

## METAL—AZO AND METAL—IMINE COMPOUNDS

### IV \*. CHEMICAL PROPERTIES OF CYCLOMETALLATED COMPOUNDS

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(Received December 27th, 1975)

#### Summary

The reactions of some cyclometallated azo and imino compounds have been studied. Treatment of  $[\text{IrHX}(\text{PhC}=\text{CHCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2]$  with  $\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) yields substitution products  $[\text{IrHX}(\text{PhC}=\text{CXCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2]$  without rupture of the Ir—C bond. Treatment of  $[\text{IrHCl}(5\text{-CH}_3 \cdot \text{C}_6\text{H}_3\text{CH}=\text{NCH}_3)(\text{PPh}_3)_2]$  with  $\text{AgClO}_4$  and then with  $\text{CNC}_6\text{H}_{11}$  or  $\text{CO}$  ( $= \text{L}$ ) leads to the formation of the complexes  $[\text{IrHL}(5\text{-CH}_3 \cdot \text{C}_6\text{H}_3\text{CH}=\text{NCH}_3)(\text{PPh}_3)_2]\text{ClO}_4$ , the metallocyclic ring remaining intact. Rupture of the metallocyclic ring is observed when  $[\text{PdCl}(\text{C}_6\text{H}_4\text{N}=\text{NPh})_2]$  is treated under mild conditions with  $\text{CNC}_6\text{H}_{11}$ , and the insertion product  $[\text{PdCl}(\text{CNC}_6\text{H}_{11})_2 \{(\text{C}=\text{NC}_6\text{H}_{11})_2\text{C}_6\text{H}_4\text{NNPh}\}]$  is obtained.

Possible mechanisms for the reactions are discussed.

#### Introduction

There is much current interest in the preparation [1–7] and reactions [8–12] of cyclometallated compounds. Since cyclometallated species may be of interest for organic synthesis, we have initiated a study of the chemical properties of some previously reported [1,13] cyclometallated azo and imine compounds, and the first results are presented below.

#### Experimental

##### *Preparations*

The complexes of the type  $[\text{IrHCl}(\text{L}')(\text{PR}_3)_2]$  ( $\text{L}'$  is a cyclometallated imine ligand) were prepared as described in [1]. The compound  $[\text{PdCl}(\text{C}_6\text{H}_4\text{NNPh})_2]$  was obtained by a published procedure [8,14].

\* For parts I–III see ref. 1, 13 and 22.

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1. Reactions of  $[\text{IrHCl}(\text{PhC}=\text{CHCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2]$  with  $\text{X}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) or  $\text{HCl}$

a. Reaction with gaseous chlorine \*. The complex  $[\text{IrHCl}(\text{PhC}=\text{CHCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2]$  (0.5 mmol) was dissolved in about 15 ml of  $\text{CH}_2\text{Cl}_2$  or  $\text{C}_6\text{H}_6$ . A slow stream of dry  $\text{Cl}_2$  gas was passed through the solution at room temperature. After a few minutes the reaction vessel was closed and set aside for about two days. The solution was filtered through a small amount of activated charcoal and evaporated to dryness. The residue was dissolved in about 5 ml of acetone, from which yellow crystals deposited upon cooling. The compound was filtered off and washed with hexane ( $2 \times 5$  ml), which was added to the acetone filtrate. From this acetone/hexane mixture a second fraction of crystals was obtained at lower temperatures. The combined solids were recrystallized from a dichloromethane/hexane or a benzene/hexane mixture, yielding about 60% of the yellow compound  $[\text{IrHCl}(\text{PhC}=\text{CClCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2]$ .

b. Reaction with bromine. Addition of about 1.0 mmol of bromine to 0.5 mmol of the starting complex resulted in the formation of a yellow product (A) which was isolated as described under 1a. According to the NMR spectra (see Results) A consisted of a mixture of  $[\text{IrHX}(\text{PhC}=\text{CBrCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2]$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), and so it was dissolved in 15 ml of warm acetone and an excess of  $\text{LiBr}$  was added with vigorous stirring. The mixture was boiled for several hours, after which the solution was completely evaporated and the residue dissolved in about 5 ml of  $\text{CH}_2\text{Cl}_2$ . The suspended  $\text{LiX}$  compounds were filtered off, the clear filtrate was evaporated to dryness, and the resulting yellow crystals of  $[\text{IrHBr}(\text{PhC}=\text{CBrCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2]$  \*\* were dried in vacuo.

c. Reaction with gaseous  $\text{HCl}$ . A procedure similar to that under 1a was used, except that a low temperature ( $-20^\circ\text{C}$ ) was maintained during the passage of gas. The temperature of the mixture was then slowly raised to room temperature. Further manipulations were as described under 1a. The resulting yellow compound was identified as the starting complex on the basis of its IR and NMR spectra [1].

2. Reaction of  $[\text{IrHCl}(\text{L}')(\text{PR}_3)_2]$  with  $\text{CO}$ ,  $\text{C}_6\text{H}_{11}\text{NC}$ ,  $\text{PR}_3$  or  $\text{H}_2$

The starting complexes were recovered unchanged in all cases, even when more drastic conditions such as prolonged heating (with  $\text{CH}_2\text{Cl}_2$  or  $\text{C}_6\text{H}_6$  as solvent) were used.

3. Reactions of  $[\text{IrHCl}(5\text{-CH}_3 \cdot \text{C}_6\text{H}_3\text{CH}=\text{NCH}_3)(\text{PPh}_3)_2]$  with  $\text{AgClO}_4$  and  $\text{C}_6\text{H}_{11}\text{NC}$  or  $\text{CO}$

a. Reaction with  $\text{CO}$ . To a solution of ca. 0.5 mmol of the starting complex in about 15 ml of benzene, an equimolar amount of  $\text{AgClO}_4$  (dissolved in benzene) was added dropwise with vigorous stirring. The precipitate of  $\text{AgCl}$ , which formed immediately, was filtered off. Through the resulting clear \*\*\* solution a slow stream of  $\text{CO}$  was passed for about 10 min, after which the vessel was closed. After standing overnight the white solid, which precipitated during and after the gas-supply, was collected by filtration and washed with hexane. The filtrate was

\* Carrying out the reaction in the absence of light or the presence of a radical scavenger had no significant influence.

\*\* This compound can also be prepared by the addition to the starting complex of  $\text{LiBr}$  followed by  $\text{Br}_2$ .

\*\*\* If no clear filtrate is obtained a small amount of  $\text{CH}_2\text{Cl}_2$  must be added.

evaporated until a second fraction of white crystals deposited.

The white solid was collected and dried in vacuo, yielding about 60% of the complex  $[\text{IrH}(\text{CO})(5\text{-CH}_3 \cdot \text{C}_6\text{H}_3\text{CH}=\text{NCH}_3)(\text{PPh}_3)_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_6$ .

*b. Reaction with  $\text{C}_6\text{H}_{11}\text{NC}$  [15].* This reaction yielded about 65% of the white complex  $[\text{IrH}(\text{CNC}_6\text{H}_{11})(5\text{-CH}_3 \cdot \text{C}_6\text{H}_3\text{CH}=\text{NCH}_3)(\text{PPh}_3)_2]\text{ClO}_4 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ , irrespective of the relative amounts of  $\text{C}_6\text{H}_{11}\text{NC}$  and the starting compound used (see 3a).

#### 4. Reaction of $[\text{PdCl}(\text{C}_6\text{H}_4\text{N}=\text{NPh})]_2$ with $\text{C}_6\text{H}_{11}\text{NC}$

To a suspension of ca. 0.5 mmol of  $[\text{PdCl}(\text{C}_6\text{H}_4\text{NNPh})]_2$  in 15 ml of benzene about 6 mmol of  $\text{C}_6\text{H}_{11}\text{NC}$  (dissolved in benzene) was added dropwise with vigorous stirring to give a clear red solution. Upon standing for several days, the colour of the solution gradually changed to yellow. After several weeks the solution was concentrated to about 5 ml. The yellow solid material, which eventually deposited, was filtered off and the clear solution evaporated to dryness. The residue was dissolved in about 3 ml of  $\text{CH}_2\text{Cl}_2$ , and hexane was added until a white solid precipitated. The product was recrystallized from a  $\text{CH}_2\text{Cl}_2$ /hexane or benzene/hexane mixture, yielding about 65% of the white complex  $[\text{PdCl}(\text{CNC}_6\text{H}_{11})_2\{(\text{C}=\text{NC}_6\text{H}_{11})_2\text{C}_6\text{H}_4\text{NNPh}\}]$ .

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

### Spectra

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian T-60 and a Varian CFT-20 spectrometer. Off-resonance experiments and spectra of the starting complexes [1,13] assisted in the assignments of the  $^{13}\text{C}$  NMR spectra. IR spectra were measured with a Beckman-IR 18A (7 or 12) spectrometer.

The molecular weight determination was carried out using a Hewlett-Packard vapour pressure osmometer.

TABLE 1  
ANALYTICAL DATA FOR THE NEW COMPOUNDS

Compound <sup>a</sup>	Analysis found (calcd.) (%)		
	C	H	Cl(Br)
$\text{IrHCl}(\text{PhC}=\text{CClCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2$ (IIA)	57.40 (57.89)	7.91 (8.04)	7.29 (7.14)
$\text{IrHBr}(\text{PhC}=\text{CBrCH}=\text{NC}_3\text{H}_7)(\text{PCy}_3)_2$ (IIB)	53.55 (53.15)	7.21 (7.38)	14.28 (14.74)
$[\text{IrH}(\text{CO})(5\text{-CH}_3 \cdot \text{C}_6\text{H}_3\text{CH}=\text{NCH}_3)(\text{PPh}_3)_2]\text{ClO}_4 \cdot \text{C}_6\text{H}_6$ (IVA) <sup>b</sup>	59.70 (59.17)	4.59 (4.46)	3.21 (3.37)
$[\text{IrH}(\text{CNC}_6\text{H}_{11})(5\text{-CH}_3 \cdot \text{C}_6\text{H}_3\text{CH}=\text{NCH}_3)(\text{PPh}_3)_2]\text{ClO}_4 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ (IVB) <sup>b</sup>	57.75 (57.27)	4.63 (4.82)	6.20 (6.45)
$\text{PdCl}(\text{CNC}_6\text{H}_{11})_2\{(\text{C}=\text{NC}_6\text{H}_{11})_2\text{C}_6\text{H}_4\text{NNPh}\}$ (VI)	63.27 (63.25)	7.20 (6.98)	4.59 (4.67)

<sup>a</sup> Cy = cyclohexyl. <sup>b</sup> See Fig. 2 for numbering of the carbon atoms of the metallated aromatic ring.

## Results

*Structural characterization of the compounds [IrHX(PhC=CXCH=NC<sub>3</sub>H<sub>7</sub>)-(PCy<sub>3</sub>)<sub>2</sub>] (X = Cl or Br)*

The infrared (Table 2) and <sup>1</sup>H NMR (Table 3) spectra clearly show that the hydrido ligand is still present after the reaction of [IrHCl(PhC=CHCH=NC<sub>3</sub>H<sub>7</sub>)-(PCy<sub>3</sub>)<sub>2</sub>] with Cl<sub>2</sub>. The peak positions of both the  $\nu(\text{Ir-H})$  vibration and the NMR signal of the hydrido ligand differ slightly from the corresponding values of the starting complex [1]. The <sup>1</sup>H NMR hydrido signal is still present as a triplet (due to <sup>31</sup>P coupling), indicating that this ligand is *cis* with respect to two equivalent phosphines.

Both the <sup>1</sup>H and <sup>13</sup>C NMR spectra (off-resonance) are consistent with the disappearance of the H(2) proton (see Fig. 1 for numbering of the protons and carbon atoms). Thus this proton must have been replaced by a chlorine atom as is also apparent from elementary analysis (Table 1). In the <sup>13</sup>C NMR spectrum (Table 4), the C(1) and C(2) signals in particular show a significant shift with respect to the corresponding signals of the starting complex [1].

On the basis of these observations, it may be concluded that the new chlorinated complex, IIA, is isostructural with the starting complex I (X = Cl) (see Fig. 1).

The analogous bromination reaction of I (X = Cl) probably results in the formation of a mixture (A) of products i.e. [IrHX(PhC=CBrCH=NC<sub>3</sub>H<sub>7</sub>)-(PCy<sub>3</sub>)<sub>2</sub>] (X = Cl or Br), as indicated by NMR data and the further reaction with LiBr (see below).

The hydride <sup>1</sup>H NMR signal consists of two partially overlapping triplets, while the <sup>13</sup>C NMR spectrum, which resembles that of IIA, shows a doubling of almost every signal. The data are consistent with bromination of the metallocyclic ring and a partial replacement of the chlorine ligand by bromine.

This conclusion is justified by a further reaction of A with LiBr, which yields the complex IIB (Fig. 1, X = Br) exclusively according to the spectroscopic data.

*Structural characterization of the complexes [IrHL(5-CH<sub>3</sub> · C<sub>6</sub>H<sub>3</sub>CH=NCH<sub>3</sub>)-(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (L = CO or CNC<sub>6</sub>H<sub>11</sub>)*

The presence of the hydrido ligand in these complexes is obvious from the in-

TABLE 2  
IR DATA (in cm<sup>-1</sup>) FOR THE NEW COMPOUNDS (KBr disk)

Compound <sup>a</sup>	Frequency/assignment
I(X = Cl)	2200/ $\nu(\text{Ir-H})$ <sup>b</sup>
IIA	2240/ $\nu(\text{Ir-H})$
IIB	2240/ $\nu(\text{Ir-H})$
III	2135/ $\nu(\text{Ir-H})$
IVA	2200/ $\nu(\text{Ir-H})$ ; 2035/ $\nu(\text{CO})$
IVB	2175/ $\nu(\text{CN})$ <sup>c</sup>
VI	2210/ $\nu(\text{CN})$ ; 1625/ $\nu(\text{C=N})$ ; 268/ $\nu(\text{Pd-Cl})$ <sup>d</sup>

<sup>a</sup> See Table 1 and Fig. 1–3 for the notation of the complexes. <sup>b</sup> See ref. 1. <sup>c</sup> The  $\nu(\text{Ir-H})$  frequency is probably hidden under this band. <sup>d</sup> Nujoll mull.

TABLE 3

 $^1\text{H}$  NMR DATA (ppm relative to TMS) FOR THE COMPLEXES IN  $\text{CDCl}_3$ 

Compound <sup>a</sup>	Relevant resonances (assignments)
I (X = Cl) <sup>b</sup>	8.00 (CH=N and <i>o</i> -C <sub>6</sub> H <sub>5</sub> ); 7.10 (H(2) and <i>m</i> - and <i>p</i> -C <sub>6</sub> H <sub>5</sub> ); 4.10 (N-CH <sub>2</sub> -); -18.35 (Ir-H) <sup>c</sup>
IIA	8.13 (CH=N); 7.85 ( <i>o</i> -C <sub>6</sub> H <sub>5</sub> ); 7.15 ( <i>m</i> - and <i>p</i> -C <sub>6</sub> H <sub>5</sub> ); 4.05 (N-CH <sub>2</sub> -); -18.90 (Ir-H) <sup>c</sup>
IIB	8.16 (CH=N); 7.86 ( <i>o</i> -C <sub>6</sub> H <sub>5</sub> ); 7.15 ( <i>m</i> - and <i>p</i> -C <sub>6</sub> H <sub>5</sub> ); 4.15 (N-CH <sub>2</sub> -); -19.70 (Ir-H) <sup>c</sup>
III <sup>d</sup>	6.82 (H(3)); 6.28 (H(4)); 5.83 (H(6)); 2.90 (N-CH <sub>3</sub> ); 1.50 (-CH <sub>3</sub> ); -17.50 (Ir-H) <sup>e</sup>
IVA	6.95 (H(3)); 6.57 (H(4)); 6.40 (H(6)); 3.28 (N-CH <sub>3</sub> ); 1.67 (-CH <sub>3</sub> ); -14.66 (Ir-H) <sup>f</sup>
IVB	6.90 (H(3)); 6.53 (H(4)); 6.40 (H(6)); 3.10 (N-CH <sub>3</sub> ); 1.60 (-CH <sub>3</sub> ); -17.00 (Ir-H) <sup>f</sup> ; 1.1 (CNC <sub>6</sub> H <sub>11</sub> )
VI	7.0-8.5 (C <sub>6</sub> H <sub>4</sub> NNPh); 3.40 (2H; N-CH of C <sub>6</sub> H <sub>11</sub> ); 1.0-2.0 (C <sub>6</sub> H <sub>11</sub> )

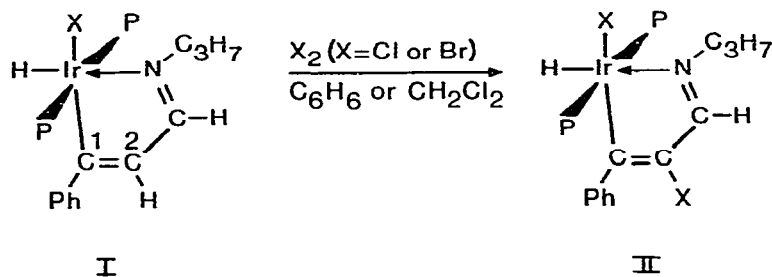
<sup>a</sup> See Table 1 and Fig. 1-3 for the notation of the complexes and for numbering of the protons. <sup>b</sup> See also ref. 1. <sup>c</sup> Triplet structure (rel. intensities 1/2/1) due to  $^{31}\text{P}$  coupling [ $J(\text{P-H})$  20 Hz]. <sup>d</sup> See also ref. 13. <sup>e</sup> Triplet structure (rel. intensities 1/2/1) due to  $^{31}\text{P}$  coupling [ $J(\text{P-H})$  16 Hz]. <sup>f</sup> Triplet structure (rel. intensities 1/2/1) due to  $^{31}\text{P}$  coupling [ $J(\text{P-H})$  13 Hz].

TABLE 4

 $^{13}\text{C}$  NMR (ppm relative to TMS) FOR THE COMPLEXES IN  $\text{CDCl}_3$ 

Compound <sup>a</sup>	Relevant resonances (assignments)
I (X = Cl) <sup>b</sup>	181.9 (C(1)); 168.3 (C=N); 127.8 (C(2)); 56.2 (N-CH <sub>2</sub> -)
IIA	167.1 (C(1)) <sup>g</sup> ; 169.9 (C=N); 116.6 (C(2)); 55.4 (N-CH <sub>2</sub> -)
IIB	173.6 (C(1)) <sup>g</sup> ; 176.2 (C=N); 108.4 (C(2)); 55.7 (N-CH <sub>2</sub> -)
III <sup>c</sup>	152.2 (C(1)); 140.9 and 141.8 (C(2) and C(5)); 126.3 (C(3)); 120.0 (C(4)); 143.2 (C(6)); 173.6 (C(7)); 44.0 (N-CH <sub>3</sub> )
IVA	C(1) <sup>d</sup> ; 146.3 (C(2)); 126.7 and 125.0 (C(3) and C(4)); 142.5 (C(5)); 143.1 (C(6)); 178.3 (C(7)); 51.2 (N-CH <sub>3</sub> )
VI	152.9; 147.7; 128.9; 128.0; 126.9; 125.5; 123.4; 121.4; 121.2; 116.8 (C <sub>6</sub> H <sub>4</sub> NNC <sub>6</sub> H <sub>5</sub> ); 158.2 and 134.8 (C=N) <sup>e</sup> ; 140.0 (CN) <sup>e</sup> ; 70.3-22.6 (C <sub>6</sub> H <sub>11</sub> ) <sup>f</sup>

<sup>a</sup> See Table 1 and Fig. 1-3 for the notation of the complexes and for the numbering of the carbon atoms. <sup>b</sup> See also ref. 1. <sup>c</sup> See also ref. 13. <sup>d</sup> C(1) could be detected. <sup>e</sup> Corresponding free ligand resonance: 155.8. <sup>f</sup> These signals show complicated splitting patterns and therefore, the peak positions are not explicitly given. <sup>g</sup> Triplet because of  $^{13}\text{P}$  coupling [ $J(\text{P-C})$  10 Hz].

Fig. 1. The reaction of a cyclometallated ene-imine with halogens in  $\text{CH}_2\text{Cl}_2$  or  $\text{C}_6\text{H}_6$ .

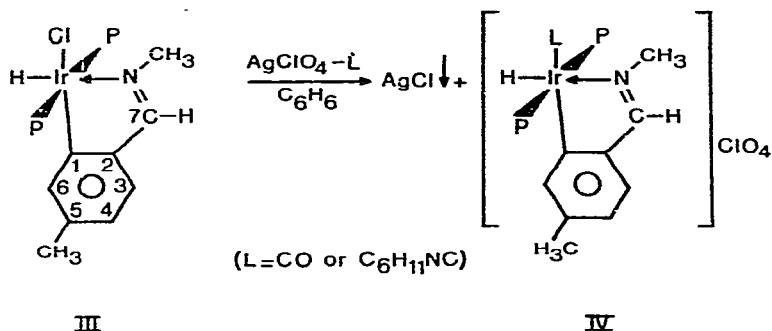


Fig. 2. The reaction of an orthometallated iridium(III) complex with CO or C<sub>6</sub>H<sub>11</sub>NC.

frared (Table 2) and <sup>1</sup>H NMR (Table 3) spectra, which, apart from a shift in peak position, show the same characteristics as the corresponding spectra of the starting complex III (Fig. 2) [13].

The  $\nu(\text{CO})$  and  $\nu(\text{CN})$  vibrations (Table 2) show that the CO- and isocyanide ligands are terminally bonded to the metal atom. The number and coupling pattern of the <sup>1</sup>H and <sup>13</sup>C NMR signals of the new complexes IV (Fig. 2) are similar to those for the initial complex [13].

Furthermore, the chemical shifts of the protons located near the metal centre and the <sup>13</sup>C shifts of the metallocyclic ring possess a large coligand dependence, as seen from the spectra of complexes III and IV (Tables 3 and 4).

The data strongly suggest that the new cationic complexes are isostructural with the starting complex, the original chloro ligand having been replaced by L (Fig. 2).

*Structural characterization of the compound [PdCl(CNC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>{(C=NC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>N=NPh}]*

Molecular weight (*M* 770) and spectroscopic data are consistent with the above formulation of complex VI, which is the result of the reaction of an excess of C<sub>6</sub>H<sub>11</sub>NC with the compound [PdCl(C<sub>6</sub>H<sub>4</sub>NNPh)]<sub>2</sub> (V) (Fig. 3).

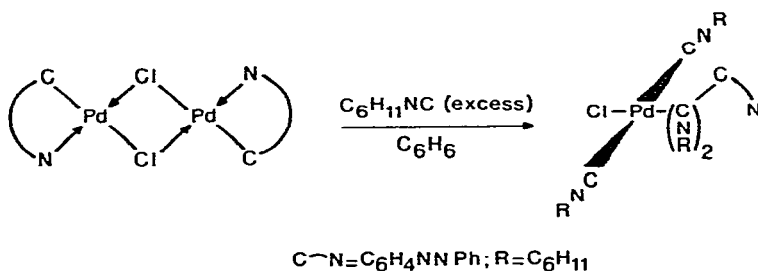


Fig. 3. The reaction of an orthometallated palladium(II) complex with C<sub>6</sub>H<sub>11</sub>NC.

The presence of the  $\nu(\text{Pd}-\text{Cl})$  vibration at  $268\text{ cm}^{-1}$  (Table 2) shows that the chloride is still acting as a ligand. Furthermore, the IR spectrum shows two more bands (at  $2210\text{ cm}^{-1}$  and  $1625\text{ cm}^{-1}$ ) than the corresponding spectrum of complex V. These bands most probably originate from  $\nu(\text{CN})$  vibrations of terminally bonded and inserted isocyanide ligands respectively [16].

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR resonances (Tables 3 and 4) in the aromatic region show that the  $\text{PhNNC}_6\text{H}_4$  moiety is still present in VI; the  $^1\text{H}$  NMR spectrum consists of a series of multiplets between 7.0 and 8.5 ppm (relative to TMS), while ten signals are observed in the  $^{13}\text{C}$  NMR spectrum. The azobenzene molecule is probably (mono) *ortho* substituted as a result of the insertion of one or more isocyanide molecules into the  $\text{Pd}-\text{C}$  bond of the original complex V.

The  $^{13}\text{C}$  NMR spectrum of VI shows three more signals in the aromatic region, which are probably due to two terminally bonded isocyanide ligands ( $\delta(\text{NC})$  140.0 ppm to TMS) and to two isocyanide molecules inserted into the  $\text{Pd}-\text{C}$  bond of V ( $\delta(\text{NC})$  158.2 and 134.8 ppm to TMS). These features and the observation of only one band at  $2210\text{ cm}^{-1}$  in the IR spectrum (see above) strongly indicate that the two terminally bonded isocyanide ligands are situated *trans* to each other as represented schematically in Fig. 3.

Finally, the  $^{13}\text{C}$  NMR spectrum in the aliphatic region suggests that there may be some steric hindrance involving the cyclohexyl groups of the inserted isocyanide molecules, as seen from the complicated splitting pattern of the corresponding signals. A single crystal X-ray investigation of complex VI will be necessary to resolve its structure in more detail.

## Discussion

The chemical properties of cyclometallated iridium(III) and palladium(II) complexes show that the metallocyclic rings of the former compounds are more stable than those of the latter (compare Fig. 1–3). This is clearly demonstrated by the reactions with halogens, for while the  $\text{Pd}-\text{C}$  bond of complex V (Fig. 3) is readily broken by these reagents [17], no such reaction occurs with the iridium(III) complexes. Instead, the substitution products II (Fig. 1) are obtained. A similar reaction with  $\text{Br}_2$  has recently been found for cyclometallated 2-vinylpyridine [18].

On the basis of the structural data (see Results) and in view of the reaction conditions (see Experimental), the following mechanism is proposed for this reaction. In the first step an electrophilic attack at the  $\text{C}(1)=\text{C}(2)$  moiety of the metallocyclic ring by the halogen leads to the formation of the intermediate carbonium ion I' (Fig. 4). The attack at the  $\text{C}(2)$  atom might be sterically favoured because of the presence of the two phosphines *cis* to the metal-carbon bond.

A similar reaction with the  $\text{C}=\text{N}$  group would create the intermediate carbonium ion I'' (Fig. 4), which would be much less stable than I' because of the positively charged nitrogen atom with a sextet of valence electrons. The inaccessibility of the  $\text{C}^*(1)$  atom for the  $\text{X}^-$  still present in solution will favour  $\text{H}^+(2)$  elimination\* from I' and formation of the final product II (Fig. 1).

\* This proposed mechanism would account for the fact that the cyclometallated complex I ( $\text{X} = \text{Cl}$ ) is recovered unchanged after treatment with  $\text{HCl}$ .



Fig. 4. Possible intermediate carbonium ions in the reaction of complex I with halogens (see also Fig. 1).

The difference in behaviour between the compounds of iridium(III) (III) and palladium(II) (V) is also shown by the reaction with  $C_6H_{11}NC$ . The starting complex III (Fig. 2) only reacts with isocyanide after initial treatment with  $AgClO_4$ . This silver(I) salt provides a free coordination site in the complex for an incoming  $RNC$  (or  $CO$ ) molecule by abstraction of the chloro ligand, which will be rather loosely bound to the metal atom because of the *trans* influence of the  $Ir-C$   $\sigma$ -bond [19]. Even a large excess of added ligand L (Fig. 2) leaves the metalocyclic ring intact. Therefore, the incoming ligand cannot attain a *cis* position with respect to the metal-carbon and, at least on geometric grounds, no insertion of the  $C_6H_{11}NC(CO)$  ligand into this bond can take place.

Such a reaction easily occurs, however, with the palladium(II) complex, V, in the presence of an excess of isocyanide (Fig. 3). The structural features of the final complex VI suggest the reaction scheme as shown in Fig. 5.

During the first steps the chloride bridges and the  $Pd-N$  bonds are broken by the entering ligand, resulting in the formation of intermediate  $V'$ . This proposal is based upon a similar reaction of V with phosphines [20]. In this way the  $Pd-C$  bond becomes more reactive towards isocyanide ligands, which is not the case for

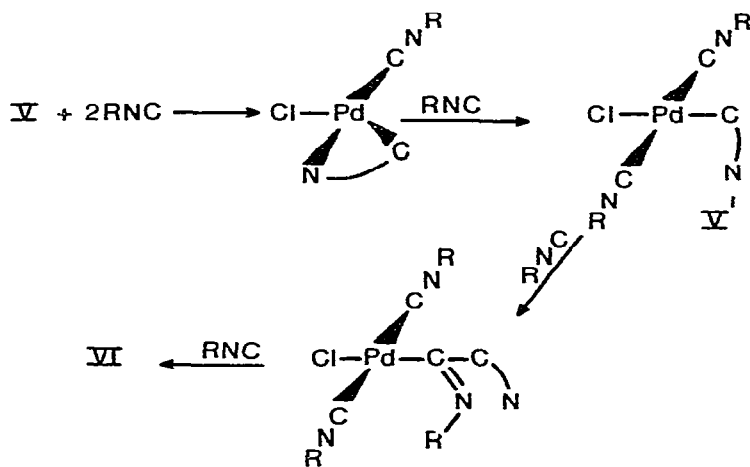


Fig. 5. Scheme proposed for the reaction of complex V with cyclohexylisocyanide (see also Fig. 3).



compound IV (Fig. 2) because of its apparent resistance towards rupture of the IR—N bond. It should be noted that the opening of the five-membered metallocyclic ring seems to be essential for any reaction of the metal—carbon bond.

Regarding the double insertion of isocyanide into the Pd—C bond of the postulated intermediate V' a parallel may be drawn between V' and the complexes *trans*-[PdI(CH<sub>3</sub>)(PR<sub>3</sub>)<sub>2</sub>] (PR<sub>3</sub> = PPh<sub>3</sub> or PMe<sub>2</sub>Ph), which undergo a similar reaction with C<sub>6</sub>H<sub>11</sub>NC [21]. More detailed studies on reaction systems, analogous to that depicted in Fig. 3, are necessary in order to obtain a clear picture of the precise course of the reaction.

We expect that it will be possible to utilize the results described above in the synthesis of new organic compounds.

### Acknowledgements

We are indebted to Mr. J. Berke for his accurate preparations, Mr. D. Prins for the elementary analysis, and Mr. J. Wever for recording the <sup>13</sup>C NMR spectra.

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