ were used in the analyses.

Table 1. *Microanalytical Data for the Complexes* [Pt(**2**)L] Calc. (Found)

L	% C	% H	% N
PBu^n_3	49.34 (49.35)	5.96 (6.02)	2.30 (2.30)
PPh_3	55.69 (55.71)	3.62 (3.69)	2.09 (2.11)
$P(OEt)_3$	39.86 (40.00)	4.23 (4.14)	2.45 (2.30)
$AsEt_3$	40.15 (40.29)	4.26 (4.28)	2.46 (2.56)
$AsPh_3$	52.26 (52.08)	3.40 (3.24)	1.97 (1.96)
C≡N(cyclohexyl)	46.60 (46.65)	3.91 (3.87)	5.43 (5.49)
DMSO[a])	37.19 (36.70)	3.12 (3.04)	2.89 (2.87)
Pyridine	44.54 (44.37)	2.91 (2.93)	5.77 (5.78)
$NHEt_2$	42.59 (42.57)	4.20 (4.21)	5.84 (5.80)
Piperidine	43.99 (44.17)	4.10 (4.20)	5.70 (5.79)

[a]) % S: 6.62 (6.64).

Structure Analysis and Refinement. The structures were solved by *Patterson* and *Fourier* methods and refined by least-squares analysis. The isotropic refinements converged at R = 0.078 and 0.085 for I and II respectively. In the subsequent cycles the H-atoms were fixed. Other atoms (except phenyl rings in II) were assigned anisotropic vibration parameters. The H-atoms were then repositioned and included in the final structure factor calculations: R = 0.060 and 0.052 (R_w = 0.047 and 0.039) for I and II, respectively. A two-block approximation of the normal-equations matrix was used in both cases. The quantity minimized was $\sum w(|Fo| - |Fc|)^2$ with $w = 4\,Fo^2/\sigma^2(Fo^2)$. The phenyl rings of II were refined as rigid groups (D_{6h}, C–C = 1.392 Å). Atomic scattering factors including anomalous dispersion terms were taken from International Tables for X-ray Crystallography [7]. The calculations were done with local programmes on the UNIVAC 1100/20 computer of the University of Rome [8] and on the HP 21MS minicomputer of the *CNR. Research Area* [9]. Final positional parameters for the non-hydrogen atoms of the two compounds are given in *Table 2.*

3. Results. – a) *^{1}H-NMR. Results.* The ^{1}H-NMR. spectra of [Pt(**1**)L] and [Pt(**2**)L] contain a signal for the imine proton, HC=N-, at δ 7.6–9.0 which is well resolved from the remaining aromatic protons. These chemical shift values are consistent with literature data for salicylaldehyde [10] and salicylaldehyde *Schiff*'s base complexes of platinum [11] [12]. Where the L ligand has a phosphorus donor atom, this resonance is further split by ^{31}P-coupling. Similarly, when [Pt(**1**)L] was prepared enriched in ^{15}N (>95 atom % ^{15}N), coupling to the ^{15}N-isotope was also observed.

For both [Pt(**1**)L] and [Pt(**2**)L] with all L ligands except $SbPh_3$, a coupling to ^{195}Pt was detectable. A tabulation of these ^{1}H-NMR. data may be found in *Table 3.*

The most salient feature of this *Table* stems from the three-bond coupling, $^3J(^{195}Pt, ^1H)$, which shows an inverse dependence on the *trans* influence of L ($^3J(^{195}Pt, ^1H)$ for PBu^n_3 = 45.5 Hz, for pyridine = 74.0 Hz. The sense of this change in coupling constant is similar to that for $^1J(^{195}Pt, ^{15}N)$ in [Pt(**1**)L] [4] and for many other one-, two- and three-bond platinum coupling constants [1].

A connection between the nitrogen donor atoms in **1** and **2** can be seen from the plot of $^3J(^{195}Pt, ^1H{-}C(7))$ in [Pt(**1**)L] *vs.* $^3J(^{195}Pt, ^1H{-}C(7))$ in [Pt(**2**)L], shown in *Figure 1.* The linear correlation of these two coupling constants suggests that both nitrogen functions react in an identical way when L is altered and therefore that the presence of the second aromatic ring does not influence the donor capacity of the nitrogen to a significant extent.

Table 2. *Crystal data and final positional parameters for the non-hydrogen atoms for I and II* (standard deviations are given in parentheses)

	I	II
Cell constants[a])	a = 11.866(5)A	15.721(4)A
	b = 9.353(2)	9.106(2)
	c = 15.302(5)	18.500(5)
	β = 101.58(3)°	106.05(2)°
Space group	$P2_1/a$	$P2_1/n$ (monoclinic: Z = 4)
Density (gcm^{-3})	1.914 (calc.); 1.95 (found)	1.745 (calc); 1.73(**1**)(found)[b])
μ(Mo$K\alpha$) (cm^{-1})	85.29	56.59

	x	y	z		x	y	z
Complex I							
Pt	0.2318(0)	0.0152(0)	0.2469(0)	C(7)	0.4399(14)	0.1481(17)	0.2407(12)
O(1)	0.3410(8)	−0.0867(10)	0.3425(6)	C(8)	0.2863(12)	0.2513(14)	0.1360(9)
O(2)	0.1204(7)	0.1176(9)	0.1518(6)	C(9)	0.1685(12)	0.2223(13)	0.1104(10)
N	0.3397(11)	0.1585(12)	0.2090(8)	C(10)	0.1024(11)	0.2962(14)	0.0417(10)
N(1)	0.1070(9)	−0.1259(11)	0.2718(7)	C(11)	0.1536(13)	0.3966(15)	−0.0021(10)
C(1)	0.4523(12)	−0.0472(14)	0.3584(10)	C(12)	0.2711(14)	0.4278(16)	0.0234(10)
C(2)	0.5265(14)	−0.1258(14)	0.4285(10)	C(13)	0.3382(11)	0.3519(14)	0.0927(10)
C(3)	0.6420(13)	−0.0934(18)	0.4506(11)	C(14)	0.0078(12)	−0.0625(17)	0.3008(11)
C(4)	0.6881(12)	0.0111(19)	0.4039(13)	C(15)	0.0437(12)	0.0230(16)	0.3850(11)
C(5)	0.6206(13)	0.0853(17)	0.3393(11)	C(16)	0.0679(15)	−0.2266(15)	0.1931(10)
C(6)	0.5009(13)	0.0608(15)	0.3152(10)	C(17)	0.1642(17)	−0.3124(16)	0.1708(13)

	x	y	z		x	y	z	
Complex II								
Non group atoms				*Rigid group atoms* (derived parameters)				
Pt	0.3548(0)	0.3380(1)	0.0291(0)	C(14)	0.1883(6)	0.3798(10)	0.1125(4)	Ph(1)
P	0.2138(2)	0.3946(3)	0.0228(2)	C(15)	0.1260(5)	0.4704(9)	0.1307(5)	
O(1)	0.3167(5)	0.1867(9)	−0.0488(4)	C(16)	0.1065(5)	0.4531(8)	0.1991(5)	
O(2)	0.4004(5)	0.4832(9)	0.1122(4)	C(17)	0.1494(6)	0.3453(10)	0.2494(4)	
N	0.4879(7)	0.3152(12)	0.0378(6)	C(18)	0.2117(5)	0.2546(9)	0.2312(5)	
C(1)	0.3718(8)	0.1215(12)	−0.0803(6)	C(19)	0.2312(5)	0.2719(8)	0.1627(5)	
C(2)	0.3371(8)	0.0220(13)	−0.1389(6)	C(20)	0.1269(4)	0.2912(8)	−0.0440(4)	Ph(2)
C(3)	0.3868(10)	−0.0527(15)	−0.1761(6)	C(21)	0.1327(4)	0.2750(8)	−0.1173(4)	
C(4)	0.4779(9)	−0.0356(14)	−0.1562(6)	C(22)	0.0664(5)	0.2009(8)	−0.1703(3)	
C(5)	0.5163(8)	0.0603(15)	−0.1002(7)	C(23)	−0.0057(4)	0.1431(8)	−0.1501(4)	
C(6)	0.4661(8)	0.1409(12)	−0.0606(5)	C(24)	−0.0115(4)	0.1593(8)	−0.0767(4)	
C(7)	0.5152(10)	0.2364(15)	−0.0023(7)	C(25)	0.0548(5)	0.2334(8)	−0.0237(3)	
C(8)	0.5397(8)	0.4093(13)	0.1001(6)	C(26)	0.1898(5)	0.5872(6)	−0.0058(4)	Ph(3)
C(9)	0.4877(9)	0.4928(14)	0.1341(6)	C(27)	0.1221(5)	0.6245(7)	−0.0693(4)	
C(10)	0.5312(10)	0.5899(14)	0.1924(6)	C(28)	0.1088(4)	0.7707(9)	−0.0915(3)	
C(11)	0.6224(11)	0.5979(14)	0.2128(7)	C(29)	0.1631(5)	0.8796(6)	−0.0502(4)	
C(12)	0.6721(9)	0.5088(20)	0.1793(7)	C(30)	0.2308(5)	0.8424(7)	0.0133(4)	
C(13)	0.6327(9)	0.4194(16)	0.1225(7)	C(31)	0.2442(4)	0.6962(9)	0.0355(3)	

	x	y	z	ϕ	θ	ψ
Rigid group parameters[c])						
Ph(1)	0.1689(4)	0.3625(6)	0.1809(3)	42.3(3)	0.9(3)	76.5(3)
Ph(2)	0.0606(3)	0.2172(5)	−0.0970(3)	119.9(3)	0.1(2)	97.1(3)
Ph(3)	0.1765(3)	0.7334(6)	−0.0280(3)	−8.4(3)	−1.3(3)	140.4(3)

[a]) Determined by least-squares from the measured angular positions of 15 reflections, centered on an automatic diffractometer *Syntex* $P2_1$.

[b]) Measured by flotation in ZnI_2 solution.

[c]) The coordinates x, y and z give the ring centers, and the angles ϕ, θ and ψ (in degress) describe rotations about an internal coordinate system.

Table 3. *^{1}H-NMR. Parameters*[a]) *in $CDCl_3$*

L	[Pt(**1**)L]				[Pt(**2**)L]		
	δ(H–C(7))	$^3J(^{195}Pt,H–C(7))$	$^2J(^{15}N,H–C(7))$	$^4J(P,H–C(7))$	δ(H–C(7))	$^3J(^{195}Pt,H–C(7))$	$^4J(P,H–C(7))$
$P(OEt)_3$	8.18	44.4	2.2	21.6	8.86[b])	44.4	21.1
PBu_3^n	8.21	45.5	2.4	13.7	8.94[c])	45.2	13.9
$P(pCH_3C_6H_4)_3$	8.14	52.0	1.7	14.8	8.94[d])	53.2	14.7
C≡N(cyclohexyl)	8.06	54.0	1.4		8.76	53.6	
$AsBu_3^n$	8.21	62.0	2.2		8.94[e])	61.2	
$As(pCH_3C_6H_4)_3$	8.21	70.0	2.2		8.93[f])	69.8	
DMSO	8.00	70.0			8.45	69.3	
Piperidine	7.91	71.0	1.6		8.45	71.3	
Pyridine	7.96	74.0	1.6		8.62	73.1	
$^{15}NH_2(CH_2)_5CH_3$	7.63	70.0		$NHEt_2$	8.71	72.9	
$SbPh_3$	8.32		2.2		9.0		

a) Chemical shifts are in ppm, coupling constants in Hz.
b) $\delta\,^{31}P = 80.5$, $^1J(^{195}Pt,^{31}P) = 5941$ Hz.
c) $\delta\,^{31}P = 0.1$, $^1J(^{195}Pt,^{31}P) = 3.739$ Hz.
d) Data are for PPh_3; $\delta\,^{31}P = 10.6$; $J(^{195}Pt,^{31}P) = 3918$ Hz.
e) Data are for $AsEt_3$.
f) Data are for $AsPh_3$.

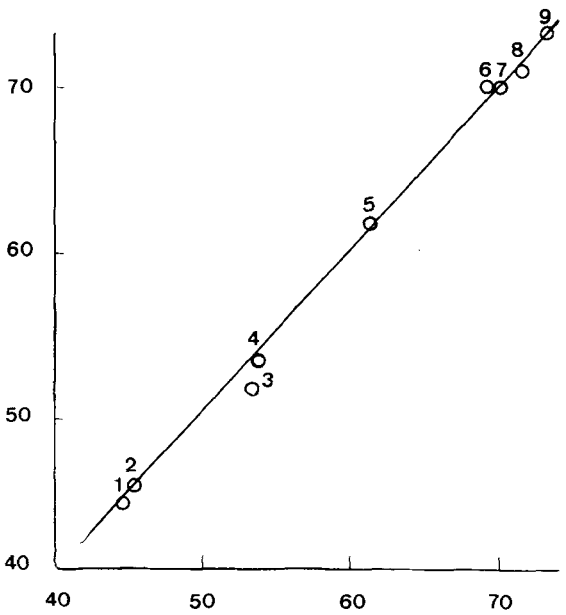
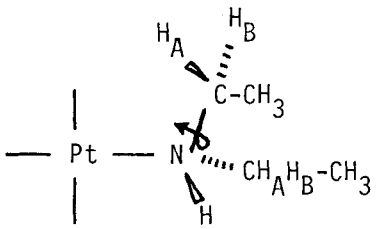


Fig. 1. *Plot of $^3J(^{195}Pt,H–C(7))$ in [Pt(**1**)L] vs. $^3J(^{195}Pt,H–C(7))$ in [Pt(**2**)L]*
L = 1) $P(OCH_2CH_3)_3$, 2) PBu_3^n, 3) PPh_3, 4) C≡N(cyclohexyl), 5) $AsEt_3$, 6) DMSO, 7) $AsPh_3$, 8) Piperidine and 9) Pyridine.
For 3 and 7 the complexes had $P(p\text{-}CH_3C_6H_4)_3$ and $As(p\text{-}CH_3C_6H_4)_3$ with **1**. Values are in Hz.

There is no immediately obvious correlation between δ(H–C(7)) and $^3J(^{195}Pt, ^1H–C(7))$[2]).

The ^{1}H-NMR. spectrum of the complex [Pt(**2**)(NHEt$_2$)] in the aliphatic region is somewhat unusual in that the absorption is extremely complicated at 90 MHz and not at all suggestive of the A-part of a simple A_2X_3 spin system (we exclude ^{195}Pt in this description). The spectrum at 360 MHz is still complex, but interpretable. At this magnetic field the methylene protons on each of the CH_2's are obviously inequivalent and are best written as: CH_AH_B. Since the NH and CH_3 protons couple to each of the H_A- and H_B-protons, the spin system, at 90 MHz, is $ABMX_3$ and consequently less recognizable. The chemical shifts for the protons H_A and H_B are: (360 MHz) δ 3.38 and 3.02, whereas the NH and CH_3 protons appear at δ 3.83 and 1.53, respectively. Irradiation (360 MHz) at the freqeunce of H_A collapses the deceptively simple CH_3 resonance into a doublet as does irradiation at H_B. Further support for the idea that the protons are non-equivalent (and not the two CH_2CH_3 groups) comes from the ^{13}C-NMR.-spectrum which shows equivalent CH_2 and CH_3 groups.

The appearance of non-equivalent methylene protons suggests that rotation around the C, N bond (see *Scheme*) may be relatively slow on the NMR. time scale.



b) *^{13}C-NMR. Results.* A complete set of ^{13}C-NMR. data for the more soluble [Pt(**1**)L] complexes and some few data for [Pt(**2**)L] are shown in *Table 4*. As in the proton spectra, the signals are split by coupling to ^{195}Pt and, when present, ^{15}N. The following points are worth noting: (i) The chemical shifts of the C-atoms adjacent to nitrogen are more sensitive to L than those adjacent to oxygen (*trans* influence > *cis* influence); (ii) $[^2J(^{195}Pt, C_\alpha) + ^3J(^{195}Pt, C_\alpha)]$ varies markedly (21.3 to 0 Hz) as a function of L; (iii) $[^2J(^{195}Pt, C_\beta) + ^3J(^{195}Pt, C_\beta)]$, although much larger in magnitude, varies only from 58 to 68 Hz (the dependence of $J(^{195}Pt, C_\alpha)$ on L is opposite to that of $J(^{195}Pt, C_\beta)$); (iv) The aromatic C-resonances are relatively insensitive to L.

Point (i) draws attention to the well established [1] empiricism concerning the relative magnitudes of *trans* and *cis* effects; however, we note that the total range for both C(7) and C_α is small, 5 ppm or less, so that δ ^{13}C may not prove to be the NMR. parameter of choice when the C-atom under study is remote from the metal. The small change in the imine carbon, C(7), is noteworthy if one remembers that $\Delta\delta$ ^{15}N is ~45 ppm [4]. Moreover, this 5 ppm range for C(7) and C_β is only slightly

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[2]) There is only a qualitative relationship between $^1J(^{195}Pt, ^{15}N)$ and $^3J(^{195}Pt, H–C(7))$.

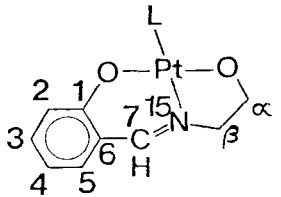
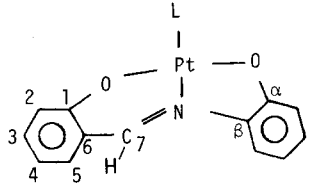


Table 4. *^{13}C-NMR. Parameters for the Complexes*[a])

L	δ C(1) J(Pt,C(1)) ^3J(N,C(1))	δ C(2) J(Pt,C(2))	δ C(3) J(Pt,C(3))	δ C(4)	δ C(5) J(Pt,C(5)) ^3J(N,C(5))	δ C(6) J(Pt,C(6)) ^2J(N,C(6))	δ C(7) J(Pt,C(7)) ^1J(N,C(7))	δ C_α J(Pt,C_α) ^2J(N,C_α)	δ C_β J(Pt,C_β) ^1J(N,C_β)	
PBu^n_3	163.4 23.5 0	122.4 46.3	133.1 11.8	115.1	133.7 0 2.9	121.8 n.o. –[c])	154.2 14.0 14.0	73.1 21.3 –[d])	63.4 58.1 5.1	[b])
$P(OEt)_3$	163.3 25.7 0	122.1 45.6	133.9 13.2	115.6	133.9 0 3.7	121.2[e]) n.o. –	156.3 15.4 14	72.9 20.6 –	63.3 60.3 4.4	[f])
$P(pCH_3C_6H_4)_3$	163.5 22.0 1.8	122.4 44.1	133.2 13.2	115.2[g])	133.4 0 1.3	121.6 n.o. –	154.5 13.2 n.o.	73.0[h]) 19.8 –	63.7 59.4 4.4	[i])
$AsBu^n_3$	163.1 22.1 1.4	122.2 41.9	133.0 12.5	115.2	133.6 0 2.2	121.6 n.o. 1.5	152.9 14.7 14.0	73.2 17.6 –	63.8 62.5 4.4	[k])
$As(pCH_3C_6H_4)_3$	162.9 n.o. 0	122.3 41.2	133.2 n.o.	115.3	133.4 0 n.o.	121.4 n.o. 0	153.3 16.2 13.2	73.3 13.2 –	64.2 68.0 4.4	[l])
C≡N–⬡	162.8 n.o. 1.5	121.9 44.1	134.3 11.8	116.1	133.9 0 2.9	121.0 n.o. 0	156.0 15.4 14.0	72.3 11.0 0	64.4 65.4 4.4	[m])
DMSO	163.0 20.6 2.2	122.0 43.4	134.6 11.8	116.4	133.9 0 2.9	121.0 n.o.	156.2 14.0 14.0	71.9 n.o. 0	65.4 66.2 5.1	[n])
DMSO	162.2 n.o. 1.4	121.5 41.2	134.2 11.8	115.8	134.6 0 2.9	n.o.	157.3 13.2 14.0	71.6 0	65.1 66.2 4.4	[o])
$SbPh_3$	162.7 n.o. n.o.	122.5 n.o.	134.5 n.o.	115.8	133.8 n.o. 2.9	121.0	153.0 13.3 14.0	73.9 12.7	63.7 n.o. 4.4	[p])
Piperidine	162.4 17.6 0	121.9 45.6	132.6 12.5	115.7	133.1 0 2.9	122.8 n.o. 1.5	151.7 12.9 14.7	71.7 0	66.7 66.2 4.4	[q])
Pyridine	162.7 n.o. 1.5	122.0 42.7	133.1 11.8	116.0	133.2 0 2.9	122.6 n.o. 1.5	153.0 14.7 15.4	71.5 0	67.7 66.9 5.1	[r])
$^{15}NH_2(CH_2)_5CH_3$	162.0 16.8 1.5	121.3 44.1	132.5 12.1	115.4	133.3 0 1.5	123.0 n.o. 1.5	151.1 11.8 15.4	71.4 0	66.2 61.0 4.4	[s])



L	δ C(1)[t])	δ C(6)	δ C(7)	δ C_α	δ C_β
C≡N(cyclohexyl)	162.1	120.4	145.6	167.7	137.4
	30.2	78.0	7	15.5	54.8
$P(OEt)_3$	162.4	120.6	145.5	168.4	136.8[u])
	29.4	61.0	n.o.	21.5	55
Piperidine	161.8	121.4	142.2	167.9	139.9[v])
	19.1	46	n.o.	n.o.	53
$NHEt_2$	162.0	122.3	142.1	168.5	139.8[w])
	19.6	n.o.	n.o.	n.o.	54.9

a) Chemical shifts are in ppm (TMS), coupling constants in Hz. Data are for $CDCl_3$ solutions unless otherwise specified. n.o. = not observed.

b) $P(C_\alpha H_2C_\beta H_2C_\gamma H_2C_\delta H_3)_3$

	C_α	C_β	C_γ	C_δ
δ C_i	21.2	25.6	24.3	13.8
$^iJ(P,C_i)$	33.8	1.5	14.0	
$^{i+1}J(Pt,C_i)$	29.4	20.6		
i	1	2	3	4

c) $\{J(P,C(6)); J(N,C(6))\} = \{1.8\text{ Hz}; 0.7\text{ Hz}\}$.

d) $\{J(P,C(1)); J(N,C(1))\} = \{1.5\text{ Hz}; 0.7\text{ Hz}\}$.

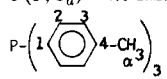
e) $J(P,C(6)) = 1.5$ Hz.

f) $P(OC_\alpha H_2C_\beta H_3)_3$

	C_α	C_β
δ C_i	62.0	16.2
$^iJ(P,C_i)$	1.5	6.6
$^{i+1}J(Pt,C_i)$	13.2	0
i	1	2

g) $J(P,C(4)) = 2.2$ Hz.

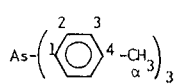
h) $J(P,C_\alpha) = 4.6$ Hz.

i) 

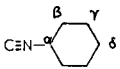
	C(1)	C(2)	C(3)	C(4)	C_α
δ C_i	126.5	134.3	128.8	140.6	21.4
$^iJ(P,C_i)$	60.3	10.3	10.3		
$^{i+1}J(Pt,C_i)$	25.0	20.6			
i	1	2	3	4	5

k) $As(C_\alpha H_2C_\beta H_2C_\gamma H_2C_\delta H_3)_3$

	C_α	C_β	C_γ	C_δ
δ C_i	19.8	26.7	24.5	13.6
$^{i+1}J(Pt,C_i)$	41.9	14.0		
i	1	2	3	4

l) 

	C(1)	C(2)	C(3)	C(4)	C_α
δ C_i	128.1	133.6	129.4	140.0	21.4
$^{i+1}J(Pt,C_i)$	47.1	10.3			
	1	2	3	4	5

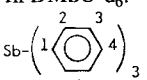
m) 

δ C(1)	δ C_α	δ C_β	δ C_γ	δ C_δ
n.b.	54.9	32.2	23.1	24.6

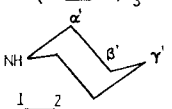
n) In $CDCl_3$

δ C_α(DMSO) = 42.2 ppm.
$^2J(Pt,C_\alpha)$ = 48.6 Hz.

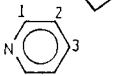
o) In DMSO-d_6.

p) 

δ C(1)	δ C(2)	δ C(3)	δ C(4)
128.2	136.3	129.1	130.2

q) 

	δ $C_{\alpha'}$	δ $C_{\beta'}$	δ $C_{\gamma'}$
	51.8	26.6	23.6
$^{i+1}J(Pt,C_i)$	19.1	32.4	

r) 

δ C(1)	δ C(2)	δ C(3)
149.6	124.9	137.9

$^3J(Pt,C(2)) = 32.4$ Hz, $^4J(Pt,C(3)) = 5.1$ Hz.

s) $^{15}NH_2C_\alpha H_2C_\beta H_2C_\gamma H_2C_\delta H_2C_\varepsilon H_2C_\varphi H_3$

δ C_α	δ C_β	δ C_γ	δ C_δ	δ C_ε	δ C_φ
45.8	31.4	26.3	31.4	22.5	14.0

$^2J(Pt,C_\alpha) = 7.0$ Hz, $^3J(Pt,C_\beta) = 32.4$ Hz, $^1J(N,C_\beta) = 2.2$ Hz.

t) Not all of the remaining eight aromatic resonances can be unambiguously assigned.

u) δ C_α = 62.7, $^2J(P,C_\alpha) = 1.5$ Hz, $^3J(Pt,C_\alpha) = 10$ Hz; δ C_β = 16.3, $^3J(P,C_\beta) = 6.6$ Hz.

v) δ C_α = 52.5, $^2J(Pt,C_\alpha) = 20.6$ Hz; δ C_β = 26.7, $^3J(Pt,C_\beta) = 30.9$ Hz; δ C_γ = 23.6.

w) δ C_α = 49.5, $^2J(Pt,C_\alpha) = 19.1$ Hz; δ C_β = 14.4, $^3J(Pt,C_\beta) = 12.5$ Hz.

larger than the 2.6 ppm difference found for the first C-atom in the hexyl amine complexes *trans*-[$PtCl_2(NH_2(CH_2)_5CH_3)L$] [3] and the 3.9 ppm change found for the C-atom adjacent to nitrogen in the *trans*-[$PtCl_2$(piperidine)L] derivatives (see below).

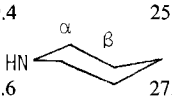
Points (ii) and (iii) suggest the possibility that the two- and three-bond couplings may have opposite sign and/or a large configurational dependence; indeed *Sarneski et al.* [13] have found that these couplings do have opposite signs in ethylenediamine complexes of platinum(II).

Point (iv) confirms that sites removed from the metal are less likely to provide useful information related to the *trans* influence of L.

We have previously reported ^{13}C-chemical shifts and $^nJ(^{195}Pt, ^{13}C)$ coupling constants for platinum(II) complexes of tertiary phosphines [14] and arsines [15] and therefore considered whether these data could be used to help evaluate the *trans* influence of the *Schiff*'s base imine nitrogen.

In *Table 5* we show some ^{13}C-data for the sets of complexes: *trans*-[$PtCl_2(PBu^n_3)L$], *trans*-[$PtCl_2(NH_2(CH_2)_5CH_3)L$] and *trans*-[$PtCl_2$(piperidine)L]. These data confirm that δ ^{13}C is not a sensitive indicator for differences in M-L bonding, but do reveal marked differences (30–50%) in both $^2J(^{195}Pt, ^{13}C)$ and $^3J(^{195}Pt, ^{13}C)$, as a function of L. For the PBu^n_3 compounds, the two- and three-bond coupling constants place the *Schiff*'s base nitrogen with piperidine and *p*-toluidine, as ligands with a relatively small *trans* influence. Similar conclusions are reached when the α and β C-atoms of the nitrogen ligands $NH_2(CH_2)_5CH_3$ and piperidine are used as probes. There is, therefore, nothing especially noteworthy in the *trans* influence of our sp^2 nitrogen donor.

Table 5. *^{13}C-NMR. Data*[a]) *as a Measure of the* trans *Influence of the* Schiff's *Base Nitrogen*

L	δ C_α	$^1J(^{195}Pt, C_\alpha)$	δ C_β	$^2J(^{195}Pt, C_\beta)$
trans-[$PtCl_2(PBu^n_3)L$]	$P(C_\alpha-C_\beta-CH_2-CH_3)_3$			
PBu^n_3	20.6	22.7	26.1	15.3
$P(pCH_3C_6H_4)_3$	20.7	25	26.1	16.8
Piperidine	21.5	36.4	25.6	19.5
p-Toluidine	21.8	32	25.8	21.2
[Pt(**1**)(PBu^n_3)]	21.2	29.4	25.6	20.6
trans-[$PtCl_2$(piperidine)L]				
PBu^n_3	48.9	6.6	27.3	24.6
$AsBu^n_3$	49.9	n.o.	27.3	30.9
Piperidine	52.8	13.2	27.3	33.8
[Pt(**1**)(piperidine)]	51.6	19.1	26.3	32.4
trans-[$PtCl_2(NH_2(CH_2)_5CH_3)L$]		$H_2N-C_\alpha-C_\beta-CH_2-CH_2-CH_3$		
PBu^n_3	44.0	n.o.	31.5	21.3
$AsBu^n_3$	44.5	8.8	31.4	26.4
$NH_2(CH_2)_5CH_3$	46.7	14.7	31.1	31.6
[Pt(**1**)($NH_2(CH_2)_5CH_3$)]	45.8	7.0	31.4	32.4

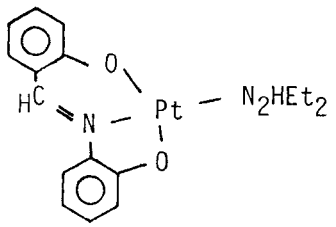
[a]) Chemical shifts are in ppm (TMS) coupling constants in Hz ($\pm$ 1). Data are for $CDCl_3$ solutions at room temperature. C_α and C_β refer to the α and β C-atoms of the Ligand L.

c) *X-ray Results.* Given the >30% change in $^3J(^{195}Pt, H_7)$ as a function of L there seemed little doubt that the electronic characteristics of the metal-nitrogen bonds were different. Since there was sufficient precedence, *e.g.* the case of Pt-P bonds [16], we expected that the solid state structures of our complexes would reflect these differences and therefore undertook an X-ray diffraction study of several of our compounds.

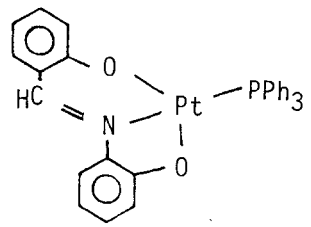
Crystals of the complexes [Pt(**2**)($NHEt_2$)] (I) and [Pt(**2**)(PPh_3)] (II) consist of discrete molecules (see *Fig. 2*) separated by normal *van der Waals* contacts. Bond

Table 6. *Bond lengths* (Å) *and valence angles* (°) *in the molecules* I *and* II (standard deviations are given in parentheses)

	I	II		I	II
Bond lengths			O(1)–Pt–N	99.9(5)	94.8(4)
Pt–P	–	2.248(3)	O(2)–Pt–N	80.7(5)	82.4(4)
Pt–O(1)	1.992(10)	1.964(9)	Pt–P–C(14)	–	113.5(4)
Pt–O(2)	2.002(10)	2.005(9)	Pt–P–C(20)	–	117.3(3)
Pt–N	2.017(12)	2.064(12)	Pt–P–C(26)	–	110.8(3)
Pt–N(1)	2.076(10)	–	C(14)–P–C(20)	–	105.5(4)
O(1)–C(1)	1.346(18)	1.312(13)	C(14)–P–C(26)	–	104.7(4)
O(2)–C(9)	1.354(15)	1.322(17)	C(20)–P–C(26)	–	104.0(4)
C(6)–C(1)	1.395(19)	1.435(19)	Pt–N(1)–C(14)	116.4(8)	–
C(1)–C(2)	1.445(23)	1.403(18)	Pt–N(1)–C(16)	111.3(8)	–
C(2)–C(3)	1.378(24)	1.358(17)	C(14)–N(1)–C(16)	110.7(12)	–
C(3)–C(4)	1.387(23)	1.385(22)	Pt–O(1)–C(1)	118.1(8)	122.5(8)
C(4)–C(5)	1.334(26)	1.362(20)	Pt–O(2)–C(9)	114.0(9)	113.5(7)
C(5)–C(6)	1.413(23)	1.421(16)	Pt–N–C(7)	117.8(11)	122.8(12)
C(6)–C(7)	1.469(24)	1.433(20)	Pt–N–C(8)	114.4(10)	109.2(7)
C(7)–N	1.194(23)	1.193(17)	C(7)–N–C(8)	127.2(19)	128.0(14)
N–C(8)	1.455(19)	1.486(18)	C(7)–C(6)–C(1)	125.8(15)	124.7(11)
C(8)–C(9)	1.399(21)	1.388(16)	C(7)–C(6)–C(5)	115.2(13)	116.2(12)
C(9)–C(10)	1.366(22)	1.416(20)	C(5)–C(6)–C(1)	118.9(15)	119.2(11)
C(10)–C(11)	1.365(19)	1.380(25)	O(1)–C(1)–C(6)	126.7(14)	126.4(11)
C(11)–C(12)	1.401(24)	1.396(20)	O(1)–C(1)–C(2)	115.1(12)	118.1(12)
C(12)–C(13)	1.386(24)	1.342(22)	C(6)–C(1)–C(2)	118.2(14)	115.5(10)
C(13)–C(8)	1.367(18)	1.407(21)	C(1)–C(2)–C(3)	119.9(13)	124.0(13)
P–C(14)	–	1.816(7)	C(2)–C(3)–C(4)	120.3(16)	120.4(13)
P–C(20)	–	1.829(9)	C(3)–C(4)–C(5)	120.5(15)	118.9(11)
P–C(26)	–	1.841(7)	C(4)–C(5)–C(6)	122.1(14)	122.0(12)
N(1)–C(14)	1.464(17)	–	C(6)–C(7)–N	131.0(15)	128.4(15)
N(1)–C(16)	1.526(20)	–	N–C(8)–C(9)	110.8(11)	113.7(12)
C(14)–C(15)	1.503(24)	–	N–C(8)–C(13)	127.9(14)	124.5(10)
C(16)–C(17)	1.492(24)	–	C(9)–C(8)–C(13)	121.3(14)	121.7(12)
			O(2)–C(9)–C(8)	120.0(13)	121.1(12)
Valence angles			O(2)–C(9)–C(10)	119.7(13)	121.1(11)
P–Pt–O(1)	–	91.5(2)	C(8)–C(9)–C(10)	120.3(12)	117.8(13)
P–Pt–O(2)	–	91.5(3)	C(9)–C(10)–C(11)	118.8(14)	119.2(12)
P–Pt–N	–	172.4(3)	C(10)–C(11)–C(12)	121.5(15)	121.7(14)
N(1)–Pt–O(1)	86.7(4)	–	C(11)–C(12)–C(13)	119.5(13)	119.7(15)
N(1)–Pt–O(2)	92.7(4)	–	C(12)–C(13)–C(8)	118.6(14)	119.2(12)
N(1)–Pt–N	173.1(5)	–	N(1)–C(14)–C(15)	111.6(13)	–
O(1)–Pt–O(2)	179.2(3)	176.1(4)	N(1)–C(16)–C(17)	112.8(15)	–



I



II

lengths and valence angles are given in *Table 7*. In both complexes platinum has the expected square-planar coordination with three coordination sites occupied by the dianionic tridentate ligand 2, the fourth by Et_2NH in I and Ph_3P in II. In both compounds, the largest deviations from the regular square-planar coordination concern the angles O(**1**)-Pt-N and O(**2**)-Pt-N, which are internal to a six- and five-membered rings respectively.

The two Pt-N bonds in I are significantly different. The Pt-N(1) bond length [2.076(10)Å] is similar to other Pt(II)-N bonds involving sp^3-hybridized N-atoms [17]. Pt-N [2.017(12)Å] is shorter, in accordance with the usual difference (~0.05 Å) observed between the atomic radii of sp^3 and sp^2-hybridized N-atoms [18]. A value of 1.973(7)Å for Pt-N has been observed in the cation *trans*-$[PtCl(HNNC_6H_4F)(PEt_3)_2]^+$ [19]. In II the Pt-N bond [2.064(12)Å] is longer than the corresponding one in I, and its length approximates that of Pt-N(1). The Pt-O(1) bond in II [1.964(9)Å] is slightly shorter than the other three Pt-O bonds in the two compounds, which average 2.000(9)Å. Values ranging between 2.0 and 2.3 Å have been observed for Pt-O distances [20–22]. The Pt-P bond in II [2.248(3)Å] is towards the low end of the range found for other Pt(II) complexes [23–25]. Apart from the ethyl and phenyl groups, the two molecules are almost planar and the Pt(2) moieties are very similar. The lengths of the Pt-N bonds [2.017(12)Å in I, 2.064(12)Å in II] provide the most relevant difference between these complexes. This change reflects the higher *trans*

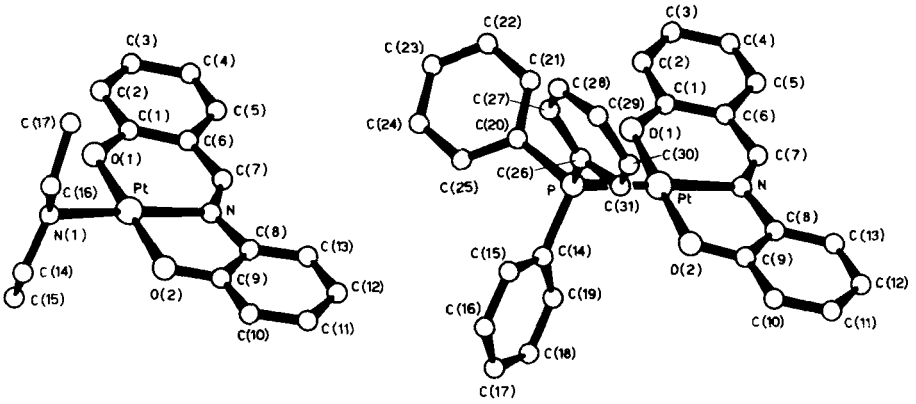


Fig. 2. *The molecular structures of I (left) and II*

Thermal parameters of I

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
PT	0.0070(0)	−0.0017(1)	0.0029(0)	0.0113(1)	−0.0011(1)	0.0041(0)
O(1)	0.0100(10)	−0.0003(21)	0.0048(13)	0.0142(13)	0.0004(15)	0.0044(6)
O(2)	0.0068(9)	0.0008(17)	0.0049(11)	0.0119(12)	0.0045(14)	0.0051(6)
N	0.0112(14)	0.0015(29)	0.0067(17)	0.0166(18)	−0.0073(20)	0.0042(7)
N(1)	0.0087(12)	−0.0070(23)	0.0067(15)	0.0134(16)	−0.0003(18)	0.0043(7)
C(1)	0.0095(15)	0.0026(30)	0.0030(20)	0.0104(19)	−0.0062(23)	0.0057(10)
C(2)	0.0133(18)	0.0073(34)	0.0017(21)	0.0125(20)	−0.0004(23)	0.0041(9)
C(3)	0.0082(16)	0.0085(37)	−0.0050(22)	0.0207(28)	−0.0052(30)	0.0059(11)
C(4)	0.0079(15)	0.0019(41)	−0.0013(21)	0.0213(32)	−0.0032(37)	0.0092(13)
C(5)	0.0091(16)	0.0008(35)	−0.0005(23)	0.0171(25)	−0.0009(29)	0.0070(12)
C(6)	0.0114(17)	0.0098(33)	0.0017(20)	0.0137(21)	−0.0023(22)	0.0039(8)
C(7)	0.0108(18)	0.0142(39)	0.0032(24)	0.0192(26)	−0.0124(30)	0.0071(13)
C(8)	0.0079(15)	0.0068(27)	0.0018(18)	0.0095(16)	−0.0000(20)	0.0034(7)
C(9)	0.0075(15)	0.0011(27)	0.0047(19)	0.0099(18)	−0.0015(20)	0.0044(8)
C(10)	0.0062(14)	0.0014(27)	0.0010(18)	0.0120(19)	0.0024(22)	0.0049(9)
C(11)	0.0112(17)	0.0072(34)	−0.0003(22)	0.0138(23)	0.0033(24)	0.0051(10)
C(12)	0.0129(18)	0.0014(33)	0.0061(23)	0.0118(20)	0.0010(25)	0.0062(11)
C(13)	0.0070(14)	0.0001(28)	0.0018(19)	0.0120(20)	−0.0011(24)	0.0057(10)
C(14)	0.0083(15)	−0.0015(32)	0.0046(20)	0.0185(24)	0.0051(27)	0.0060(10)
C(15)	0.0129(17)	−0.0018(38)	0.0098(22)	0.0187(26)	−0.0043(32)	0.0074(11)
C(16)	0.0152(21)	−0.0064(34)	0.0020(23)	0.0129(21)	−0.0018(23)	0.0037(8)
C(17)	0.0221(26)	−0.0036(43)	0.0085(29)	0.0147(24)	−0.0027(29)	0.0065(12)

$T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Thermal parameters of II

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Pt	0.0035(0)	0.0041(1)	0.0025(0)	0.0117(1)	0.0028(1)	0.0030(0)
P	0.0036(2)	0.0019(5)	0.0021(2)	0.0088(5)	0.0006(4)	0.0025(1)
O(1)	0.0041(4)	0.0055(16)	0.0055(7)	0.0173(16)	0.0046(14)	0.0049(4)
O(2)	0.0045(5)	0.0051(16)	0.0007(7)	0.0148(14)	−0.0002(12)	0.0038(3)
N	0.0076(8)	0.0092(24)	0.0051(11)	0.0169(22)	0.0081(19)	0.0045(5)
C(1)	0.0047(8)	0.0003(21)	0.0014(10)	0.0109(23)	0.0017(16)	0.0024(5)
C(2)	0.0048(8)	0.0037(22)	0.0014(11)	0.0123(21)	−0.0040(18)	0.0034(5)
C(3)	0.0067(10)	0.0026(27)	0.0022(12)	0.0152(24)	−0.0001(19)	0.0030(5)
C(4)	0.0060(9)	0.0044(25)	0.0047(12)	0.0144(23)	0.0017(19)	0.0029(5)
C(5)	0.0031(7)	0.0038(23)	0.0025(11)	0.0184(26)	0.0070(21)	0.0041(6)
C(6)	0.0051(7)	−0.0006(22)	0.0000(9)	0.0081(19)	0.0010(16)	0.0019(4)
C(7)	0.0088(11)	0.0052(28)	0.0044(12)	0.0163(25)	0.0074(20)	0.0028(5)
C(8)	0.0044(8)	−0.0034(21)	−0.0017(11)	0.0106(20)	0.0019(16)	0.0025(5)
C(9)	0.0053(8)	0.0029(24)	0.0010(11)	0.0115(21)	0.0040(17)	0.0025(5)
C(10)	0.0085(11)	−0.0005(28)	0.0001(13)	0.0154(24)	−0.0027(18)	0.0022(5)
C(11)	0.0099(12)	−0.0092(30)	−0.0017(14)	0.0150(25)	0.0034(18)	0.0025(5)
C(12)	0.0052(10)	−0.0106(33)	−0.0007(12)	0.0344(40)	0.0058(26)	0.0031(6)
C(13)	0.0048(9)	0.0025(27)	0.0011(11)	0.0258(30)	0.0082(20)	0.0024(5)

Rigid-group atoms

	B(Å^2)
C(14)–C(19)	5.5(1)
C(20)–C(25)	4.0(1)
C(26)–C(31)	4.2(1)

$T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Table 7. *Torsion angles defining the arrangements of Et_2NH in I and Ph_3P in II*

I		II	
O(1)–Pt–N(1)–C(14)	119.5(10)	O(1)–Pt–P–C(14)	123.7(4)
O(1)–Pt–N(1)–C(16)	– 112.4(9)	O(1)–Pt–P–C(20)	0.1(4)
Pt–N(1)–C(14)–C(15)	– 58.6(15)	O(1)–Pt–P–C(26)	– 118.9(4)
Pt–N(1)–C(16)–C(17)	58.5(14)		

influence of Ph_3P with respect to Et_2NH and suggests that the Pt-N bond has more *p*-character in II than in I. A difference of ~0.05 Å as a function of the *trans* ligand is quite reasonable and indeed values in excess of 0.10 Å are known to occur for Pt-Cl [26] and Pt-P [27] separations. Further, the Pt-N–C(7) and Pt-N–C(8) angles in I[117.8(11) and 114.4(10)°] differ significantly from the corresponding angles in II[122.8(12) and 109.2(7)°]. This may also be a consequence of the longer Pt-N bond in II.

Comparing the structure of the coordinated *Schiff*'s base in the present compounds with the structures of other compounds containing the Ph-CH=N-Ph system [28–32], one finds: (a) a shortening, by 0.05–0.1 Å, of the C=N double bond; (b) an enlargement, by about 10°, of the C–C=N and C=N–C angles. These differences may be due to variations in the electronic structure of the C=N double bond, as a consequence of the coordination at the metal atom followed by the closure of two rings. The arrangements of Et_2NH in I and Ph_3P in II are defined by the torsion angles given in *Table 7*.

d) *IR. Results.* In the hope of finding a change in ν (C=N) we have measured some IR. spectra of our complexes. In the region 1520–1620 cm^{-1} there are four intense bands, any one of which might be ν (C=N). These appear at ≈1605, 1600, 1580–1590 and 1520–1530 cm^{-1}. The width of the band at ≈1605 cm^{-1}, by comparison with that of the free ligand, suggests that this may be the sought after signal; in any case, all of these bands are almost (± 5 cm^{-1}) independent of L[3]). Thus, as with the $^{13}C(7)$ chemical shift and C=N bond length data there is no evidence for a large change in the electronic structures within the carbon skeleton from the IR. data.

4. Discussion. – The complexes [Pt(**1**)L] and [Pt(**2**)L] fulfill the required conditions for a classical *trans* influence study. The *cis* ligands can be held constant and the *trans* ligand can be varied such that complexes containing a variety of L donor atoms can be prepared. Further, these are favorable molecules in that several physical methods can be readily applied, thereby providing a more complete picture of their ground state structures. The ^{1}H-NMR. data, through the values $^3J(^{195}Pt,H)$, show that the *trans* ligand, L, significantly affects the other side of the molecule. The available ^{15}N-data [4] specifically reveal a large effect at the chelate N-atom and the ^{13}C studies suggest that there is only a small change due to L as one moves away from the *Schiff*'s base N-atom. This latter point is a negative, but useful, observation. In the event of a major $d\pi$-$p\pi$ metal-imine back-bonding interaction

[3]) We have fewer data for the complexes [Pt(**1**)L] since these were more often oils. The comparison was made only for measurements made on KBr pellets.

one might expect δ $^{13}C(7)$ to change markedly[4]). This negative effect at C(7) is supported by the IR. and X-ray solid-state work in which no noteworthy change in either ν(C=N) or the C=N bond length is found, however, a large change in Pt-N bond length *is* observed, in agreement with $^3J(^{195}Pt, ^1H)$ and $^1J(^{195}Pt, ^{15}N)$ [4]. These results speak for a localized change in the Pt-N bond which propagates itself primarily through the Pt-N σ-bond. Following previous suggestions [19] it seems likely that there is a change at platinum, as a function of L, which reveals itself in the NMR. data as larger (or smaller) s-coefficients in that part of the molecular orbital involving Pt-N overlap, and therefore a larger (or smaller) coupling constant. This same redistribution produces a change in the Pt-N bond length but only a secondary effect at remote sites. Our conclusion with regard to the NMR. data is in agreement with recent calculations by *Shustorovich* [34], and there is now general theoretical support [35] for the importance of σ bonding in determining the *trans* influence of a ligand.

Assuming a minimal π bond and the relative importance of the σ component in the Pt-N bond, the linear correlation found [4] between $^1J(^{195}Pt, ^{15}N)$ in [Pt(**1**)L] and the same parameter in *trans*-[$PtCl_2$ ($^{15}NH_2(CH_2)_5CH_3$)L] is now readily understandable. Neither of the nitrogen ligands markedly interferes with Pt-L ligand π bonding and therefore the interaction of L with Pt is similar in both cases. It is not possible, or even reasonable, to completely exclude platinum-imine π back bonding; such bonding can be constant, zero or only slightly dependent on L, but there is no compelling evidence in its favor. It would be interesting to have both solution- and solid state data for some R–C≡^{15}N complexes for comparison with the existing sp^3 and sp^2 nitrogen studies.

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