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METAL—AZO AND METAL—IMINE COMPOUNDS

III*. THE INFLUENCE OF METAL BASICITY ON THE CLEAVAGE OF C—H BONDS BY Rh^I AND Ir^I

J.F. van BAAR, K. VRIEZE** and D.J. STUFKENS

Anorganisch Chemisch Laboratorium, Van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam (The Netherlands)

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Summary

From the reaction of R'X=NR (X = N or CH) with $[MCl(C_8H_{14})_2]_2$ in the presence of CO or PR_3, $\sigma(N)$-coordinated complexes *cis*-$RhCl(CO)_2(R'CH{=}NR)$ and cyclometallated complexes $MHCl(L')(PR_3)_2$ [L' is cyclometallated R'X=NR; R = Ph or Cy when M = Ir; R = Cy when M = Rh] were isolated.

The ease of C—H bond breaking by M^I appears to be strongly dependent on the basic properties of M^I, and decreases as follows: aromatic CH > olefinic CH > aliphatic CH. On the basis of the chemical and structural information, the metallation can be explained in terms of Pearson's symmetry rules for chemical reactions.

For the cyclometallated azo compounds, $\nu(N{=}N)$ shows resonance enhancement in the Raman spectra, and appears to be very sensitive to the basicity of M^I in the reactant system.

I. Introduction

At the moment there is only scant knowledge of the mechanistic aspects of *ortho*-metallation reactions of aromatic N-donor ligands [2,3]. Very recently it was deduced, from *ortho*-metallation reactions of various asymmetrically substituted azobenzenes, that both nucleophilic and electrophilic behaviour of the metal atom in these reactions are possible [3].

First steps towards a clearer picture of the reaction course were given by our recent results, obtained from the reactions of aromatic azo and imine ligands

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* For Part II see ref. 1.

** To whom correspondence should be sent.

R'X=NR (X = CH or N) with Pt^{II} and Ir^{I} compounds [1,4]. With the Pt^{II}-compounds, $\sigma(N)$-coordinated complexes were formed, in which close range non-bonded interactions occur between the metal atom and *ortho*-CH-groups [4,5] of R'. In the case of Ir^{I}, insertation of the metal atom into these C—H bonds occurs, as was concluded from spectroscopic and structural data [1,6].

The general relevance of these observations becomes clear in this paper, which presents convincing chemical evidence for the importance of metal basicity in the C—H bond breaking reactions of Rh^{I} and Ir^{I}. Furthermore, enimines and ene—azo compounds undergo similar metallation reactions, as firstly reported in the preceding paper of this series [1].

In addition, these results suggest a description of the reaction path in terms of the symmetry rules for chemical reactions, recently presented by Pearson [7].

II. Experimental

A. Preparations

The azo and imine ligands were obtained pure by methods previously cited [1]. The complex *trans*-$PtCl_2(PhCH{=}CH{-}CH{=}NC_3H_7)(PEt_3)$ was readily prepared according to an earlier method [4].

The complexes *cis*-$RhCl(CO)_2(R'X{=}NR)$, which can only be prepared for X = CH and not for X = N, result from the reaction between the $RhCl(CO)_2$-dimer and the imine ligand, as described earlier by Kang and Maitlis [8]. Using the dimer of $RhCl(C_8H_{14})_2$ [9] as starting compound these complexes are readily obtainable, as is shown below for *cis*-$RhCl(CO)_2$(*p*-tolylCHNCH$_3$).

130 mg (0.33 mmol) of the dimer of $RhCl(C_8H_{14})_2$ was added to a solution of 95 mg of *p*-tolylCH=NCH$_3$ (0.71 mmol) in 20 ml of benzene under argon. A slow stream of pure CO was passed through the solution at room temperature. Within a few moments the solution turned yellow. The gas-flow was continued for about ten minutes, after which the filtered solution was completely evaporated. The resulting solid was recrystallized from a benzene/hexane mixture, yielding 185 mg (85%) of yellow crystals.

There was no indication of metallation of the imine ligands after standing for several days in benzene at room temperature. Refluxing the compounds *cis*-$RhCl(CO)_2(R'CH{=}NR)$ either in benzene or in petroleum ether (b.p. 120°C) did not yield complexes like $RhHCl(CO)_2(L')$ (L' = cyclometallated R'CH=NR). Further, under similar reaction conditions and also upon prolonged heating no metallation occurs in the $\sigma(N)$-coordinated complexes *trans*-$PtCl_2(R'X{=}NR)(L)$ [4].

The complexes $IrHCl(L')(PPh_3)_2$* (L' = cyclometallated R'X=NR) may be prepared from the reaction of *trans*-$IrCl(N_2)(PPh_3)_2$ with R'X = NR [1]. A new general method of synthesis via the species $MCl(PR_3)_2(S)$ [S = solvent molecule], obtained from the reaction of the dimer of $MCl(C_8H_{14})_2$ [M = Rh, Ir] with PR_3 [11], is illustrated below for the compound IrHCl $(PhC{=}CH{-}CH{=}NC_3H_7)(PCy_3)_2$.

$PhCH{=}CH{-}CH{=}NC_3H_7$ (190 mg, 1.1 mmol) was dissolved in 20 ml of well-degassed benzene. The dimer of $IrCl(C_8H_{14})_2$ [447 mg, 0.5 mmol] was added to

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* Recently, the preparation of $IrHCl(C_6H_4N{=}NPh)(PPh_3)_2$ from the reaction of *trans*-IrCl(CO)-$(PPh_3)_2$ with azobenzene was reported [10].

TABLE 1

ANALYTICAL DATA FOR $RhCl(CO)_2(R'CHNR)$ AND $MHCl(L')(PR_3)_2$[a] (M = Rh, Ir)

Compound[b]	Colour	Analysis found (calcd.) (%)		
		C	H	Cl
$RhCl(CO)_2$(*p*-tolyl-$CHNCH_3$)	yellow	40.42	3.37	10.71
		(40.31)	(3.36)	(10.84)
$RhCl(CO)_2(PhCH{=}CH{-}CHNC_3H_7)$	yellow	46.12	4.07	9.35
		(45.77)	(4.08)	(9.65)
$PtCl_2(PhCH{=}CH{-}CHNC_3H_7)(PEt_3)$	yellow	39.05	5.50	12.42
		(38.75)	(5.39)	(12.75)
$RhHCl(5\text{-}CH_3C_6H_3CHNCH_3)(PCy_3)_2$	white	65.40	9.21	4.09
		(64.95)	(9.26)	(4.27)
$RhHCl(5\text{-}CH_3C_6H_3NN$-*p*-tolyl)$(PCy_3)_2$	orange	66.41	8.67	3.79
		(66.04)	(8.81)	(3.91)
$IrHCl(5\text{-}CH_3C_6H_3NN$-*p*-tolyl)$(PCy_3)_2$	red	60.50	8.10	3.39
		(60.15)	(8.20)	(3.56)
$IrHCl(PhC{=}CH{-}CHNC_3H_7)(PCy_3)_2$	yellow	60.40	8.27	3.50
		(59.97)	(8.43)	(3.70)
$IrHCl(PhC{=}CH{-}CHNC_3H_7)(PPh_3)_2$	yellow	61.84	4.99	3.89
		(62.30)	(4.87)	(3.84)

[a] See Fig. 2 for numbering of the carbon atoms of the metallated ring. [b] Cy = cyclohexyl.

this solution, which was kept under argon and continuously stirred. After addition of tricyclohexylphosphine (560 mg, 2 mmol) under vigorous stirring the resulting red solution was refluxed for about two hours and after cooling to room temperature the filtered solution was evaporated to dryness. The residue which was washed with n-pentane and recrystallized from a benzene/n-pentane mixture yielded 480 mg (50%) of air-stable yellow crystals.

The analytical data and the colours of the new complexes are listed in Table 1. The metallation reactions may also be carried out at room temperature (about three days), which in general gave lower yields. The reactions of Ir^I with azotoluene, which are characterized by intense coloration, clearly show that they proceed much faster at room temperature with PCy_3 than with PPh_3 as coligand. Attempted reactions with aliphatic azo compounds (azoethane and azoisopropane) afforded no metallated products, even upon prolonged heating. Using similar conditions no metallated products could be isolated from the reaction of olefinic azo or imine compounds with Rh^I in the presence of PPh_3 or PCy_3, while the aromatic ligands undergo *ortho*-metallation only in the presence of PCy_3.

B. Spectra

Spectra were recorded on a Varian HA-100 proton NMR apparatus, a Varian XL-100 with Fourier Transform (^1H and ^{13}C), a Cary-14 (UV), a Beckman-IR 18A (Infrared) and a Coderg pH1 spectrometer (Raman).

The experimental details for the resonance Raman spectra have been reported elsewhere [1]. Off-resonance (^{13}C) and NMDR (^1H) techniques assisted in the assignments of the NMR signals.

III. Results

A. Structural characterization of the compounds cis-RhCl(CO)$_2$(R'CH=NR)

1. Infrared spectra. The relative *cis*-orientation of the CO ligands in these complexes is apparent from the occurrence of two ν(CO) vibrations located at about 2000 and 2075 cm^{-1} respectively.

The ν(C=N) vibrations of the imine ligands of the complexes *p*-tolyl-CH=NCH$_3$ and PhCH=CH—CH=NC$_3$H$_7$ (respectively at 1640 and 1630 cm^{-1}) hardly differ from the corresponding free ligand vibrations (respectively at 1650 and 1640 cm^{-1}), which is similar to the observations for the analogous complexes *trans*-PtCl$_2$(R'CH=NR)(PEt$_3$). These data are consistent with a σ(*N*)-coordination mode [4,8].

2. ^{1}H and ^{13}C NMR spectra. The NMR spectra unequivocally establish the geometry of the σ(*N*)-coordinated ligands in the complexes *cis*-RhCl(CO)$_2$-(*p*-tolyl-CH=NCH$_3$) (I) and *cis*-RhCl(CO)$_2$(PhCH=CH—CH=NC$_3$H$_7$) (II) if compared with the data for *trans*-PtCl$_2$(*p*-tolyl-CH=NCH$_3$)(PEt$_3$) (III) and *trans*-PtCl$_2$(PhCH=CH—CH=NC$_3$H$_7$)(PEt$_3$) (IV).

The CH=N absorptions show low-field shifts with respect to the corresponding free ligand resonances in the ^{13}C NMR spectra, while the corresponding proton signal is located very near to the free ligand singal (Table 2).

It appears that the *ortho* protons H(2) in complex I are shifted downfield (about 0.6 ppm) compared with the free ligand resonance (see Fig. 1 for the numbering of the protons and carbon atoms), Furthermore, the *ortho* carbon (C(2)) and the neighbouring carbon atom (C(1)) undergo respectively downfield

TABLE 2a

^{1}H NMR DATA (ppm RELATIVE TO TMS) FOR RhCl(CO)$_2$(R'CH=NR)[a] IN CDCl$_3$

Compound	CH=N	H(1)[c]	H(2)[c]	other
RhCl(CO)$_2$(*p*-tolyl-CHNCH$_3$) (I)[e]	8.30		8.30 (d)	3.78 (NCH$_3$) 2.40 (CH$_3$)
RhCl(CO)$_2$(PhCH=CH—CHNC$_3$H$_7$) (II)[b,d]	7.95	7.10 (d)	7.60 (d)	3.72 (NCH$_2$—)
PtCl$_2$(PhCH=CH—CHNC$_3$H$_7$)(PEt$_3$) (IV)[b]	8.17	7.08 (d)	8.17 (d)	3.87 (NCH$_2$—)

[a] See Fig. 1 for numbering of the protons; d = doublet. [b] Free ligand resonances: 8.10 (CH=N); 7.5 (H(2) and aryl protons), 7.05 (H(1)), 3.60 (NCH$_2$—). [c] *J*(H(1)—H(2)) = 15 Hz. [d] Resonances in C$_7$D$_8$: 7.54 (H(2)) and 6.60 (H(1)). [e] See ref. 4 for free ligand resonances.

TABLE 2b

^{13}C NMR DATA (ppm RELATIVE TO TMS) FOR RhCl(CO)$_2$(R'X=NR)[a] IN CDCl$_3$

Compound	CH=N	C(2)	C(1)[b]	other
RhCl(CO)$_2$(*p*-tolyl-CHNCH$_3$)[d]	171.69	130.91	130.13	51.08 (NCH$_3$)
RhCl(CO)$_2$(PhCH=CH—CHNC$_3$H$_7$)[c]	169.38	148.67	125.65	178.46; 182.11 (CO) 65.39 (NCH$_2$—)
PtCl$_2$(PhCH=CH—CHNC$_3$H$_7$)(PEt$_3$)[c]	166.32	145.64	126.11(32.7)	65.14 (NCH$_2$—)

[a] See Fig. 1 for numbering of the carbons. [b] Value in parentheses represents *J*(Pt). [c] Free ligand resonances: 62.35 (NCH$_2$—), 127.40 or 127.89 (C(1)), 139.93 (C(2)), 161.08 (CH=N). [d] See ref. 4 for free ligand resonances.

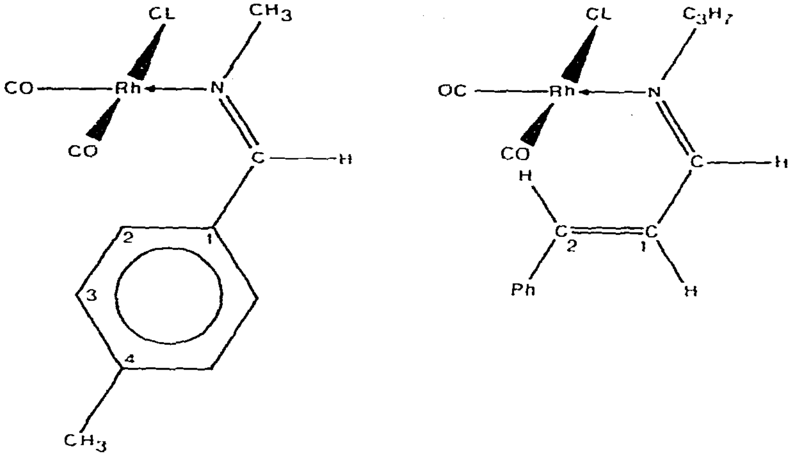

Fig. 1. The structure of the complexes *cis*-$RhCl(CO)_2$(*p*-tolyl-$CH{=}NCH_3$) (I) and *cis*-$RhCl(CO)_2$-($PhCH{=}CH{-}CH{=}NC_3H_7$) (II).

and upfield shifts upon complexation, paralleling earlier observations in $\sigma(N)$-coordinated Pt^{II}-complexes like III [4].

The remarkable low-field shifts of the *ortho* CH-groups in complex I show that they are situated close to the metal atom and above the bonding plane of the square planar molecule (Fig. 1) i.e. the coordinated ligand has a *trans* geometry [4,5].

On the basis of similar observations for the $(CH)_2$ group and because of the size of the coupling between the H(1) and H(2) protons ($J(H(1){-}H(2)) = 15$ Hz) it is concluded that the ligand $PhCH{=}CH{-}CH{=}NC_3H_7$ has a *trans—trans* geometry in complex IV. From Table 3, which contains the chemical shift difference (Δ) between the H(2) resonance of the complexed and free ligands both for the Pt^{II} and the Rh^{I} complexes, it is clear that on going from Pt^{II} to Rh^{I} the same trends are observed for both these ligands. From this Table it may therefore be deduced that the coordinated ligand in complex II has a *trans—trans* geometry, although the Δ-value for this complex, if taken as an absolute, is not conclusive for this assignment. Only ^{13}C NMR provides the evidence for such a geometry, because of the observation of the specific C(2) shift (Table 2).

Temperature-dependent ^{1}H NMR spectroscopic measurements shed some more light on the reason for the failure to isolate analogous $\sigma(N)$-coordinated

TABLE 3

^{1}H NMR CHEMICAL SHIFT DIFFERENCE[a] Δ BETWEEN THE H(2)[b] RESONANCE OF THE $\sigma(N)$-COORDINATED AND OF THE FREE IMINE LIGAND ($R'CH{=}NR$) IN THE COMPLEXES $PtCl_2$-($R'CH{=}NR$)(PEt_3) AND $RhCl(CO)_2(R'CH{=}NR)$

Ligand ($R'CH{=}NR$)	Δ (Pt^{II} complex)	Δ (Rh^{I} complex)
p-tolyl-$CHNCH_3$	1.1	0.6
$PhCH{=}CH{-}CHNC_3H_7$	0.7	0.1

[a] Compare Table 2a and ref. 4 (Tables 4 and 8). [b] See Fig. 1 for numbering of the protons.

azo complexes of Rh^{I} under similar reaction conditions (section II). A $CDCl_3$-solution of a mixture of ca. 0.1 mmol of the $RhCl(CO)_2$-dimer and ca. 0.2 mmol of *trans*-azobenzene shows one broad *ortho* proton signal at room temperature which is located at the free ligand position (7.88 ppm relative to TMS). At lower temperatures this signal splits into two signals to lower field (peak positions at −58°C: 8.17 ppm and 8.52 ppm relative to TMS). The splitting pattern is strongly dependent on the concentration of both the complex and the ligand.

These observations are consistent with intermolecular exchange of azobenzene, which possibly indicates a relatively weaker Rh—N bond.

B. Structural characterization of the compounds $MHCl(L')(PR_3)_2$ (L' is cyclometallated R'X=NR)

1. Electronic absorption spectra. The energies and intensities of the absorption bands of the new azo compounds of Rh^{III} and Ir^{III} are presented in Table 4 together with previous results for Ir^{III}- and Pd^{II}-azo complexes [1].

The spectra are very much alike, and it may therefore be concluded that the new compounds are isostructural (Fig. 2) with the previously reported Ir^{III} complexes [1,6]. The electronic transitions at about 21 and 29 kK are hardly affected by the nature of the metal atom. These transitions are therefore assigned to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition of the complexed azo ligand, respectively.

The transition at lower energies (17—19 kK) is affected by the nature of the azo ligand, the metal atom and the coligands. The band is not found for the Pd^{II} complexes of azobenzene and is much stronger for the Ir^{III} complexes than for the Rh^{III} analogues. It is assigned to a forbidden transition within the metallocyclic ring, which gains intensity from the close lying $n \rightarrow \pi^*$ transition by vibronic coupling. The vibronic coupling is expected to be much stronger for the Ir^{III} complexes than for the Rh^{III} analogues, since the electronic transitions are closer in energy to each other for the Ir^{III} complexes.

This vibronic coupling is also evident from the resonance Raman spectra, which are discussed in the next section.

2. Infrared and resonance Raman spectra. The presence of a hydrido ligand in these complexes is shown by the appearance of ν(M—H) in the region 2050—2250 cm^{-1} of the infrared spectrum (Table 5). This ligand does not originate

TABLE 4

ELECTRONIC ABSORPTION SPECTRA OF SOME AZO LIGANDS RNNR AND THE CORRESPONDING COMPLEXES $MHCl(L')(PR_3)_2$ [L' = CYCLOMETALLATED RNNR] IN CH_2Cl_2 (ν_{max} IN 10^3 cm^{-1}, ϵ VALUES IN PARENTHESES)

Compound	ν_{max} (ϵ)
trans-p-tolyl-NN—*p*-tolyl	22.9 (400)[a]; 30.0 (23000)[b]
$RhHCl(5\text{-}CH_3C_6H_3NN\text{—}p\text{-tolyl})(PCy_3)_2$	16.8 (180); 21.3 (2600); 27.9 (9900)
$IrHCl(5\text{-}CH_3C_6H_3NN\text{—}p\text{-tolyl})(PCy_3)_2$	18.0 (1900); 21.1 (3500); 28.2 (16000)
$IrHCl(5\text{-}CH_3C_6H_3NN\text{—}p\text{-tolyl})(PPh_3)_2$[c]	19.4 (1870); 22.0 (3460); 28.4 (13000)
trans-PhNNPh	22.5 (600)[a]; 31.4 (22000)[b]
$IrHCl(C_6H_4NNPh)(PPh_3)_2$[c]	18.9 (2010); 21.6 (4080); 29.4 (12500)
trans-$PdCl(C_6H_4NNPh)(PEt_3)_2$[c]	21.5 (1900); 31.2 (19000)

[a] $n \rightarrow \pi^*$ transition. [b] $\pi \rightarrow \pi^*$ transition. [c] See ref. 1.

TABLE 5

ν(N=N) AND ν(M—H) (IN CM^{-1}) FOR MHCl(L')(PR$_3$)$_2$[a], DERIVED FROM IR (KBr DISK) AND RAMAN (CH$_2$Cl$_2$ SOLUTION) DATA

Compound	ν(N=N)[b]	ν(M—H)[c]
RhHCl(5-CH$_3$C$_6$H$_3$NN—*p*-tolyl)(PCy$_3$)$_2$	1371 (1458)	2150
IrHCl(5-CH$_3$C$_6$H$_3$NN—*p*-tolyl)(PPh$_3$)$_2$[e]	1362 (1458)	2140
IrHCl(5-CH$_3$C$_6$H$_3$NN—*p*-tolyl)(PCy$_3$)$_2$	1334 (1458)	2270
IrHCl(PhC=CH—CHNC$_3$H$_7$)(PCy$_3$)$_2$	[d]	2200
IrHCl(PhC=CH—CHNC$_3$H$_7$)(PPh$_3$)$_2$	[d]	2135

[a] See Fig. 2 for numbering of the carbon atoms of the metallated ring. [b] Raman results. Values in parentheses are for the corresponding free ligand vibrations. [c] Infrared results. [d] Not assigned, see ref. 1. [e] See ref. 1.

from solvent molecules, because ν(M—H) is also found when the reactions are carried out in C$_6$D$_6$.

Because the infrared spectra are too complicated for further assignments, resonance Raman spectra [1] were taken which only show seven bands in the region 0-2000 cm^{-1}. One band (1330-1370) cm^{-1}) is fairly intense and is assigned to ν(N=N) of the complexed azo ligand in accordance with previous results [1].

When the laser-line is varied through the region of the two low energy absorption bands (450—650 nm), the ν(N=N) of the Ir^{III} complexes shows a resonance enhancement of intensity in both of the electronic transitions. This resonance effect is demonstrated by the variation of $I[\nu(\text{N=N})]/I[1422(\text{CH}_2\text{Cl}_2)]$ (I = intensity) with the laser frequency in Table 6. For the Rh^{III} complexes, ν(N=N) only shows a resonance Raman effect in the 21.3 kK band and not in the 16.9 kK band. This is consistent with the assumed vibronic coupling of the lowest energy band in the Ir^{III} compounds (see previous section).

From Table 5 it is seen that the ν(N=N) vibration in the d^6 complexes is lowered by (more than) 100 cm^{-1} with respect to the free ligand vibration, as also observed previously [1]. Furthermore, the size of this decrease increases on going from Rh to Ir and on changing from PPh$_3$ to PCy$_3$ as coligands. These facts might be explained by the extra negative charge, which the azo ligands

TABLE 6

RELATIVE INTENSITIES OF ν(N=N) IN MHCl—(5-CH$_3$C$_6$H$_3$NN—*p*-tolyl)(PCy$_3$)$_2$ WITH RESPECT TO THE 1422 CM^{-1} BAND OF CH$_2$Cl$_2$ FOR DIFFERENT LASER LINES (CONCENTRATIONS ABOUT 10^{-3} *M*)

Exciting wavelength (Å)	I(1334 cm^{-1})/I(1422 cm^{-1})[a]	I(1371 cm^{-1})/I(1422 cm^{-1})[b]
6471	1.0	1.0
5682	1.7	1.9
5145	1.0	9.9
4880	2.1	6.9
4727	1.2	—
4579	0.8	2.6

[a] M = Ir; value for $\lambda_{\text{exc.}}$ = 6471 Å is set equal to 1. [b] M = Rh; value for $\lambda_{\text{exc.}}$ = 6471 Å is set equal to 1.

TABLE 7a

^{1}H NMR DATA (ppm RELATIVE TO TMS) FOR SOME $\mathrm{MHCl(L')(PCy_3)_2}$[a] COMPOUNDS IN $\mathrm{CDCl_3}$

M; L′	M—H[b]	H(6)	H(4)	H(3)	other[c]
Rh; 5-$\mathrm{CH_3C_6H_3CHNCH_3}$	—15.26	7.38 (s)	6.70 (d)	7.14 (d)	3.94 ($\mathrm{NCH_3}$) 2.28 ($\mathrm{CH_3}$)
Rh; 5-$\mathrm{CH_3C_6H_3NN}$—*p*-tolyl	—14.66	7.49 (s)	6.92 (d)	7.97 (d)	2.36, 2.39 (—$\mathrm{CH_3}$)
Ir; 5-$\mathrm{CH_3C_6H_3NN}$—*p*-tolyl	—19.28	7.60 (s)	6.88 (d)	8.02 (d)	2.40 (—$\mathrm{CH_3}$)
Ir; PhC=CH—$\mathrm{CHNC_3H_7}$	—18.35				4.08 (N—$\mathrm{CH_2}$—)

[a] See Fig. 2 for numbering of the protons; s, singlet; d, doublet. [b] Quartet structure (rel. intensities 1/3/3/1) due to ^{31}P coupling [*J*(P—H) = 15 Hz] and ^{103}Rh coupling [*J*(Rh—H) = 15 Hz], when M = Rh; whenM = Ir, triplet structure (rel. intensities 1/2/1) due to ^{31}P coupling [*J*(P—H) = 19 Hz]. [c] The $\mathrm{PCy_3}$ resonances appear as a broad signal between 1.00 and 2.00 ppm.

TABLE 7b

^{13}C NMR DATA (ppm RELATIVE TO TMS) FOR SOME $\mathrm{MHCl(L')(PCy_3)_2}$[a] COMPOUNDS IN $\mathrm{CDCl_3}$

M; L′	C(1)[b]	$\mathrm{NCH_2}$—R	Other
Rh; 5-$\mathrm{CH_3C_6H_3NN}$—*p*-tolyl[c]	170.40		
Ir; PhC=CH—CH=$\mathrm{NC_3H_7}$	181.89	56.24	168.25 (C=N); 127.81 (C(2)) $\mathrm{PCy_3}$; 27.00; 27.76 (*J*(P—C) = 5 Hz) 30.00; 35.97 (*J*(P—C) = 13 Hz)

[a] See Fig. 2 for numbering of the carbon atoms. The free ligand values are given in ref. 4 (Table 5) and in Table 2b (footnote *c*). [b] Doublet of triplets because of ^{103}Rh coupling [*J*(Rh—C) = 33 Hz] and ^{31}P coupling [*J*(P—C) = 8 Hz], when M = Rh; triplet because of ^{31}P coupling [*J*(P—C) = 8 Hz], when M = Ir. [c] See ref. 1 for complete ^{13}C NMR data of analogous $\mathrm{Ir^{III}}$ complexes.

should obtain as a consequence of an oxidative addition to the d^8 metal $\mathrm{M^I}$. This effect should become greater upon enhancing the basicity of $\mathrm{M^I}$ (section IV). The extra electron density should occupy the π^* level of the azo ligand , which is mainly localized on the N=N group, and as a result ν(N=N) will be lowered.

3. *^{1}H and ^{13}C NMR spectra.* The most important NMR data are given in Table 7. The ^{1}H NMR spectra show a high field triplet (relative intensities 1/2/1) for the complexes $\mathrm{IrHCl(L')(PR_3)_2}$, arising from a metal hydride coupling with two equivalent ^{31}P atoms ($J(^{31}\mathrm{P}$—$^1\mathrm{H})$ = 19 Hz). For the complexes $\mathrm{RhHCl(L')(PCy_3)_2}$, this signal appears as a quartet (rel. intensities 1/3/3/1) owing to the equivalence of the ^{103}Rh—^{1}H and ^{31}P—^{1}H coupling constants ($J(^{103}\mathrm{Rh}$—$^1\mathrm{H})$ = $J(^{31}\mathrm{P}$—$^1\mathrm{H})$ = 15 Hz).

These data strongly indicate that the hydrido ligand is *trans* to a ligand of low *trans* influence and *cis* to both the phosphorus atoms [12].

In the ^{13}C NMR spectra it is easily seen that the $\mathrm{PCy_3}$ groups are mutually *trans* because for the Ir complexes four phosphine carbon signals are observed, of which the P—C resonance appears as a triplet at about 36 ppm [1]. The metallated carbon C(1) resonates at very low field as a triplet for M = Ir owing to the coupling with two equivalent ^{31}P atoms ($J(^{31}\mathrm{P}$—$^{13}\mathrm{C})$ = 8 Hz) and as a doublet of triplets for M = Rh owing to ^{103}Rh coupling ($J(^{103}\mathrm{Rh}$—$^{13}\mathrm{C})$ = 33 Hz) and ^{31}P coupling ($J(^{31}\mathrm{P}$—$^{13}\mathrm{C})$ = 8 Hz).

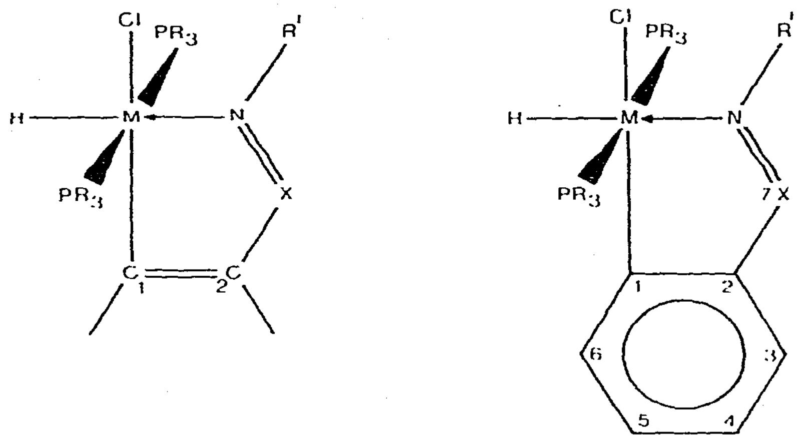

Fig. 2. The structure of the complexes $MHCl(L')(PR_3)_2$ (L' = cyclometallated $R'X{=}NR$).

The specific shifts of the $N{-}CH_3$ or NCH_2R groups strongly indicate the presence of a metal—nitrogen bond [1].

These observations and those of the previous sections are consistent with the structure of the complexes as shown in Fig. 2 [1,6].

IV. Discussion

The new chemical information obtained from this investigation (Table 8) shows that the attack of C—H bonds of azo and imine ligands $R'X{=}NR$ (X = N or CH) by Rh^I and Ir^I is strongly dependent on (*a*) the electronic properties of the metal atom and (*b*) the type of C—H bond (the ease of C—H bond cleavage decreases as follows: aromatic > olefinic > aliphatic).

For cyclometallation to occur the metal atom must be electron-rich; this is encouraged by basic phosphines as coligands. Using an electron-accepting coligand like CO, $\sigma(N)$-coordinated complexes of the type *cis*-$RhCl(CO)_2(R'X{=}NR)$*

TABLE 8

THE REACTIVITY OF SEVERAL d^8 COMPLEXES TOWARDS C—H BONDS OF $R'X{=}NR$

Reactant system[a]	Type of C—H bond[d]	Behaviour of metal atom
$IrCl(S)(PR_3)_2 + R'X{=}NR$	aromatic and olefinic	nucleophilic
$RhCl(S)(PCy_3)_2 + R'X{=}NR$	aromatic	nucleophilic
$RhCl(S)(PPh_3)_2 + R'X{=}NR$	—	borderline
$RhCl(CO)_2(R'X{=}NR)$[b]	—	borderline
$PtCl_2(R'X{=}NR)(L)$	—	borderline
$PdCl_2(R'X{=}NR)_2$[c]	aromatic	electrophilic

[a] See section II for experimental details. [b] See also note at the bottom of this page. [c] See refs. 2 and 3. [d] In all cases there was no indication for an attack of an aliphatic C—H bond of the compounds $(H_3C)_{3-n}CH_nNNCH_n(CH_3)_{3-n}$ [n = 1, 2] (see section II).

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* It is known that the $RhCl(CO)_2$ dimer reacts with $PhX{=}NR$ at elevated temperatures to give $RhCl(CO)_2RhCl(C_6H_4X{=}NR)_2$ [13,14]. Most likely, the intermediates I and $RhCl(CO)(PhX{=}NR)_2$ are formed successively and followed by CO extrusion and cyclometallation (metal basicity enhanced by N-donor ligands).

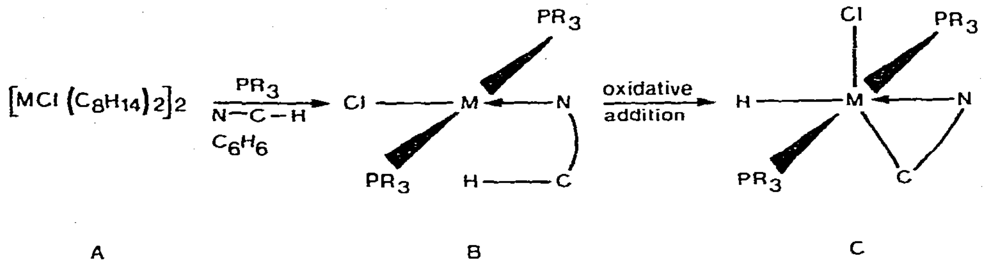

Fig. 3. Reaction scheme for metallation of the aromatic and olefinic azo or imine compounds. Using CO instead of PR_3 as coligand at room temperature the reaction stops at stage B (compare Fig. 1).

(section II) were isolated, in which CH groups come into close proximity to the metal atom (Fig. 1). These data and the structural information (section III and refs. 1 and 6) provide strong evidence that these cyclometallation reactions proceed via a $\sigma(N)$-coordinated intermediate, B, followed by the intramolecular oxidative addition of a CH group to the metal atom (Fig. 3).

This nucleophilic behaviour of the metal atom contrasts with the apparently electrophilic behaviour of Pd^{II} in *ortho*-metallation with azobenzene [2,3]. Higher oxidation states of the metal atom evidently favour electrophilic rather than nucleophilic attack, as intuitively expected.

The absence of cyclometallation upon heating the $\sigma(N)$-coordinated complexes *trans*-$PtCl_2(R'X{=}NR)(L)$ or upon treating the $RhCl(C_8H_{14})_2$ dimer with the N-donor ligands in the presence of PPh_3 (section II) may find its origin in the fact that the electronic properties of the species B are borderline cases for either of the two mechanisms.

Our results can be readily explained in terms of the symmetry rules for chemical reactions which were recently presented by Pearson [7]. In his description, the MO theory is used as a basis, but chemical reaction is considered as a perturbation of the reactant system. Reaction takes place if compatible symmetry of the highest energy (E_o) occupied MO(HOMO) and a low energy (E_k) unoccupied MO(LUMO) leads to positive total overlap and thus to the possibility of HOMO—LUMO electron transfer.

In terms of second order perturbation theory it follows that the stabilizing effect of this electron excitation will be larger if $|E_o - E_k|$ becomes smaller.

On the basis of the structural properties of the compounds B and the metallated compounds C (Figs. 1-3) it may be concluded that the latter compounds are formed by C—H bond breaking and M—H and M—C bond formation in the compounds B (*cis* addition of the C—H bond to the metal atom). Therefore, according to Pearson's concept the HOMO in B should be a metal *d* orbital (M is the nucleophile) and the LUMO should be the σ^*(CH) orbital, restricted to the CH bond since it is the only unoccupied orbital possessing the possibility of sterically favoured overlap with the HOMO, as may be concluded from a recent crystallographic study [5]. In Fig. 4 it is shown that both the d_{z^2} orbital (situation *a*) and the d_{xz} orbital (situation *b*), either of which might be the HOMO in the distorted square planar d^8 complex B, have compatible symmetry for overlap with the σ^*(CH) orbital. Crystal structural data [5,15,16], however, strongly indicate that situation (*a*) should be favoured.

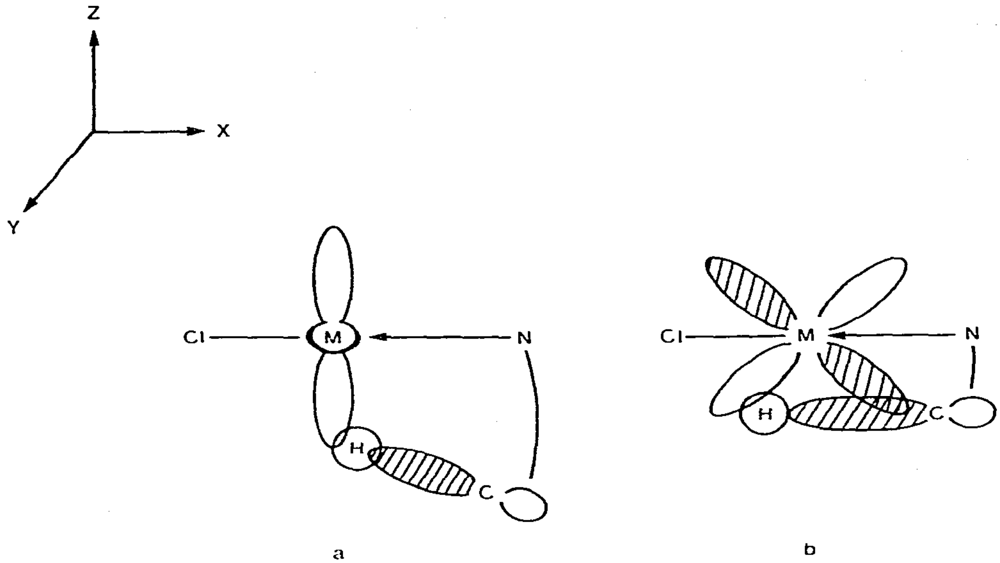

Fig. 4. Molecular orbitals for the reaction between M and a C—H bond in compounds B (compare Fig. 3; the PR_3 ligands along the Y axis are omitted). The shaded and unshaded lobes of the orbitals stand for opposite signs of the orbital function.

On going from Ir^{I} to Rh^{I} and on changing from very basic to much less basic coligands, the d_{z^2} (d_{xz}) level will move to lower energy, i.e. $|E_o - E_k|$ becomes larger for a specific C—H bond, resulting in a lower (or zero) reactivity towards that C—H bond. Furthermore, the spatial extent of the d orbitals decreases on going from Ir^{I} to Rh^{I}, making the metal d—σ^*(CH) overlap less favourable.

Because of the further lowering of the d levels in energy, these trends become even more pronounced upon going from Rh^{I} to $\mathrm{Pd}^{\mathrm{II}}$, which might explain the change-over to electrophilic behaviour by the second metal atom. The latter process can then be described by an electron transfer from the σ(C—H) orbital (HOMO) to a metal orbital (LUMO) of proper symmetry, the corresponding $|E_o - E_k|$ value apparently being lower than that for the metal $d \rightarrow \sigma^*$(CH) transition.

There is a lack of knowledge of the position of the σ^*(CH) energy levels for different kinds of CH bonds and therefore no reasonable explanation can be given for the absence of reactivity of the Rh^{I} and Ir^{I} complexes towards aliphatic C—H bonds in terms of Pearson's concept, if it is assumed that these reactions proceed according to the same mechanism as for aromatic and olefinic C—H bonds. Regarding the metal atom as a base in our reactions, an explanation of the latter phenomenon might be the less acidic nature of aliphatic hydrocarbons with respect to aromatic hydrocarbons [19]. However, further speculation should be suspended until more information is obtained. Therefore, detailed research is being done at the moment into the possibility of the cleavage of aliphatic C—H bonds by d^8 metals. In addition the possibility of a radical mechanism, as proposed for the oxidative addition reactions of low-valent metal complexes with alkyl halides [17,18], will be investigated.

Finally it may be concluded that this investigation gives further insight into the factors which determine the possibility of cleavage of several types of C–H bonds by d^8 metals. Furthermore it allows systematization according to the concepts of Pearson and might lead to new approaches to further research in this field.

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