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METAL-AZO AND METAL-IMINE COMPOUNDS

I. σ-(*N*)-COORDINATED PLATINUM(II) COMPLEXES

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Summary

The reaction of aliphatic azo $(CH_3)_nCH_{3-n}N=NCH_{3-n}(CH_3)_n$ (n = 0, 1, 2), aromatic azo (ArN=NAr), aromatic imine (ArCH=NAr or $ArCH=NCH_3$) compounds with $[LPtCl_2]_2$ (L = C_2H_4, $AsEt_3$ or PEt_3) yields a series of *trans*-$[PtCl_2(R'X=NR)L]$ complexes (X = CH or N; R, R′ = alkyl or aryl) in which the ligands are coordinated through a nitrogen atom.

Vibrational and electronic absorption spectra show that the azo compounds retain their *trans* geometry on coordination, and that azobenzene is much less affected in the complexes with palladium and platinum than in its conjugated acid or $SbCl_5$ complex. ^1H and ^{13}C NMR spectra indicated the close proximity to the metal atom of the aliphatic or *ortho* CH-groups of the non-coordinated end of the azo and imine ligands.

I. Introduction

Owing to the presence of the nitrogen lone pair(s) and the π electrons, the azo or imine compounds can form either σ-(*N*)-coordinated [1, 2, 3] or π-coordinated [1, 4, 5] complexes. A third possibility is the formation of *ortho*-metallated complexes, in which coordination occurs through a σ bond at an *ortho* carbon atom of the aromatic ring and through the lone pair of a nitrogen atom [1, 6, 7]. We are studying the factors influencing the occurrence of these three types of coordination, and investigating systematically the spectroscopic and chemical properties of each type of coordination. In the first part of this series we present the results for σ-(*N*)-coordinated azo— and imino—transition metal complexes, with emphasis on their spectroscopic properties.

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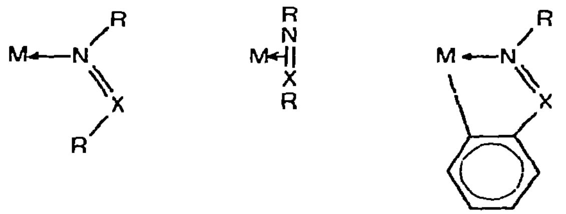

σ-(*N*)-coordination π coordination *ortho*-metallation

(X = CH or N)

Fig. 1.

II. Experimental

*Preparations**

The complexes *trans*-[PtCl$_2$(R'X=NR)L] were prepared according to the method given below for *trans*-[PtCl$_2$(*p*-CH$_3$C$_6$H$_4$CH=NCH$_3$)(AsEt$_3$)]. 430 mg of the complex [(Et$_3$As)PtCl$_2$]$_2$ (0.5 mmol) was dissolved at room temperature in 15 ml of dichloromethane. Upon addition of 160 mg of *p*-CH$_3$C$_6$H$_4$CH=NCH$_3$ (1.2 mmol) with vigorous stirring, the orange solution immediately turned yellow. After evaporation of a part of the solvent, 15 ml of diethyl ether was added to the residual solution (5 ml). After cooling to −20°C, 525 mg of yellow crystals of [PtCl$_2$(*p*-CH$_3$C$_6$H$_4$CH=NCH$_3$)(AsEt$_3$)] were isolated. The compound was recrystallized from a dichloromethane/hexane or dichloromethane/ether mixture.

The analytical data for the new complexes are listed in Table 1.

Spectra

Spectra were recorded by means of Varian HA-100 apparatus (^{1}H NMR), a Varian XL-100 with Fourier transform (^{13}C/NMR), a Cary-14 (UV), a Coderg PH1 (Raman), Beckman IR-7 and IR-12 apparatus (IR).

The electronic absorption spectra (section III.A.2) were also recorded for CH$_2$Cl$_2$ solutions at concentrations at which no dissociation occurs as indicated by the NMR spectra (10^{-2} *M*). The spectra did not show much change on dilution, so the data in Table 3 do refer to the complexes and not to dissociated species.

III. Results

A. Azo compounds

1. Raman and IR spectra

The monomeric complexes [PtCl$_2$(R'N=NR)L] (R, R' = alkyl or aryl) show a *trans* geometry, as shown by the occurrence of one Pt—Cl stretching vibration in the far infrared region at about 335 to 350 cm^{-1}.

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* The ligands were prepared and purified by published methods [22, 23].

TABLE 1

ANALYTICAL DATA FOR $[PtCl_2(R'X{=}NR)L]$[a]

Compound	Analysis found (calcd.) (%)		
	C	H	Cl
$PtCl_2(CH_3NNCH_3)(AsEt_3)$	20.00	4.21	14.48
	(19.75)	(4.32)	(14.61)
$PtCl_2(CH_3NNCH_3)(PEt_3)$	22.01	4.63	15.98
	(21.74)	(4.75)	(16.06)
$PtCl_2(C_2H_5NNC_2H_5)(PEt_3)$	25.20	5.18	15.31
	(25.53)	(5.32)	(15.11)
$PtCl_2(i\text{-}C_3H_7{-}NN{-}i\text{-}C_3H_7)(PEt_3)$	29.00	5.66	13.99
	(28.91)	(5.82)	(14.06)
$PtCl_2(PhNNPh)(AsEt_3)$	35.72	4.30	11.21
	(35.41)	(4.13)	(11.62)
$PtCl_2(p\text{-}CH_3C_6H_4{-}NN{-}p\text{-}CH_3C_6H_4)(AsEt_3)$	37.22	4.65	10.90
	(37.63)	(4.58)	(11.10)
$PtCl_2(PhNNPh)(C_2H_4)$	35.04	2.80	15.21
	(35.29)	(2.94)	(14.92)
$PtCl_2(p\text{-}CH_3C_6H_4{-}NN{-}p\text{-}CH_3C_6H_4)(C_2H_4)$	38.19	3.40	14.35
	(38 10)	(3.57)	(14.09)
$PtCl_2(PhCHNCH_3)(AsEt_3)$	30.74	4.53	12.84
	(30.72)	(4.42)	(12.95)
$PtCl_2(p\ CH_3C_6H_4CHNCH_3)(AsEt_3)$	32.08	4.65	12.75
	(32.11)	(4.63)	(12.63)
$PtCl_2(p\text{-}CH_3C_6H_4{-}CHN{-}p\text{-}CH_3C_6H_4)(AsEt_3)$	39.50	4.87	10.86
	(39.56)	(4.74)	(11.12)
$PtCl_2(PhCHNPh)(AsEt_3)$	37.02	4.42	11.65
	(37.45)	(4.30)	(11.64)
$PtCl_2(PhCHNCH_3)(C_2H_4)$	28.70	2.93	16.99
	(29.06)	(3.15)	(17.19)
$PtCl_2(p\text{-}CH_3C_6H_4CHNCH_3)(C_2H_4)$	30.23	3.58	16.71
	(30.92)	(3.51)	(16.60)
$PtCl_2(p\text{-}CH_3C_6H_4{-}CHN{-}p\text{-}CH_3C_6H_4)(C_2H_4)$	40.19	3.85	14.50
	(40.55)	(3.80)	(14.08)
$PtCl_2(PhCHNPh)(C_2H_4)$	37 81	3.25	14.82
	(37.89)	(3.18)	(14.92)

[a] All the complexes have a yellow colour.

For the preparations of the complexes the stable *trans* azo compounds were used. The $\nu(N{=}N)$ vibrations of the free *cis* and *trans* azo compounds have been unambiguously assigned by IR (^{15}N) [20] and Raman [19, 21] spectroscopy.

In *trans*-azobenzene, $\nu(N{=}N)$ at 1442 cm^{-1} is only Raman active and differs markedly from $\nu(N{=}N)$ for the *cis* isomer at 1511 cm^{-1}. Upon coordination, the $\nu(N{=}N)$ vibration hardly changes from that for the corresponding free *trans* azo compound (Table 2). These and other spectroscopic data considered below show that the azo compound is σ-(*N*)-coordinated and has retained its *trans* geometry. In contrast, the conjugated acid [8] and the $SbCl_5$ complex [9] of azobenzene show large shifts of $\nu(N{=}N)$ to lower frequencies (Table 2). Evidently the energy levels of azobenzene are much more affected by the proton and main group elements than by palladium and platinum.

TABLE 2

ν(X=N) OF [$PtCl_2(R'X{=}NR)L$] FROM THE IR (KBr DISK) AND RAMAN DATA (powdered samples)

Compound	ν(X=N) (cm^{-1})	
trans-CH_3NNCH_3[c]	1576	(Raman)
$PtCl_2(CH_3NNCH_3)(AsEt_3)$	1590	(IR)
trans-PhNNPh[c]	1442	(Raman)
$PtCl_2$(PhNNPh) ($AsEt_3$)	1448	(Raman)
$PtCl_2$(PhNNPh) (PEt_3)	1450	(Raman)
trans-$PdCl_2(PhNNPh)_2$	1446	(Raman)
trans $PdBr_2(PhNNPh)_2$	1446	(Raman)
$SbCl_5\cdot$(PhNNPh)[a]	1390	(Raman)
$(PhNNPhH^+)_2(PtCl_6^{2-})$[b]	1390	(Raman)
trans *p*-$CH_3C_6H_4$—NN—*p* $CH_3C_6H_4$[c]	1458	(Raman)
$PtCl_2$(*p*-$CH_3C_6H_4$—NN—*p*-$CH_3C_6H_4$) ($AsEt_3$)	1450	(Raman)
$PtCl_2$(*p*-$CH_3C_6H_4$—NN—*p*-$CH_3C_6H_4$) (C_2H_4)	1455	(Raman)
trans $PdCl_2$(*p*-$CH_3C_6H_4$—NN—*p*-$CH_3C_6H_4$)$_2$	1466	(Raman)
trans $PdBr_2$(*p*-$CH_3C_6H_4$—NN—*p*-$CH_3C_6H_4$)$_2$	1464	(Raman)
$PhCHNCH_3$[c]	1650	(IR)
$PtCl_2(PhCHNCH_3)(AsEt_3)$	1643	(IR)
$PtCl_2(PhCHNCH_3)(C_2H_4)$	1638	(IR)
p-$CH_3C_6H_4CHNCH_3$[c]	1650	(IR)
$PtCl_2$(*p*-$CH_3C_6H_4CHNCH_3$) ($AsEt_3$)	1633	(IR)
$PtCl_2$(*p*-$CH_3C_6H_4CHNCH_3$) (C_2H_4)	1633	(IR)
PhCHNPh[c]	1640	(IR)
$PtCl_2$(PhCHNPh) ($AsEt_3$)	1618	(IR)
$PtCl_2$(PhCHNPh) (C_2H_4)	1618	(IR)
p-$CH_3C_6H_4$—CHN—*p*-$CH_3C_6H_4$[c]	1635	(IR)
$PtCl_2$(*p*-$CH_3C_6H_4$—CHN—*p*-$CH_3C_6H_4$) ($AsEt_3$)	1613	(IR)
$PtCl_2$(*p*-$CH_3C_6H_4$—CHN—*p*-$CH_3C_6H_4$) (C_2H_4)	1610	(IR)

[a] See ref. 9. [b] See ref. 8. [c] See ref. 19-22 for the assignments of ν(X=N) of the free ligands; for comparison, the ν(N=N) of *cis*-azobenzene [20] is located at 1511 cm^{-1}.

2. *Electronic absorption spectra*

trans-Azomethane only possesses a very weak absorption band in the UV. In the spectrum of [$PtCl_2(CH_3NNCH_3)(PEt_3)$], only ligand-field (LF) transitions are observed (Table 3), and these are situated close to the corresponding transitions of [$PtCl_2$ (piperidine) (P-n-Pr_3)] [10]. This indicates that azomethane is coordinated to the platinum atom like piperidine, i.e. through a nitrogen lone pair.

The weak and strong absorption bands of *trans*-azobenzene and *trans-p,p'*-azotoluene have been assigned respectively to the $n_s \rightarrow \pi^*$ (symmetrically forbidden) and the $\pi \rightarrow \pi^*$ (fully allowed) transitions [11]. The spectra of the azobenzene and azotoluene complexes of platinum and palladium (also included in Table 3) all possess a strong band at about 30 000 cm^{-1}, which we assign to the $\pi \rightarrow \pi^*$ transition of the complexed ligands, because it agrees in position and intensity with the $\pi \rightarrow \pi^*$ transition of the free azo compounds. The much weaker band at longer wavelengths of the spectra of the platinum complexes is assigned to the $n \rightarrow \pi^*$ transition of the coordinated azo ligand by the same arguments, and because it is too low in energy and too intense to be assigned

ABELE 3

LECTRONIC ABSORPTION SPECTRA OF $[PtCl_2(R'X{=}NR)L]$ IN CH_2Cl_2 (absorption maxima in ^{3} cm^{-1}, ϵ values in brackets).

mpound	$\lambda_{max}(\epsilon)$
ns-CH_3NNCH_3	28.0(13)
$Cl_2(CH_3NNCH_3)(PEt_3)$	30.5(450); 32.3(500), 38.3(950)
$Cl_2(CH_3NNCH_3)(AsEt_3)$	30.9(600)
$lCl_2(CH_3NNCH_3)_2$[a]	26.0(245); 33.1(3840); 36.1(5170)
$lBr_2(CH_3NNCH_3)_2$[a]	25.0(292), 32.0(3700), 39.8(36800)
ns-PhNNPh	22.5(600); 31.4(22000)
Cl_2(PhNNPh)$(AsEt_3)$	23.9(1150); 31.3(19500)
lCl_2(PhNNPn)$_2$	25.3(9500), 31.6(39000)
lBr_2(PhNNPh)$_2$	25.1(6050); 31.6(23000)
hNNPh)H^+[b]	23.9(27000), 33.9(3000)
hNNPh)$SbCl_5$[c]	24.4(28500)
ns p $CH_3C_6H_4{-}NN{-}p{\cdot}CH_3C_6H_4$	22.9(400), 30.0(23000)
$Cl_2(p\ CH_3C_6H_4{-}NN{-}p{\cdot}CH_3C_6H_4)(AsEt_3)$	24.3(3200), 30.0(17500)
$lCl_2(p\ CH_3C_6H_4{-}NN{-}p{\text -}CH_3C_6H_4)_2$	24.6(15500), 30.6(27500)
$lBr_2(p{\text -}CH_3C_6H_4{-}NN{-}p{\text -}CH_3C_6H_4)_2$	24.4(17500); 30.1(32000)

See ref 2. [b] See ref. 12. [c] See ref. 9.

a LF-transition. The analogous band of the palladium complexes is tentatily assigned to a ligand to metal charge transfer transition coinciding with the → π* transition, because it is too high in intensity to be assigned to the → π* transition alone.

Clearly the spectra of these azo complexes hardly differ from those of the rresponding free *trans* azo ligands. Thus the ligands must retain their *trans* nfiguration in the complexes, since the π → π* transition is strongly shifted wards longer wavelengths in the corresponding free *cis* azo compound [24]. hese results differ from those of the conjugated acid [12] and the $SbCl_5$ comlex [9] of azobenzene, which are also included in Table 3. The last two compounds show a strong shift of the π → π* transition as a result of a lowering f the π* level.

BLE 4

NMR DATA[a] FOR $R'X{=}NR$ IN $CDCl_3$ (ppm from TMS).

mpound	$NCH_{3-n}(CH_3)_n$	*ortho'*	*ortho*	*meta'* (*para'*)	*meta* (*para*)	CH=N
H_3NNCH_3	3.75s					
$H_5NNC_2H_5$	3.79q[b]; 1.30t[b]					
$_3H_7{-}NN{-}i{\cdot}C_3H_7$	3.55m[b]; 1.22d[b]					
NNPh		7.88m	7.88m	7.37m	7.37m	
$CH_3C_6H_4{-}NN{-}p{\cdot}CH_3C_6H_4$[d]		7.82d	7.82d	7.29d	7.29d	
$CHNCH_3$	3.45d[c]	7.68m		7.33m		8.18q[c]
$CH_3C_6H_4CHNCH_3$[d]	3.47d[c]	7.64d		7.22d		8.24q[c]
CHNPh		7.78m	7.33m	7.33m	7.33m	8.40s
$CH_3C_6H_4CHN{-}p{\text -}CH_3C_6H_4$[d]		7.74d	7.11s	7 22d	7.11s	8.37s

, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. [b] J(H—H) 7 Hz. [c] J(H—H) 1.5 Hz. $J_{A,B}$(A,B quadruplet) 8-13 Hz.

TABLE 5

^{13}C NMR DATA FOR R'X=NR IN CDCl$_3$ (ppm from TMS)

Compound	NCH$_{3-n}$(CH$_3$)$_n$ NCH$_{3-n}$; (CH$_3$)$_n$	*ortho'*	*ortho*	*meta'* and *meta*	*para'*	*para*	X–C'	N–C	CH=N
CH$_3$NNCH$_3$	55.65								
C$_2$H$_5$NNC$_2$H$_5$	63.14; 12.29								
i-C$_3$H$_7$–NN–i-C$_3$H$_7$	67.43; 19.36								
PhNNPh		122.65	122.65	128.77	130.63	130.63	152.38	152 38	
p-CH$_3$C$_6$H$_4$–NN–p-CH$_3$C$_6$H$_4$		122.54	122.54	129.48	140.87	140.87	150.60	150 60	
PhCHNPh		128.55	120.65	128.91	131.08	125.70	136.07	161 90	159.95
p-CH$_3$C$_6$H$_4$–CHN–p-CH$_3$C$_6$H$_4$		128 65	121.63	129.64, 129.37	141.35	135.20	134.01	149 60	159.12
PhCHNCH$_3$	47.98	127.70		128.31	130.18		136.19		161.93
p-CH$_3$C$_6$H$_4$CHNCH$_3$	48.02	127.69		129.09	140.39		133.59		162.02

ABLE 6A

H NMR DATA FOR $[PtCl_2\{(CH_3')_nCH'_{3-n}NNCH_{3-n}(CH_3)_n\}L]^a$ IN $CDCl_3$ (ppm from TMS)

	n	NCH'_{3-n} [b]	NCH_{3-n} [b]	$(CH_3)_n$ resonances
sEt$_3$	0	4.52 (12.5 Hz)[c]	4.33 (14 Hz)[c]	
Et$_3$	0	4.45	4.18[d]	
Et$_3$	1	4.72	4.46[d]	1.55
Et$_3$	2	5.65	4.88[d]	1.39, 1.48

Accent denotes protons at the non-coordinated end of the azo ligand. [b] $J(H-H)$ 1.5 Hz; the other H—^{1}H coupling constants are the same as observed in the free ligands (Table 4). [c] $J(Pt)$ noted in rackets. [d] These resonances show P coupling.

TABLE 6B

^{1}H CHEMICAL SHIFT DIFFERENCE Δ BETWEEN THE LOW FIELD $N-CH'_{3-n}$ RESONANCE OF $[PtCl_2\{(CH'_3)_nCH'_{3-n}NNCH_{3-n}(CH_3)_n\}(PEt_3)]$ AND THE $N-CH_{3-n}$ RESONANCE OF $(CH_3)_n$-$CH_{3-n}NNCH_{3-n}(CH_3)_n$

n	$m = 3-n$	Δ	$\Delta \times m$
0	3	0.65	1.95
1	2	0.93	1.86
2	1	1.83	2.10

3. *^{1}H and ^{13}C NMR spectra*

The ^{1}H and ^{13}C NMR spectra of the free azo ligands are listed in Tables 4 and 5. Off-resonance experiments and methyl substitution at an aromatic ring carbon atom have assisted in the assignment of the ^{13}C signals of the aromatic azo compounds.

Features of the ^{1}H and ^{13}C NMR spectra of the complexes *trans*-$[PtCl_2(CH_3)_nCH_{3-n}NNCH_{3-n}(CH_3)_n(PEt_3)]$ (n = 0, 1, 2) are listed in Tables 6 and 7. The ^{1}H NMR spectra (Table 6A) show the existence of two non-equivalent $N-CH_{3-n}$ groups, which both absorb at lower field than the corresponding groups in the free ligand, and which show a long range ^{1}H—^{1}H coupling (1.5 Hz). This is consistent with the σ-(*N*)-coordination mode. The ^{31}P coupling and the larger ^{195}Pt coupling, clearly resolved for $[PtCl_2(CH_3NNCH_3)(AsEt_3)]$, for the high field $N-CH_{3-n}$ signal, strongly indicate that this signal arises from the coordinated $N-CH_{3-n}$ group.

If we take the chemical shift difference between the lower field $N-CH_{3-n}$ resonance and the corresponding free ligand resonance and multiply these

TABLE 7

^{13}C NMR DATA FOR $[PtCl_2\{(C'H_3)_nC'H_{3-n}NNCH_{3-n}(CH_3)_n\}L]^a$ IN $CDCl_3$ (ppm from TMS) (coupling constants in Hz)

L	n	NCH_{3-n}; $J(Pt)$; $J(P)$	$NC'H_{3-n}$, $J(Pt)$; $J(P)$	$(CH_3)_n$ resonances
AsEt$_3$	0	60.40, 45	56.24; 56	
PEt$_3$	0	59.40; 36.5; 2.7	55.67, 46; 3.6	
PEt$_3$	1	66.61; 30; 3.6	63.16; 40; 2.6	12.73
PEt$_3$	2	71.45; 32; 3.1	68.87; 39; 2.9	19.54; 21.37

[a] The C' denotes a carbon atom at the non-coordinated end of the azo ligand

TABLE 8

^{1}H NMR DATA[a] FOR [PtCl$_2$(R'X=NR)L][b] IN CDCl$_3$ (ppm from TMS) (coupling constants[c] in Hz)

Compound	*ortho'*	*ortho*	*meta'* (*para'*)	*meta* (*para*)	CH=N; *J*(Pt)	NCH$_3$; *J*(Pt)
PtCl$_2$(PhNNPh) (AsEt$_3$)	8.65m	8.36m	7.50m	7.50m		
PtCl$_2$(*p*-CH$_3$C$_6$H$_4$—NN—*p*-CH$_3$C$_6$H$_4$) (AsEt$_3$)	8.55d	8.39d	7.35d	7.35d		
PtCl$_2$(PhNNPh) (C$_2$H$_4$)	8.40m	8.40m	7.60m	7.60m		
PtCl$_2$(*p*-CH$_3$C$_6$H$_4$—NN—*p*-CH$_3$C$_6$H$_4$) (C$_2$H$_4$)	8.37d	8.37d	7.10d	7.40d		
PtCl$_2$(PhCHNCH$_3$) (AsEt$_3$)	8.91m		7.48m		8.57q, 74	3.88d; 19
PtCl$_2$(PhCHNCH$_3$) (C$_2$H$_4$)	8.64m		7.57m		8.69q, 100	3.88d; 19
PtCl$_2$(*p*-CH$_3$C$_6$H$_4$CHNCH$_3$) (AsEt$_3$)	8.87d		7.29d		8.51q; 76	3.88d; 19
PtCl$_2$(*p*-CH$_3$C$_6$H$_4$CHNCH$_3$) (C$_2$H$_4$)	8.55d		7.36d		8.61; 100	3.84d; 19
PtCl$_2$(PhCHNPh) (AsEt$_3$)	9.11m	7.44m	7.44m	7.44m	8.58s; 76	
PtCl$_2$(PhCHNPh) (C$_2$H$_4$)	8.87m	7.56m	7.56m	7.56m		
PtCl$_2$(*p*-CH$_3$C$_6$H$_4$CHN—*p*-CH$_3$C$_6$H$_4$) (AsEt$_3$)	9.06d	7.60d	7.32d	7.19d	8.60s; 75	
PtCl$_2$(*p*-CH$_3$C$_6$H$_4$CHN—*p*-CH$_3$C$_6$H$_4$) (C$_2$H$_4$)	8.74d	7.56d	7.41d	7.23d	8.67s, 96	

[a] s, singlet; d, doublet; m, multiplet. [b] Accent denotes protons at the non-coordinated end of the azo or imine ligand. [c] the H—H coupling constants are the same as observed in the free azo or imine ligands (Table 4).

igures by 3, 2 and 1, respectively, for n = 0, 1 and 2 we obtain a fairly contant value for the downfield shift of about 2.00 ppm (Table 6B). A similar obervation was made in the case of one of the isomers of *trans*-[$PtCl_2$(RN=S=NR)-] [17]. By analogy with the interpretation given for those complexes, we ascribe our observations to the close proximity of the metal to the protons of the noncoordinated $N{-}CH_{3-n}$ group and to the occurrence of restricted rotation about his $N{-}CH_{3-n}$ bond for n = 1 or 2 arising from the *trans* geometry of the coordinated ligand (Section IV).

In the ^{13}C NMR spectrum two $N{-}CH_{3-n}$ signals are again observed (Table 7). No assignment could be made on the basis of the ^{195}Pt and ^{31}P coupling data, but off-resonance experiments showed that the lower field signal belongs to the coordinated $N{-}CH_{3-n}$ group.

The ^1H and ^{13}C spectra of the complexes [$PtCl_2$(PhNNPh)L] and [$PtCl_2$-(p-$CH_3C_6H_4{-}NN{-}p$-$CH_3C_6H_4$)L] (Tables 8 and 9) show that the largest downfield shifts in comparison with the free ligand signals (Tables 4 and 5) are observed for the *ortho* resonances. The lower field *ortho* proton signal undergoes an upfield shift going from L = $AsEt_3$ to L = C_2H_4, while no such shifts are observed for the other resonances. The same observations are made for the analogous imine complexes (section III.B.3), and in the light of this analogy the lower field *ortho* ^1H and ^{13}C signals are assigned to the *ortho* CH-groups of the noncoordinated end of the ligand.

B. Imine compounds

1. Infrared spectra

By the arguments used for the azo complexes, it can be deduced, that the imine complexes [$PtCl_2$(R'CHNR)L] possess a *trans* geometry and that the imine ligands are $\sigma(N)$-coordinated (Table 2)*.

2. Electronic absorption spectra

No interpretation could be made of the absorption spectra, because of the overlap between ligand and charge transfer transitions.

3. ^1H and ^{13}C NMR spectra

The ^1H and ^{13}C NMR spectra of the free imine ligands are summarized in Tables 4 and 5. The ^{13}C results (Table 5) lead to a clear distinction to be made between the signals of the *N*-aryl ring and the *C*-aryl ring, except for the *meta* carbon signals.

Comparison of the ^1H and ^{13}C NMR spectra of the complexes [$PtCl_2$-(p-$CH_3C_6H_4CH{=}NCH_3$)L] with those of [$PtCl_2$(p-$CH_3C_6H_4CH{=}N{-}p$-$CH_3C_6H_4$)L] (Tables 8 and 9) lead to significant conclusions. From the proton spectra (Tables 4 and 8) it is clear that the $N{-}CH_3$ signal moves downfield with respect to the free ligand signal (see also Fig. 2), and shows ^{195}Pt coupling (19 Hz). The imine (CH=N)-proton absorption also moves downfield upon coordination and shows a quite large ^{195}Pt coupling (75-100 Hz). These results confirm the σ-(N)-coordination mode of the imine ligand. Marked downfield shifts are ob-

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* No definite conclusions can be drawn about the geometry of the imine ligands in the complexes by IR, because there is doubt about the geometry of the free ligands themselves [22].

TABLE 9

^{13}C NMR DATA FOR [PtCl$_2$(R'X=NR)L]^a IN CDCl$_3$ (ppm from TMS) (coupling constants in Hz)

Compound	*ortho'*;J(Pt)	*ortho*;J(Pt)	*meta'* and *meta*^{b}	*para'*	*para*	X—C';J(Pt)	N—C	CH=N	N—CH$_3$;J(Pt)
PtCl$_2$(PhNNPh) (AsEt$_3$)	125.39	122.52	128.17; 128.67	131.78 (130.94)^c		154.41 (152.97)			
PtCl$_2$(p-CH$_3$C$_6$H$_4$—NN—p-CH$_3$C$_6$H$_4$)(AsEt$_3$)	125.34	123.07	128.87; 129.22	142.21 (140.81)^c		152.67 (150.99)			
PtCl$_2$(PhNNPh) (C$_2$H$_4$)	125.37	122.55	129.00	132.81^c					
PtCl$_2$(p-CH$_3$C$_6$H$_4$—NN—p-CH$_3$C$_6$H$_4$)(C$_2$H$_4$)	125.70	122.87	129.70	143.79 (143.50)^c					
PtCl$_2$(PhCHNCH$_3$)(AsEt$_3$)	130.99; 14		127.93	132.13		132.74; 19		167.32	51.74; 12.5
PtCl$_2$(PhCHNCH$_3$)(C$_2$H$_4$)	130.94; 15		128.68	133.23				169.72	51.54; 13
PtCl$_2$(p-CH$_3$C$_6$H$_4$CHNCH$_3$)(AsEt$_3$)	131.25; 13		128.80	143.04		130.05; 19		167.15	51.68; 12.5
PtCl$_2$(p-CH$_3$C$_6$H$_4$CHNCH$_3$)(C$_2$H$_4$)	131.15; 14		129.50	144.10				169.40	51.50; 12.5
PtCl$_2$(PhCHNPh)(AsEt$_3$)	131.95; 14	123.41, 8	128.22; 128.77	133.04	127.45	133.04; 19	151.44	168.20	
PtCl$_2$(PhCHNPh)(C$_2$H$_4$)	131.75; 13	123.42, 9	128.92; 129.33	133.96	128.29		149.46	170.10	
PtCl$_2$(p-CH$_3$C$_6$H$_4$CHN—p-CH$_3$C$_6$H$_4$) (AsEt$_3$)	132.24; 15	123.31; 9	129.02; 129.37	143.95	137.15	130.45; 19	149.30	167.32	
PtCl$_2$(p-CH$_3$C$_6$H$_4$CHN—p-CH$_3$C$_6$H$_4$)(C$_2$H$_4$)	132.04; 13	123.41; 9	129.71; 129.87	145.29	138.30		147.22	169.54	

[a] Accent denotes carbons at the non-coordinated end of the azo or imine ligand. [b] No distinction could be made between the two types of *meta* carbons.
[c] No distinction could be made between the two types of *para* carbons, if X is N.

TABLE 10

^{13}C CHEMICAL SHIFT DIFFERENCE Δ BETWEEN THE ARYL RESONANCES OF THE COMPLEXED ([PtCl$_2$(R'X=NR) (AsEt$_3$)])^a AND OF THE FREE IMINE LIGAND (R'X=NR)^a (X = CH)

Compound	Δ(*ortho'*)	Δ(*ortho*)	Δ(*meta'*)^b	Δ(*para'*)	Δ(*para*)	Δ(X—C')	Δ(N—C)
PtCl$_2$(PhCHNCH$_3$) (AsEt$_3$)	3.29		−0.38	1.95		−3.45	
PtCl$_2$(PhCHNPh) (AsEt$_3$)*	3.40	2.76		1.95	1.75	−3.15	−0.46
PtCl$_2$(p-CH$_3$C$_6$H$_4$CHNCH$_3$) (AsEt$_3$)	3.56		−0.29	2.65		−3.54	
PtCl$_2$(p-CH$_3$C$_6$H$_4$CHN—p-CH$_3$C$_6$H$_4$) (AsEt$_3$)*	3.59	1.68		2.60	1.95	−3.56	−0.30

[a] Accent denotes carbons at the non-coordinated end of the imine ligand (compare Tables 5 and 9). [b] No Δ values are given for the *meta* resonances of the marked (*) complexes for the same reason mentioned in Table 9 (footnote *b*).

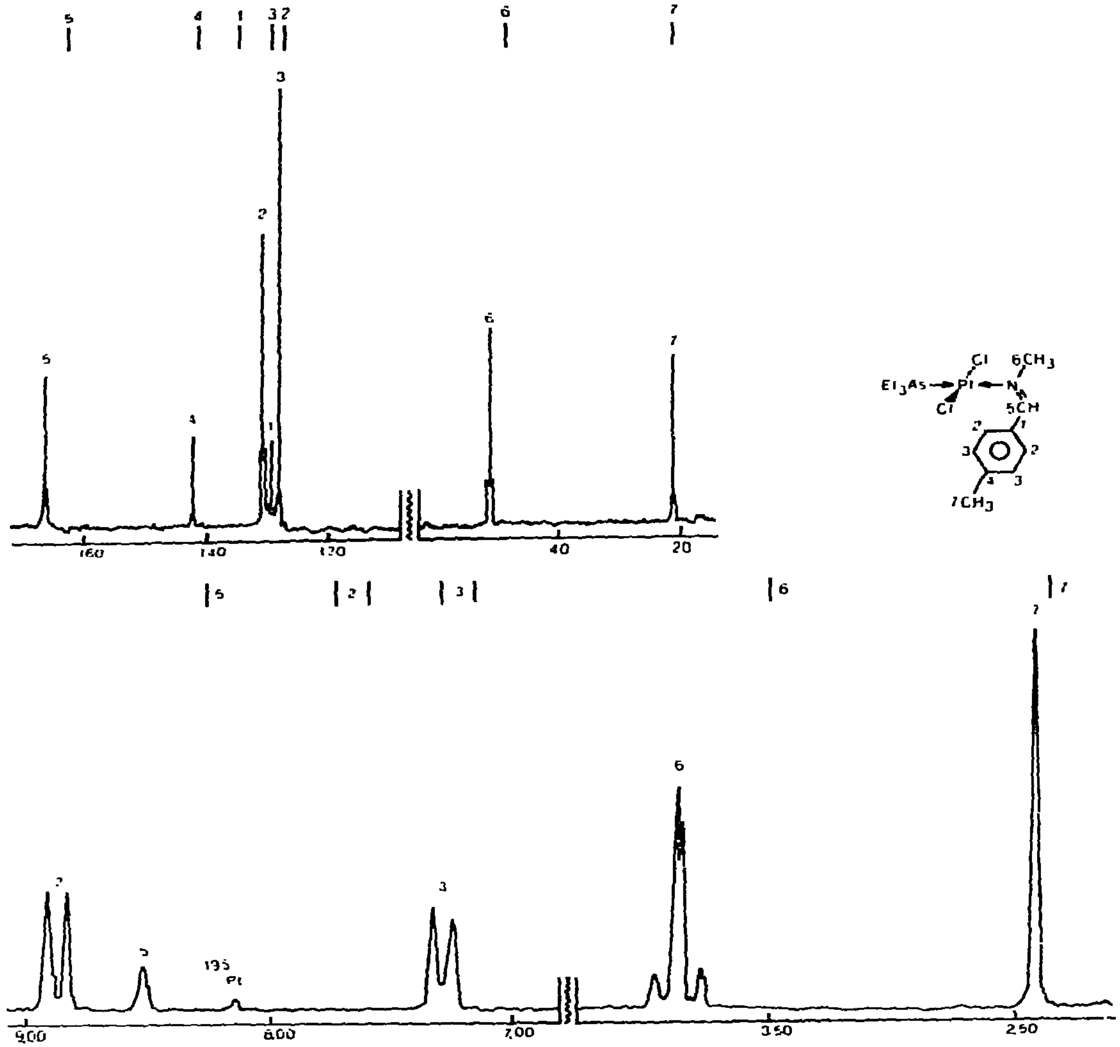

Fig. 2. ${}^1H$ (below) and ${}^{13}C$ (above) NMR spectra of *trans*-[$PtCl_2(p\text{-}CH_3C_6H_4CH{=}NCH_3)(AsEt_3)$] in $CDCl_3$ at room temperature. The δ-values relative to TMS are shown on each baseline. The vertical lines above each spectrum indicate the position of the corresponding free ligand signals.

served for the *ortho* protons. The *ortho* protons of the non-coordinated end of the ligand show the largest downfield shift (ca. 1.2 ppm). This low field *ortho* proton signal is shifted slightly upfield going from $L = AsEt_3$ to $L = C_2H_4$.

Similar features appear in the ${}^{13}C$ NMR spectra (Tables 5 and 9). The $N{-}CH_3$ absorption moves downfield upon coordination (see also Fig. 2) and shows ${}^{195}Pt$ coupling (ca. 12.5 Hz). The imine ($CH{=}N$) absorption shows a downfield chemical shift compared with the free ligand signal. However, no ${}^{195}Pt$ coupling is observed for this carbon signal, in contrast to the large ${}^{195}Pt$ coupling for the analogous proton signal.

From Table 10, which lists the chemical shift difference between the aryl absorptions of the complexed and the free ligands, it is clear that the *ortho* carbons at the non-coordinated end of the ligand show the largest downfield shift. It is striking that the signal of the carbon atom directly attached to the functional group carbon (C—X) shows an upfield shift of similar magnitude. Both these signals show ^{195}Pt coupling, while a lower or no ^{195}Pt coupling respectively is observed for the analogous carbon absorptions of the *N*-aryl ring.

Thus, both in the ^{1}H and in the ^{13}C NMR spectra the *ortho* CH-groups of the non-coordinated end of the imine ligand show a marked low-field shift. This observation can only be rationalized if we assume a *trans* geometry of the coordinated ligand, as explained in the next section.

IV. Discussion

Some interesting points have emerged from this spectroscopic investigation All the data are consistent with σ-(*N*)-coordination of the azo and imine ligands in the complexes *trans*-[$PtCl_2(R'X=NR)L$]. The vibrational and electronic absorption spectra show that azobenzene is affected in a different way upon coordination to Sb^V and H^+ than upon coordination to Pd^{II} and Pt^{II}. Because azobenzene is a hard base, much stronger interactions are expected for this compound with hard acids such as Sb^V and H^+ than with the soft acids Pd^{II} and Pt^{II} [13].

On coordination to Sb^V and H^+ the (N=N) bond in azobenzene will be polarized causing a decrease of ν(N=N) and a shift to longer wavelengths of the $\pi \rightarrow \pi^*$ transition. No such effects are found for the much weaker complexes with Pd^{II} and Pt^{II}.

The vibrational and electronic absorption spectra strongly indicate that the azo ligands retain their *trans* geometry. This also accounts for the unexpected, large low field proton shift of the $N—CH_{3-n}$ group and of the *ortho* protons of the non-coordinated end of the azo or imine ligands. This effect, observed in only a few other cases [14-17], is probably attributable to the paramagnetic anisotropy of the platinum atom, which causes downfield shifts if the protons are situated close to the metal and above the bonding plane of the planar molecule (Fig. 3).

Preliminary results on the crystal structure of *trans*-[$PtCl_2$(*p*-$CH_3C_6H_4$-$CH=NCH_3$) $AsEt_3$)], reveal a short distance between the platinum atom and the *ortho* proton [18]*; the specific dependence of the position of the peaks, observed only for the low field *ortho* proton signals in the ^{1}H NMR spectra of the azo and imine complexes, support this explanation. Possibly the paramagnetic anisotropy of

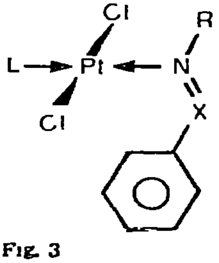

Fig. 3

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* The Pt—C_{ortho} distance is 3.24 (0.05) Å.

the platinum atom is also a major cause of the low field ^{13}C shift of the *ortho* carbons of the non-coordinated aryl ring.

The close range non-bonded Pt · · · HC interactions in the σ-(*N*)-coordinated complexes point to the possibility of intramolecular formation of metal—carbon bonds. The next papers in this series will deal with *ortho*-metallation and with the more general formation of metal—carbon bonds.

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