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METAL—AZO AND METAL—IMINE COMPOUNDS II*.

II*. INSERTION OF Ir^I INTO AROMATIC AND OLEFINIC C—H BONDS

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Summary

The reaction of the aromatic azo or imine compounds PhX=NR (X=N or CH; R = alkyl or aryl) and 2-(methylazo)propene, $H_2C=C(CH_3)—N=NCH_3$, with *trans*-$IrCl(N_2)(PPh_3)_2$ yields the (*ortho*) metallated complexes IrHCl-$(C_6H_4X=NR)(PPh_3)_2$ and $IrHCl[CH=C(CH_3)—N=NCH_3](PPh_3)_2$ respectively.

The ν(N=N) vibration in $IrHCl(C_6H_4N=NPh)(PPh_3)_2$ appears to be drastically lowered with respect to the free ligand vibration. Furthermore, Resonance Raman experiments show that this vibration is strongly coupled to both of the electronic transitions of this compound at longer wavelengths, which therefore must be closely connected with the azo group.

^1H and ^{13}C NMR spectroscopic data and crystallographic studies of IrHCl-$(C_6H_4N=NPh)(PPh_3)_2$ give strong evidence about the nature of the mechanism of these (*ortho*) metallation reactions.

Introduction

Our investigation of σ (*N*)-coordinated aromatic azo or imine Pt^{II}-complexes revealed spectroscopic (NMR)[1] and structural [2] evidence for close range non-bonded interactions between the metal atom and the *ortho* CH groups of the non-coordinated end of the ligand. This observation points to the possibility of subsequent intramolecular formation of a metal—carbon bond, i.e. *ortho* metallation [3-7], which might proceed via an oxidative addition of one of these *ortho* CH groups to the metal atom with subsequent reductive elimination, as was recently suggested by Stone et al. [8] for the *ortho* metallation reaction of azobenzene with Rh^I.

We now report the *ortho* metallation reactions of aromatic azo and imine

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* For part I see ref. 1.

compounds with an Ir^{I} complex, which occur without reductive elimination and provide additional support to the proposed mechanism for low-valent metal complexes [8, 9].

2-(Methylazo)propene is shown to undergo a similar metallation reaction which is new for this compound. Up to now, such reactions with olefinic ligands containing a hetero donor-atom have only been known for *N,N*-dimethylallylamines [10] and 2-vinylpyridine [11].

In addition to the chemical aspects the spectroscopic properties of the new compounds are discussed and compared with those of known complexes of the type *trans*-$PdCl(C_6H_4N{=}NPh)(PEt_3)_2$ [12].

Experimental

The aromatic azo and imine ligands were prepared and purified according to literature methods. [13, 14].

2-(Methylazo)propene was obtained pure following the method of Matveeva et al. [15]. Pure samples of complexes of the type *trans*-$(PdCl(C_6H_4N{=}NPh)(PEt_3)_2$ were obtained according to the method of Crociani et al. [16].

The complexes $IrHCl(C_6H_4X{=}NR)(PPh_3)_2$ (X = N or CH; R = alkyl or aryl) and $IrHCl[CH{=}C(CH_3){-}N{=}NCH_3](PPh_3)_2$ can be prepared by a slow (A) or a rapid (B) method as illustrated below for $IrHCl(C_6H_4CH{=}NPh)(PPh_3)_2$.

Method A

Benzylidene aniline PhCH=NPh (60 mg, 0.33 mmol), was added to a suspension of the complex *trans*-$IrCl(N_2)(PPh_3)_2$ [17] (246 mg, 0.32 mmol) in 15 ml of benzene with exclusion of oxygen. The reaction mixture, which was stirred continuously at room temperature. gradually became clearer and orange-red in colour.

After about three days the reaction was complete and the resulting solution was orange-yellow in colour. After evaporation of part of the solvent, hexane was added to the residual solution (5 ml) until complete precipitation had occurred. The yellow, air-stable solid was washed with hexane and recrystallized from a dichloromethane/hexane mixture (yield 55%).

Method B

The reaction mixture was refluxed for about two hours. After the solution was cooled to room temperature the product was isolated in the same manner as described in method A (yield 70%).

Analytical data for the new complexes are given in Table 1. The aromatic azo and imine complexes are wine-red and yellow respectively, while the complex $IrHCl[CH{=}C(CH_3){-}N{=}NCH_3](PPh_3)_2$ is greenish-yellow in colour.

Attempted reactions with aliphatic azo compounds and azomesitylene, which has all its *ortho* protons substituted by a methyl group, afforded no metallated products. The results were also negative in reactions of the azo or imine ligands with $RhCl(PPh_3)_3$ [18] and $RhCl(N_2)(PPh_3)_2$, which was prepared in situ as described by Maitlis et al [19].

Spectra were recorded on a Varian HA-100 proton NMR apparatus, a Varian XL-100 with Fourier transform (^{1}H and ^{13}C), a Cary-14 (UV), and a

TABLE 1

ANALYTICAL DATA[a] FOR $IrHCl(L')(PPh_3)_2$

L'[b]	Analysis found (calcd.) (%)		
	C	H	Cl
$C_6H_4CHNCH_3$	60.42	4.40	4.28
	(60.64)	(4.48)	(4.08)
$5\text{-}CH_3C_6H_3CHNCH_3$	60.69	4.68	4.35
	(61.02)	(4.63)	(4.01)
C_6H_4CHNPh	62.60	4.32	3.68
	(63.02)	(4.39)	(3.81)
$5\text{-}CH_3C_6H_3CHN$—*p*-tolyl	63.35	4.61	3.85
	(63.68)	(4.68)	(3.70)
C_6H_4NNPh	62.02	4.13	3.98
	(61.69)	(4.28)	(3.80)
$5\text{-}CH_3C_6H_3NN$—*p*-tolyl	61.93	4.38	3.94
	(62.38)	(4.58)	(3.69)
$4,6\text{-}(CH_3)_2C_6H_2NN$—*m*-xylene	62.81	4.88	3.82
	(63.04)	(4.85)	(3.59)
$CH{=}C(CH_3)$—$NNCH_3$	57.21	4.49	4.42
	(57.44)	(4.55)	(4.25)

[a] The excess recrystallization solvent (CH_2Cl_2) contained in the crystals was removed in boiling hexane.
[b] See Fig. 2 for numbering of the carbon atoms of the metallated aromatic ring.

Beckman IR-18A (infrared). The Raman spectra were recorded with a Coderg PH1 spectrometer. The Resonance Raman spectra [20, 21] were recorded on a 4×10^{-3} *M* solution of $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ in CH_2Cl_2 with a Cary-81 spectrophotometer. In this experiment a CRL Ar^+/Kr^+ laser was used with exciting lines ranging from 647 to 458 nm. The solvent CH_2Cl_2 was used as an internal standard because it does not absorb in the visible or near UV regions and has a Raman band within 75 cm^{-1} of the 1348 cm^{-1} band of the complex (at 1422 cm^{-1}). Corrections for absorption and wavelength dependence of the detecting system have not been applied because the 1348 and 1422 cm^{-1} bands are so close together that the corrections can be neglected with respect to the experimental errors (about 10%).

Results

Electronic absorption, infrared and Resonance Raman spectra

Electronic absorption spectra. The energies and intensities of the absorption bands of the azo compounds and their Ir^{III} complexes are presented in Table 2, together with the results for *trans*-$PdCl(C_6H_4N{=}NPh)(PEt_3)_2$. The spectra of the corresponding imine complexes are not discussed here because in the UV, they consist of a series of overlapping bands which are not easy to assign.

trans-Azobenzene [22], *trans-p,p'*-azotoluene [22] and 2-(methylazo)-propene posses a strong absorption band which is assigned to the $\pi \rightarrow \pi^*$ transsition (intramolecular charge transfer from the aromatic or olefinic group to the N=N group). At longer wavelengths they all show a much weaker band

TABLE 2

ELECTRONIC ABSORPTION SPECTRA OF SOME AZO LIGANDS L AND THE CORRESPONDING COMPLEXES $IrHCl(L')(PPh_3)_2$[a] AND *trans*-$PdCl(L')PEt_3)_2$ in CH_2Cl_2 (ν_{max} IN 10^3 cm^{-1}, ϵ-VALUES IN PARENTHESES)

Azo ligand	M	ν_{max} (ϵ)
trans-PhNNPh (L)		22.5 (600); 31.4(22000)
C_6H_4NNPh (L')	Pd	21.5 (1900); 31.2(19000)
C_6H_4N:NPh (L')	Ir	18.9(2010), 21.6 (4080); 29.4(12500)
trans-*p*-tolyl—NN-*p*-tolyl (L)		22.9 (400); 30.0(23000)
5-$CH_3C_6H_3NN$-p-tolyl (L')	Ir	19.4(1870); 22.0 (3460); 28.4(13000)
CH_2=C(CH_3)—$NNCH_3$ (L)		25.3 (40), 42.6 (7850)
CH=C(CH_3)—$NNCH_3$ (L')	Ir	22.2 (410); 24.7 (850);[b]

[a] L' = (*ortho*) metallated L. [b] Coincides with other bands.

(ϵ <1000) which is assigned to an $n \rightarrow \pi^*$ transition (the n level originates from the nitrogen lone-pair orbitals).

From the crystal structure of the square-planar complex *trans*-$PdCl(C_6H_4N$=NPh)$(PEt_3)_2$ [12] it is known that azobenzene is coordinated to the metal atom by means of only an *ortho* carbon atom and retains its *trans* geometry. The bond lengths and angles do not differ significantly from those of *trans*-azobenzene itself; only the N=N bond distance is slightly elongated with respect to the (mean) distance in the corresponding free ligand. These structural similarities are reflected in the absorption spectrum of this complex, which closely resembles the spectrum of *trans*-azobenzene. The $\pi \rightarrow \pi^*$ transition is found at the same position with intensity nearly equal to that of the free ligand. The $n \rightarrow \pi^*$ transition shows a small blue shift presumably due to a drift of some negative charge from Pd to the azo ligand.

In $IrHCl(C_6H_4N$=NPh)$(PPh_3)_2$ azobenzene is coordinated to the metal atom by means of a metal—carbon and a metal—nitrogen σ bond (see Fig. 4), resulting in more drastic structural changes within the azo ligand. The spectrum of this complex shows little resemblance to the spectrum of the free ligand. It shows a strong absorption band at about 29000 cm^{-1} which by analogy with the band of the Pd^{II} complex is assigned to the $\pi \rightarrow \pi^*$ transition of the complexed ligand. In contrast to the results for the Pd^{II} complex this band is now shifted to longer wavelengths with respect to the free ligand.

At longer wavelengths two bands are found, strongly shifted to the red with respect to the $n_s \rightarrow \pi^*$ transition of *trans*-azobenzene. The same observations are made for the corresponding azotoluene complex. In the spectrum of $IrHCl[CH=C(CH_3)—N=NCH_3](PPh_3)_2$ these bands are also present and are shifted in the same way with respect to the $n \rightarrow \pi^*$ transition of the free ligand. Apparently these bands are closely connected with the lone-pair or anti-bonding orbitals localized on the azo group. This conclusion is also drawn from the Resonance Raman spectra (see next section) which show that both of the long wavelength transitions are strongly coupled to the ν(N=N) of the azo group. Therefore, these bands may be assigned either to $n \rightarrow \pi^*$ transitions which have changed in character from the corresponding free ligand transition, or to charge transfer transitions within the metallocyclic ring (Fig. 4).

Infrared and Resonance Raman spectra. The disappearance of the N_2 ligand is demonstrated by the absence of $\nu(N{\equiv}N)$ in the infrared and Raman spectra of the new Ir^{III} complexes. Instead, another IR band which is assigned to the $\nu(Ir{-}H)$ vibration (Table 3) occurs in the region 2000 to 2200 cm^{-1}. This band is also found when the reaction is carried out in a deuterated solvent ($CDCl_3$ or C_6D_6), showing that the hydrido ligand does not originate from a solvent molecule.

From the IR spectra it is clear that the $\nu(C{=}N)$ vibrations of the complexes $IrHCl(C_6H_4CH{=}NR)(PPh_3)_2$ should be shifted to lower frequency with respect to the free ligand vibrations, because no band is found at the free ligand position [1] or at higher frequency. On the basis of the same arguments and by comparison with the spectra of the other complexes it is concluded that the stretching vibrations of the $(C{=}C{-}N{=}N)$ fragment of the free azopropene ligand [15] at 1640 and 1510 cm^{-1} are shifted to lower frequency upon complexation.

The strong, polarized band at 1442 cm^{-1} of *trans*-azobenzene which was used for the *ortho*-metallation reaction, has already been assigned to the $\nu(N{=}N)$ vibration [23]. Koide et al. [24] found that the Raman intensity of this vibration is strongly enhanced when the exciting laser line approaches the $\pi \rightarrow \pi^*$ absorption band of the compound at 320 nm, while no rigorous Resonance Raman effect [24] was observed with excitation within the $n_s \rightarrow \pi^*$ absorption band. From this Resonance Raman effect they concluded that $\nu(N{=}N)$ is strongly coupled to the $\pi \rightarrow \pi^*$ transition and not to the $n_s \rightarrow \pi^*$ transition.

For the compound $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ the same Resonance Raman technique was used. The Raman spectra are incomplete, showing only four bands at 1192, 1348, 1538 and 1585 cm^{-1} respectively. The band at 1442 cm^{-1} of free *trans*-azobenzene is not observed in the complex; instead a strong polarized band is found at 1348 cm^{-1} which shows a strong Resonance Raman effect, like the 1442 cm^{-1} band of the free ligand. We therefore assign this band mainly to the $\nu(N{=}N)$ vibration of azobenzene in the complex, which has been lowered by nearly 100 cm^{-1} with respect to the corresponding free ligand vibration. In comparison, the $\nu(N{=}N)$ vibration of the azo ligand is much less affec-

TABLE 3

$\nu(N{=}N)$ AND $\nu(Ir{-}H)$ (in cm^{-1}) FOR $IrHCl(L')(PPh_3)_2$ AND *trans*-$PdCl(L')(PEt_3)_2$, DERIVED FROM IR (KBr DISC) AND RAMAN (CH_2Cl_2 SOLUTION) DATA

L' [a]	M	$\nu(N{=}N)$ [b]	$\nu(Ir{-}H)$ [c]
$C_6H_4CHNCH_3$	Ir	[d]	2060
$5\text{-}CH_3C_6H_3CHNCH_3$	Ir	[d]	2100
C_6H_4CHNPh	Ir	[d]	2120
$5\text{-}CH_3C_6H_3CHN$-*p*-tolyl	Ir	[d]	2140
C_6H_4NNPh	Ir	1348(1442) [e]	2180
$5\text{-}CH_3C_6H_3NN$-*p*-tolyl	Ir	1362(1458) [e]	2140
C_6H_4NNPh	Pd	1411(1442) [e]	
$5\text{-}CH_3C_6H_3NN$-*p*-tolyl	Pd	1426(1458) [e]	
$CH{=}C(CH_3){-}NNCH_3$	Ir	[d]	2080

[a] See Fig. 2 for numbering of the carbon atoms of the metallated ring. [b] Raman results. [c] Infrared results. [d] Not assigned, see text. [e] Values in parentheses are for the corresponding free ligand vibration.

TABLE 4

RELATIVE INTENSITIES OF ν(N=N) IN $IrHCl(C_6H_4NNPh)(PPh_3)_2$ (4×10^{-3}M SOLUTION IN CH_2Cl_2) WITH RESPECT TO THE 1422 cm^{-1} BAND OF CH_2Cl_2 FOR DIFFERENT LASER LINES[a]

$I(1348\ cm^{-1})/I(1422\ cm^{-1})$	Exciting wavelength (Å)
0.14	6471
0.63	5682
0.95	5309
1.14	5208
0.88	5145
0.64	5017
0.72	4965
1.29	4880
1.32	4765
1.30	4727
1.19	4579

[a] See Experimental for further details.

ted in *trans*-$PdCl(C_6H_4N{=}NPh)(PEt_3)_2$, where it does not act as a chelate [12], and the vibration is only lowered to 1411 cm^{-1}. The same results are found for the corresponding Ir^{III}- and Pd^{II}-azotoluene complexes (Table 3).

Details of the Resonance Raman experiments were given in the Experimental, so that only the results are discussed here. The relative intensities of the 1348 cm^{-1} band of $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ with respect to the 1422 cm^{-1} band of CH_2Cl_2 are collected in Table 4 and are plotted as a function of the exciting frequencies in Fig. 1 (excitation profile) [25] together with the absorption spectrum of the compound.

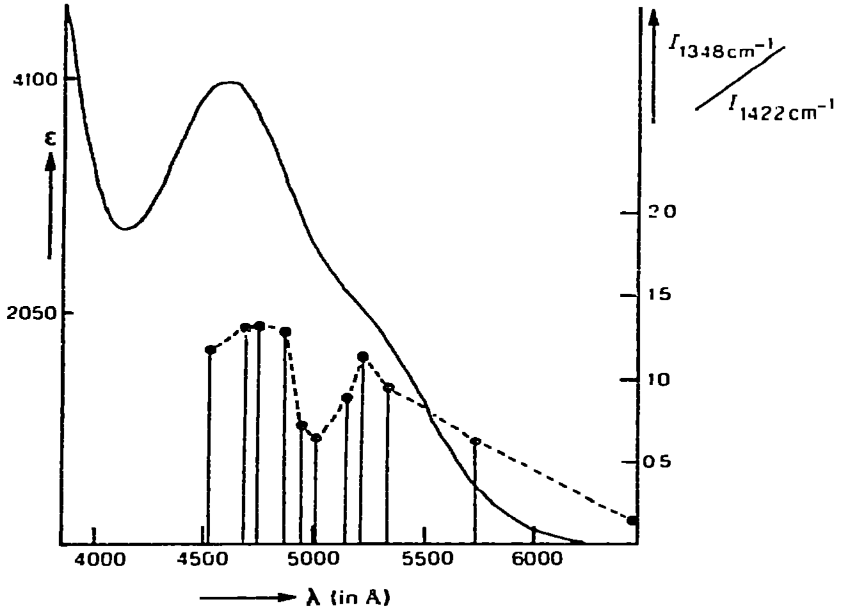

Fig. 1. Absorption spectrum (———) and Raman excitation profile (- - -) of $IrHCl(C_6H_4NNPh)(PPh_3)_2$. Numbers on the left ordinate belong to the absorption spectrum, and on the right to the excitation profile.

TABLE 5

^{1}H NMR DATA [a](ppm RELATIVE TO TMS) FOR IrHCl(L$'$)(PPh$_3$)$_2$[b] IN CDCl$_3$

L$'$	Ir—H[c]	H_6	H_5	H_4	H_3	H_7	Other
$C_6H_4CHNCH_3$	−16.36	5.92(m)	6.53(m)	6.24(m)	6.94(m)	7.77(br)	2.89(s)(N—CH$_3$)
5-$CH_3C_6H_3CHNCH_3$	−17.55	5.83(s)		6.28(d)	6.82(d)	7.75(br)	2.90(s)(N—CH$_3$)
C_6H_4CHNPh	−17.78	6.03(m)	6.55(m)	6.55(m)	6.85(m)	8.00(s)	
5-$CH_3C_6H_3CHN$-*p*-tolyl	−19.55	6.11(s)		6.25(d)	6.81(d)	7.97(s)	6.58(d), 6.81(d)(N—R)
C_6H_4NNPh	−16.86	6.00(m)	6.65(m)	6.65(m)			7.64(m), 7.76(m)(N—R)
5-$CH_3C_6H_3NN$-*p*-tolyl	−17.14	6.11(s)		6.41(d)	6.85(d)		7.64(d)(N—R)
4,6-$(CH_3)_2C_6H_2NN$-*m*-xylene	−16.85		5.89(s)		6.80(s)		7.70(s), 6.95(s)(N—R)
$CH{=}C(CH)_3{-}NNCH_3$[d]	−14.85						1.58(br)(H$_1$)2.90(s)(N—CH$_3$), 1.93(s)(C—CH$_3$)

[a] s=Singlet, d=doublet, m=multiplet, br=broad. Free ligand values are given in ref. 1 (Table 4). [b] See Figs. 2 and 3 for numbering of the protons. [c] Triplet structure (rel. intensities 1/2/1) due to ^{31}P coupling [J(P—H) 17 Hz]. [d] Free ligand resonances: 5.88(s) and 5.73(s) (H$_1$); 3.85 (N—CH$_3$) and 1.81(s)(C—CH$_3$).

It may be seen from Fig. 1 that the excitation profile follows the absorption curve of the complex and that the intensity of ν(N=N) is strongly enhanced when the excitation line falls within an absorption band of the compound (an enhancement factor of 9 is found for the 488 nm line compared with the 647 nm laser line).

Apparently, the ν(N=N) vibration at 1348 cm^{-1} is strongly coupled to both of the electronic transitions at longer wavelengths which, as a consequence must be localized on the azo ligand ($n \rightarrow \pi^*$) or are charge transfer transitions connected with the azo group. However, an assignment to pure $n \rightarrow \pi^*$ transitions is not justified because the $n_s \rightarrow \pi^*$ transition of *trans*-azobenzene itself, does not show such coupling with ν(N=N).

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

The ^{1}H and ^{13}C NMR data of the complexes $IrHCl(C_6H_4X{=}NR)(PPh_3)_2$ and $IrHCl[CH{=}C(CH_3){-}N{=}NCH_3](PPh_3)_2$ are listed in Tables 5 to 8.

Methyl substitution in the aromatic rings, variation of R, NMDR- and off-resonance experiments have assisted in the assignment of the ^{1}H and ^{13}C NMR signals of the coordinated azo and imine ligands. The NMR spectra of the complexes $IrHCl(5\text{-}CH_3C_6H_3CH{=}NCH_3)(PPh_3)_2$ (I) and $IrHCl[CH{=}C(CH_3){-}N{=}NCH_3](PPh_3)_2$ (II) are shown in Figs. 2 and 3 as typical examples.

From the NMR data the following features of interest are obtained . The proton spectra (see also Table 5) show high field triplets (relative intensities 1/2/1) due to metal—hydride coupling with two equivalent phosphorus atoms, which both should have a *cis* orientation relative to the hydrido ligand (J(^{31}P—^{1}H) 17 Hz) [26]. The chemical shift of the hydrido signal indicates strongly that this ligand is *trans* to a ligand of low *trans* influence [26].

The phosphine groups are mutually *trans* as is clear from the observation of four phosphine carbon signals, which (except for the *para* carbon signal) appear as triplets in the ^{13}C NMR spectra [27].

In the ^{13}C NMR spectra of both complex I and complex II the metallated carbon C_1, (see Figs. 2 and 3 for the numbering of the ligand carbon atoms) appears as a triplet signal, which shows a very large downfield shift compared with the corresponding free ligand signal (Table 8). This triplet changes to a

TABLE 6

^{1}H METHYL RESONANCES OF THE METALLATED RING OF THE COMPLEXES $IrHCl(L')(PPh_3)_2$ AND *trans*-$PdCl(L')(PEt_3)_2$ (ppm FROM TMS)

L′	M	CH$_3$^{a}	Δδ^b
$5\text{-}CH_3C_6H_3CHNCH_3$	Ir	1.49(5)	−0.85
$5\text{-}CH_3C_6H_3CHN$-*p*-tolyl	Ir	1.56(5)	−0.81
$5\text{-}CH_3C_6H_3NN$-*p*-tolyl	Ir	1.58(5)	−0.79
$5\text{-}CH_3C_6H_3NN$-*p*-tolyl	Pd	1.70(5)	−0.67
$4,6\text{-}(CH_3)_2C_6H_2NN$-*m*-xylene	Ir	1.42(6), 2.16(4)	−0.93, −0.19
$4,6\text{-}(CH_3)_2C_6H_2NN$-*m*-xylene	Pd	3.18(6), 2.28(4)	+0.83, −0.07

[a] Numbers in parentheses represent the carbon atom to which the methyl group is attached (see Fig. 2 for numbering of the carbon atoms of the metallated ring). [b] Δδ is the chemical shift difference between the methyl proton resonance of the metallated ring and the corresponding free ligand resonance.

TABLE 7

^{13}C NMR DATA (ppm RELATIVE TO TMS) FOR IrHCl(L')(PPh$_3$)$_2$[a,b] AND *trans*-PdCl(L')(L)$_2$ IN CDCl$_3$

L':L	M	C_1[c]	C_2	C_3	C_4	C_5	C_6	$-CH_3$[d]	Relevant resonances[e]
5-$CH_3C_6H_3CHNCH_3$	Ir	152.19	140.92(141.82)	126.29	119.96	141.82(140.92)	143.16	21.50	44.00 (N—CH_3) 173.61(C_7)
5-$CH_3C_6H_3CHN$-*p*-tolyl	Ir	155.81	141.49(142.56)	126.79	120.29	142.56(141.49)	143.11	21.55	172.79(C_7)
C_6H_4NNPh	Ir	155.80	163.20	128.89	120.69	132 25(130.26)	140.70		
C_6H_4NNPh; PEt_3	Pd	156.59	155.83	122.90	120.32	128.49	137.38		
C_6H_4NNPh; $AsEt_3$	Pd	147.96	157.24	123.36	125.26	128.82	138.46		
5-$CH_3C_6H_3NN$-*p*-tolyl	Ir	156.08	160.57	129.40	121.74	141.00(138.77)	142.44	21.55	
5-$CH_3C_6H_3NN$-*p*-tolyl; PEt_3	Pd	155.87	154.76	124.13	120.37	138.37	138.02	21.31	
4,6-$(CH_3)_2C_6H_2NN$-*m*-xylene	Ir	155.20	163.80	128.49	131.38	133.22(130.46)	143.20	29.14(6)[f] 20.18(4)[f]	
CH=C(CH_3)—$NNCH_3$[g]	Ir	161.88	155.44						50.92(N—CH_3) 17.98(—CH_3)

[a] See Figs. 2 and 3 for numbering of the carbon atoms. The free ligand values are given in ref. 1 (Table 5). [b] The PPh_3 signals except for the *para* carbon signal appears as triplets: *ortho*, 134.10(5.3); *meta*, 127.10(4.8); *para*, 129.01(—), 132.16(26): (carbon bonded to P). The quoted positions represent the values for all the complexes; values in parentheses are *J*(P—C) in Hz. [c] Except for *trans*-PdCl(C_6H_4N=NPh)($AsEt_3$)$_2$. C_1 shows a triplet structure due to ^{31}P coupling [*J*(P—C) 7.5 Hz]. [d] Metallated ring. [e] Resonances of the non-metallated aromatic ring have been omitted. [f] Values in parentheses represents the carbon atom to which the methyl group is attached. [g] Free ligand resonances: 122.07(C_1), 157.85(C_2), 14.90(CH_3), 56.30(N—CH_3).

TABLE 8

^{13}C NMR CHEMICAL SHIFT DIFFERENCES[a] Δ BETWEEN THE RESONANCES OF THE METALLATED AROMATIC RING AND THE CORRESPONDING FREE LIGAND RESONANCES IN THE COMPLEXES IrHCl(L')(PPh$_3$)$_2$

L'	Δ(C_1)	Δ(C_2)	Δ(C_3)	Δ(C_4)	Δ(C_5)	Δ(C_6)	Δ(C_7)
5-$CH_3C_6H_3CHNCH_3$	24.50	8.23(7.35)[b]	−1.40	−9.13	1.43(0.53)[b]	14.07	11.59
5-$CH_3C_6H_3CHN$-*p*-tolyl	27.16	8.51(7.45)[b]	−1.86	−9.08(−9.35)[b]	1.21(0.14)[b]	13.79(13.47)[b]	13.67
5-$CH_3C_6H_3NN$-*p*-tolyl	33.54	9.97	−6.86	−7.74	−2.10(0.13)[b]	12.96	

[a] Compare Table 7 and ref. 1 (Table 5); see Fig. 2 for numbering of the carbon atoms. [b] Values in parentheses are also possible because of the uncertain assignment (Table 7).

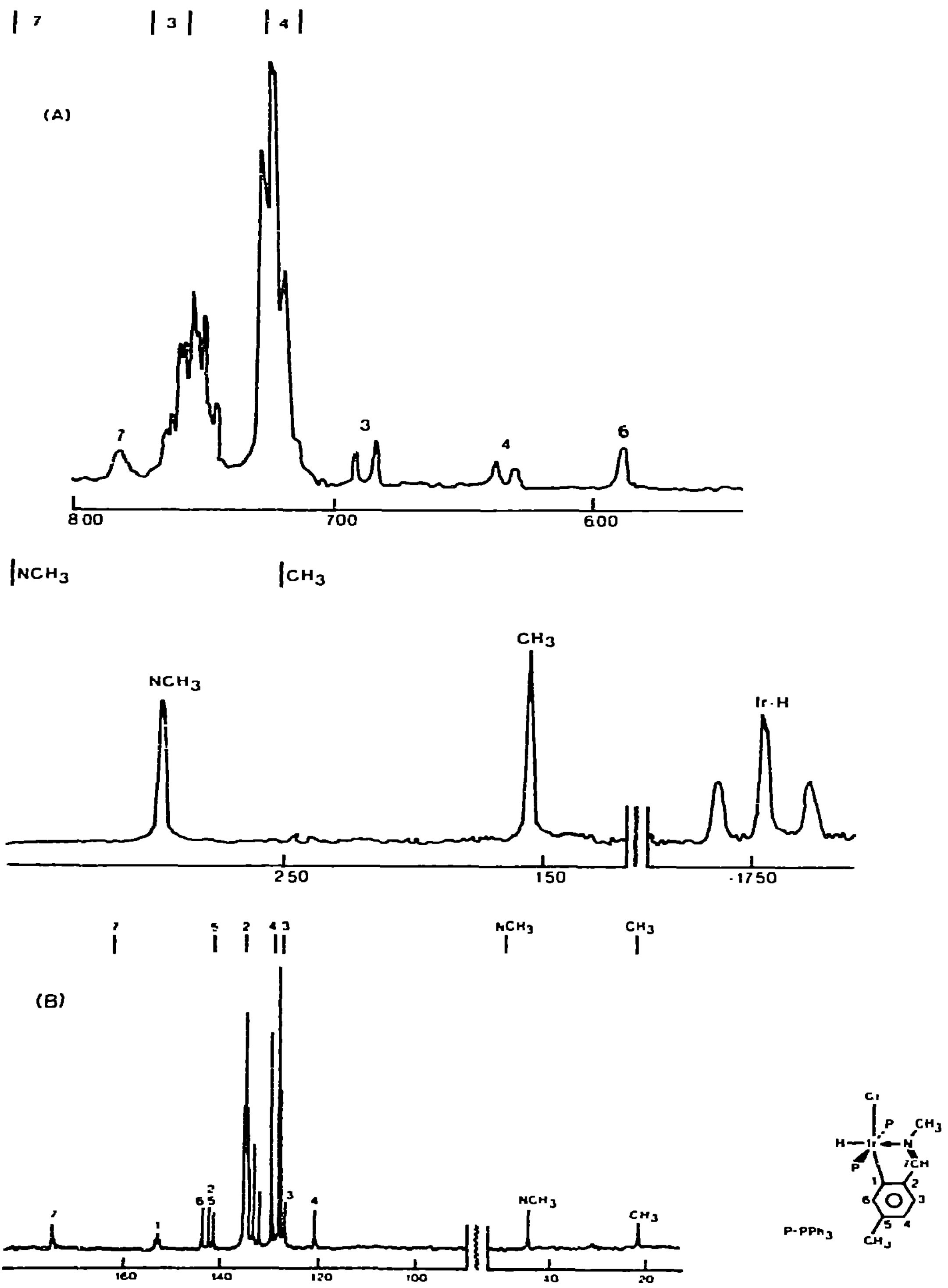

Fig. 2. (a) ^{1}H and (b) ^{13}C NMR spectra of $IrHCl(5\text{-}CH_3C_6H_3CHNCH_3)(PPh_3)_2$ in $CDCl_3$ at room temperature. The δ-values relative to TMS are given on each baseline. The vertical lines above each spectrum indicate the position of the corresponding free ligand signals.

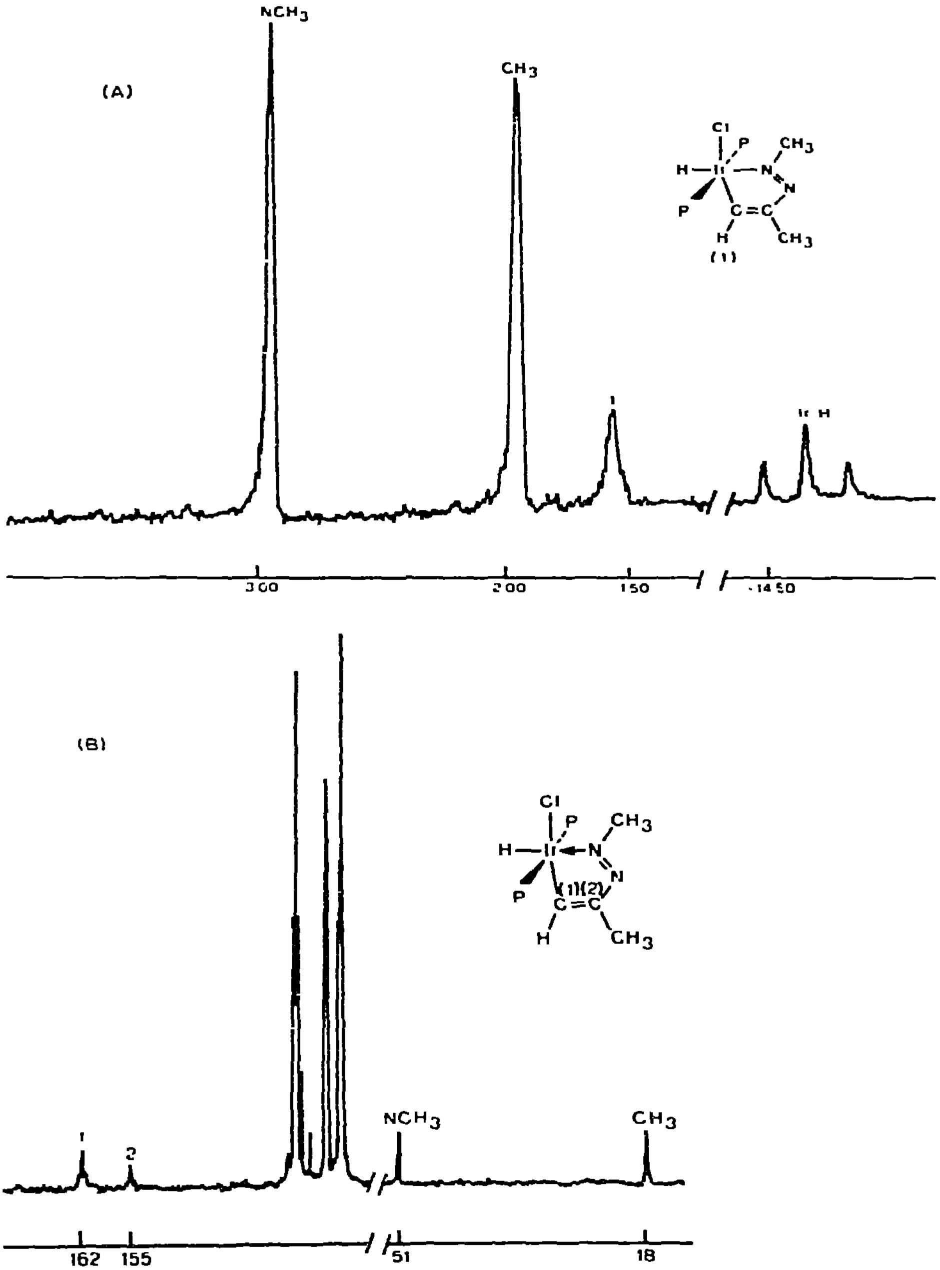

Fig. 3. (a) ^{1}H and (b) ^{13}C NMR spectra of IrHCl[CH=C(CH$_3$)—NNCH$_3$](PPh$_3$)$_2$ in CDCl$_3$ at room temperature. The δ-values relative to TMS are given on each baseline.

singlet on going from L = PEt$_3$ to L = AsEt$_3$ in the complexes *trans*-PdCl(C$_6$H$_4$N=NPh) L$_2$, the spectra of which are also included in Table 7. This observation shows that the triplet signal is due to the coupling of the metallated carbon with the two equivalent phosphorus atoms [$J(^{31}P—^{13}C)$ 7.5 Hz].

From the proton spectra of complexes I and II it is concluded that all the proton signals of the coordinated ligand (except for the C—CH_3 protons of complex II) are shifted upfield with respect to the corresponding free ligand signals. The largest upfield shift (more than 4 ppm) is experienced in complex II by the proton attached to the metallated carbon, which shows the largest downfield shift (about 40 ppm) in the ${}^{13}C$ spectrum. The upfield proton shift decreases for hydrogens, which are further removed from the metal—carbon bond, as is clear from the methyl group resonances (Table 6) of the metallated ring of the azo complexes of Ir^{III}. The methyl group at C_6 resonates at the highest field, while those at C_5 and C_4 are found to lower field than C_6. In contrast, the methyl (C_6) group in the azo complex of Pd^{II} shows a low field shift of similar magnitude to the upfield shift of the same protons in the corresponding Ir^{III} complex.

An important contribution to the remarkable shifts of the $(CH)_1$ and methyl (C_6) protons and to the upfield shift of the coordinated N—CH_3 group is most probably the paramagnetic anisotropy centred at the metal—(carbon bond) region (see Discussion).

The large upfield shift of the C_4 atoms in the ${}^{13}C$ NMR spectra of the aromatic azo and imine complexes might be an indication of increased electron density in the metallated ring by analogy with the observed shifts of the *para* carbon signals of substituted benzenes [28].

Discussion

From NMR spectroscopic data and the results of a single crystal X-ray investigation of $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ [29] it is concluded that the new Ir^{III} complexes have a nearly octahedral structure as shown in Fig. 4.

A remarkable observation is the extra lowering of the $\nu(N{=}N)$ vibration in the Ir^{III} complexes with respect to the corresponding Pd^{II} complexes, in which the azo ligand is only bonded to the metal via an *ortho* carbon atom [12]. This might be brought about by a decrease of the N=N bond order as seen from the elongation of the N=N bond upon chelation [29] and by the coupling of this vibration with other vibrations of the metallocyclic ring. The $\nu(N{=}N)$ vibration is strongly coupled to the two electronic transitions at longer wavelengths in $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ as shown by the Resonance Raman experiment, which therefore appears to be a very useful tool for the assignment of the electronic absorption bands in this and related complexes.

In ${}^{13}C$ NMR the metallated aromatic or olefinic carbon atom resonates

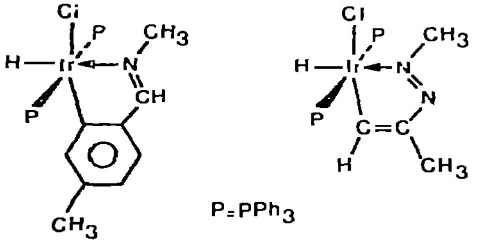

Fig. 4. The structure of the complexes $IrHCl(L')(PPh_3)_2$ (L' = *ortho*-metallated L).

at very low field with respect to the corresponding free ligand signals. This phenomenon, which occurs both in the octahedral Ir^{III} complexes and the square planar Pd^{II} complexes, has also been observed for other metallated aromatic (Ti[30]- and Li[31]-aryl compounds) or olefinic carbons (Rh) [11]. It may be explained in terms of the paramagnetic shielding [32] contribution σ_p, of which the main factors are charge polarization effects, variation of π-bond orders and the average excitation energy ΔE (σ_p varies inversely with ΔE). For both the Li-aryl and Ti-aryl compounds it has previously been argued that the shielding of C_1 is dominated by a decrease in the ΔE factor. This might indeed be the main factor contributing to the observed C_1 shift of the Ir^{III}- and Pd^{II}-complexes, although charge polarization effects cannot be excluded, as might be concluded from the strikingly large upfield proton and downfield carbon shifts of the $(CH)_1$ moiety of the complex $IrHCl[CH{=}C(CH_3){-}N{=}NCH_3](PPh_3)_2$. In this respect it is noteworthy that the NMR data which are available at present show a remarkable difference between the resonances of the metallated aromatic or olefinic carbons and those of methyl-metal carbons, which are usually found at very high field (to the right of TMS) [30, 33].

The structural data can also explain the anomalous methyl (C_6) proton shifts in the Ir^{III}-complexes and Pd^{II}-complexes. Because the positions *ortho* to the metallated carbon C_1 of the square-planar complex *trans*-$PdCl[4,6\text{-}(CH_3)_2C_6H_2N{=}N{-}$*m*-xylene$](PEt_3)_2$ are occupied by rather bulky groups [methyl(C_6) and NN-*m*-xylene] the metallated phenyl ring would be expected to be rotated out of the bonding plane of the complex [12], so that the methyl (C_6) protons are situated above (or below) this plane and rather close to the metal atom. In the octahedral Ir^{III} complex the methyl (C_6) group would be situated in the planar metallocyclic ring and would also be quite close to the metal atom. These structural arguments indicate that the major cause of the observed downfield and upfield shifts of the methyl (C_6) protons in the Pd^{II} and Ir^{III} complexes respectively is probably the paramagnetic anisotropy of the metal (—carbon bond) centre [34]. This phenomenon, which is only observed in a few other cases [1, 35, 36], causes changes in the chemical shifts which are apparently stereospecific. A similar situation occurs in the diethyldi-1-pyrazolylborato complexes of Ni (square-planar) [37] and Mo (octahedral) [38], in which the methylene protons of the ethyl group experience a downfield shift in the Ni complex and an upfield shift of similar magnitude in the Mo complex. The protons are located above and below the bonding plane of the Ni complex [37], while in the Mo complex one methylene proton approaches very close to the metal atom through a coordination site of the octahedron, shown recently by direct structural evidence [39].

The structural properties of the complexes $IrHCl(C_6H_3X{=}NR)(PPh_3)_2$ and $IrHCl(CH{=}C(CH_3){-}N{=}NCH_3)(PPh_3)_2$ provide strong evidence for the type of mechanism for the (*ortho*) metallation reactions mentioned in the Introduction.

The first step should be σ (*N*)-coordination of the azo or imine ligand, which would bring an *ortho* or olefinic CH group close to the metal atom, as has been observed for analogous aromatic azo or imine complexes of Pt^{II} [1, 2]. This property and the extra charge density on the metal atom brought about

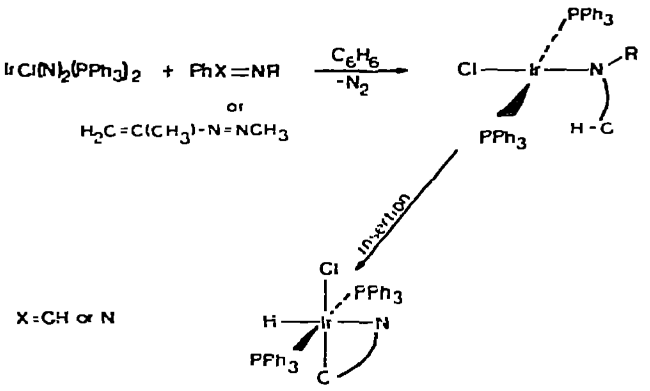

Fig. 5. Reaction scheme for metallation of the aromatic and olefinic azo or imine ligands.

by the N-donor ligand should promote the second step in the reaction sequence, namely, the oxidative addition of the *ortho* or olefinic CH group to the metal atom (Fig. 5).

No observable C—H bond cleavage occurs with the aliphatic azo compounds and azomesitylene. Apparently the activation energy for cleavage of the aliphatic C—H bond is too high for metal insertion to take place under the conditions used. The absence of reactivity of the CH groups of the azo or imine ligands towards analogous Rh^{I} complexes (see Experimental) is similar to the behaviour of the complexes $MCl(PPh_3)_3$ (M = Rh,Ir), where *ortho*-metallation has only been observed for M = Ir [40]. This parallels the increased difficulty of oxidative addition reactions on going from Ir^{I} to Rh^{I} [41, 42] and the greater basicity of Ir^{I} with respect to Rh^{I} [43].

Although from the point of view of the proposed reaction mechanism the analogous behaviour of olefinic and aromatic compounds is not surprising, it is very important to note that this metallation is unique for a system such as 2-(methylazo)propene. Very little is known of the coordination chemistry of ene-azo compounds [44], and the corresponding enimines [19, 45].

Further studies on the properties of these compounds with respect to the corresponding aromatic compounds are in progress.

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