Journal of Organometallic Chemistry, 114 (1976) 219—224
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE REACTION OF TRIHYDRIDOTRIS(TRIPHENYLPHOSPHINE)IRIDIUM WITH *p*-ANISYLDIAZONIUM TETRAFLUOROBORATE

M. ANGOLETTA, L. MALATESTA *, P.L. BELLON
Istituto di Chimica Generale dell'Università di Milano (Italy)
and G. CAGLIO
Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei bassi Stati di Ossidazione, C.N.R., Via Venezian 21, Milano (Italy)

(Received January 30th, 1976)

Summary

The reaction of $IrH_3(PPh_3)_3$ with *p*-anisyldiazonium tetrafluoroborate gives an insertion product which very easily undergoes orthometalation, yielding $[\underline{IrH(PPh_3)_3NHNC}_6H_3OMe]^+BF_4^-$ (V), the structure of which is tentatively assigned. By reaction with halides X^-, the metalated fluoborate gives the neutral $\underline{IrHX(PPh_3)_2NHNC}_6H_3OMe$, which with halogens X_2 affords $\underline{IrX_2(PPh_3)_2NHNC}_6H_3OMe$, the structure of which has previously been determined.

The reaction of transition metal compounds containing only triphenylphosphine and hydrido ligands with diazonium cations may occur [1] by oxidative or reductive addition of the diazonium cation, or by insertion of the aryldiazonium group between the metal and one of the hydrogen atoms to form aryldiazene derivatives. In particular, the reaction between IrH_3L_3 ($L = PPh_3$) and RN_2BF_4 (R = a substituted aryl) gives insertion products.

We now report that in the case where R = *p*-anisole the compound obtained upon insertion loses two atoms of hydrogen under rather mild conditions and undergoes an *ortho*-metalation reaction. In addition, the *ortho*-metalated salt may be transformed into its neutral derivatives, the structures of which have been confirmed by X-rays.

Results and discussion

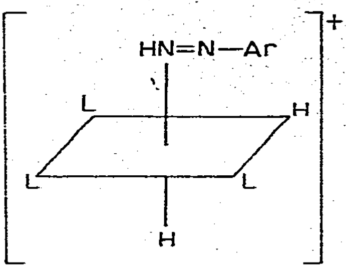
The insertion compound I mentioned in the brief communication [2] is obtained in two isomeric forms, according to the reaction:

$$IrH_3L_3 + RN_2^+ \rightarrow \underset{(I)}{[IrH_2L_3NHNR]^+}$$

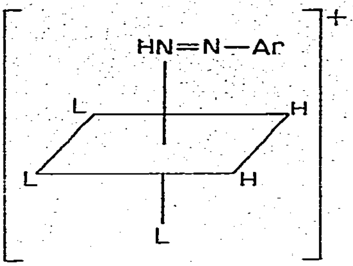
---

* To whom correspondence should be addressed.

To the isomer having m.p. 132° C and obtained from chloroform, a *mer* configuration Ia is assigned on the basis of IR and NMR data. To the other, crystallized from ethanol and having a m.p. of 169° C, the *fac* structure Ib is tentatively assigned on the basis of IR data, which exclude an alternative structure having two *trans* hydrogen atoms.



(Ia)



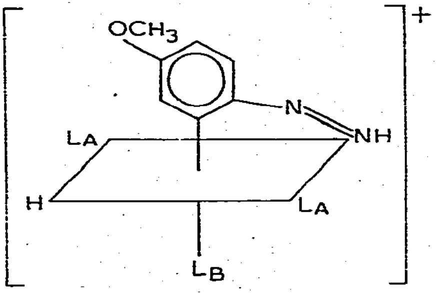
(Ib)

Both Ia and Ib give the original diazonium salt on reaction with chlorine in solution, while reaction with alcoholic KOH or with $NaBH_4$ leads to the starting hydride complex.

On prolonged boiling in benzene, chloroform or ethanol, I undergoes *ortho*-metalation to give V:

$$\mathrm{I} \rightarrow \mathrm{H_2} + (\underset{\text{(V)}}{\underline{\mathrm{IrHL_3NHNC}}}\mathrm{_6H_3OMe})\mathrm{BF_4} \qquad (1)$$

Compound V (L = phosphine) is obtained as a mixture of isomers. Using chromatographic techniques it was possible to separate only one of these, to which is



(Va)

assigned structure Va on the following evidence:

(i). In the NMR spectrum, Va exhibits a hydride proton signal, centred at $\tau = 25$, as a complex multiplet having an integrated intensity 1/3 that of the methyl group. This multiplet may be considered as arising from the overlap of a triplet ($J(P_A,H) \simeq 18$ Hz) of doublets ($J(P_B,H) \simeq 10$ Hz) in turn split into doublets ($J(H(N),H) \simeq 4$ Hz).

The methoxy protons show a singlet at $\tau = 7.8$, while in chloroform solution the proton bonded to the nitrogen atom appears as a doublet centred at $\tau = 4.21$ with $J = 4$ Hz.

(ii). No bands assignable with certainty to Ir—H stretching vibrations appear in the IR spectrum (see Table 1), which shows ν(N—H) at 3240 cm^{-1}. The N=N

TABLE 1

FORMULAE, ANALYTICAL AND PHYSICAL DATA OF COMPOUNDS I—XI

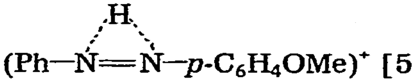
Number	Formula	Analysis found (calcd.) (%)			M.p. (°C)	Molar conductivity Λ (Ω^{-1} cm^2 mol^{-1})	Infrared (cm^{-1})		
		C	H	N			ν(Ir—H)	ν(N—H)	ν(C—O—C)
Ia	$[\mathrm{IrH_2(PPh_3)_3NHNC_6H_4OCH_3}]\mathrm{BF_4}$	60.67	5.01	2.11	132	28.4	2150	3515	1270
		(61.0)	(4.60)	(2.34)					
Ib	$[\mathrm{IrH_2(PPh_3)_3NHNC_6H_4OCH_3}]\mathrm{BF_4}$	59.91	4.62	2.22	169	29.1	2210— 2120	3515	1270
		(61.0)	(4.60)	(2.34)					
II	$[\mathrm{IrH_2(PPh_3)_3NHNC_6H_4CH_3}]\mathrm{BF_4}$	61.87	4.54	2.37	133	32.4	2130	3500	1270
		(61.7)	(4.72)	(2.40)					
III	$[\mathrm{IrH_2(PPh_3)_3NHNC_6H_4F}]\mathrm{BF_4}$	61.0	4.12	2.41		24.6	2130	3500	1270
		(60.4)	(4.37)	(2.35)					
IV	$[\mathrm{IrH_2(PPh_3)_3NHNC_6H_4N(C_2H_5)_2}]\mathrm{BPh_4}$	71.29	5.5	2.81	75	23.1	2130		1270
		(72.4)	(5.62)	(2.89)					
V	$[\underline{\mathrm{IrH(PPh_3)_3NHNC}}\mathrm{_6H_3OCH_3}]\mathrm{BF_4}$	60.52	4.18	2.09				3240	1230
		(61.0)	(4.41)	(2.34)					
Va	$[\underline{\mathrm{IrH(PPh_3)_3NHNC}}\mathrm{_6H_3OCH_3}]\mathrm{BF_4}$	60.83	4.21	2.18		27.3		3240	1230
		(61.0)	(4.41)	(2.34)					
VIa	$\underline{\mathrm{IrHCl(PPh_3)_2NHNC}}\mathrm{_6H_3OCH_3}$	58.26	4.22	3.10			2120	3200	1230
		(58.2)	(4.28)	(3.16)					
VIb	$\underline{\mathrm{IrHCl(PPh_3)_2NHNC}}\mathrm{_6H_3OCH_3 \cdot CHCl_3}$	51.64	3.38	2.73			2055	3230	1230
		(52.7)	(3.8)	(2.8)					
VII	$\underline{\mathrm{IrHBr(PPh_3)_2NHNC}}\mathrm{_6H_3OCH_3}$	55.32	3.91	3.01	160		2110	3190	1230
		(55.3)	(4.08)	(3.0)					
VIII	$\underline{\mathrm{IrHI(PPh_3)_2NHNC}}\mathrm{_6H_3OCH_3}$	51.87	3.67	2.78	145		2100	3170	1230
		(52.8)	(3.88)	(2.86)					
IX	$\underline{\mathrm{IrCl_2(PPh_3)_2NHNC}}\mathrm{_6H_3OCH_3 \cdot CHCl_3}$	50.2	3.69	2.66				3230	1230
		(50.6)	(3.65)	(2.68)					
X	$\underline{\mathrm{IrBr_2(PPh_3)_2NHNC}}\mathrm{_6H_3OCH_3 \cdot CHCl_3}$	46.60	3.21	2.54	>230			3210	1230
		(46.7)	(3.36)	(2.48)					
XI	$\underline{\mathrm{IrI_2(PPh_3)_2NHNC}}\mathrm{_6H_3OCH_3 \cdot CHCl_3}$	43.21	2.89	1.83	>230			3190	1230
		(43.1)	(3.10)	(2.29)					

stretching mode, found at 1500 cm^{-1} in I, is not easily identified in V and presumably lies at lower frequencies and is covered by triphenylphosphine bands. (iii). The band characteristic of 1,2,4-trisubstituted phenyl groups, often taken as diagnostic for *ortho*-metalation [3], lies at 810 cm^{-1}. In addition, the band attributed to C—O—C (phenyl—methoxy) stretching, present at 1270 cm^{-1} in compound I, moves to 1230 cm^{-1} in V. This band also falls at 1230 cm^{-1} in compounds VI, VII and VIII (see below) in which *ortho*-metalation has been confirmed by structure determination.

Further support for the *ortho*-metalation of V lies in the fact that the compound is diamagnetic. If the Ir—C bond were not present, the iridium would be in oxidation state II, which should be paramagnetic.

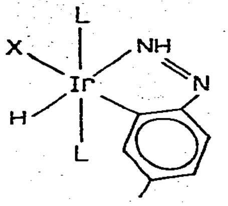
Deprotonation of V is not possible since the action of even weak alkalis leads to the formation of IrH_3L_3. Compound I behaves similarly.

The most convincing proof of *ortho*-metalation comes from a comparison between the reactions of I and V with halides X^- (X = Cl, Br and I). In fact I gives IrH_2XL_3 complexes, while V gives $IrHXNHNC_6H_3OMeL_2$ (VI, VII, VIII). Thus, in the former, a substitution of the monodentate aryldiazene occurs, whilst in the latter the anionic chelating azo group is not displaced but instead, one of the phosphines is eliminated. We note that this reaction for I takes place readily in all organic solvents, with the exception of ethanol. Since the isomer Ib is stable in ethanol, we can account for this behaviour by assuming that this isomer is much more inert than is Ia to nucleophilic attack by halide ions.

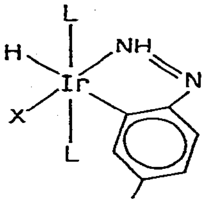
The neutral compounds, the structures of two of which (VII, VIII) have been determined crystallographically [4], are red, crystalline solids and monomeric non-conductors in solution. In the IR spectrum of VI, VII, VIII, the band attributed to the 1,2,4-substituted phenyl group is still present at 810 cm^{-1}, as is that of the C—O—C stretching of the same phenyl group at 1230 cm^{-1}. The virtually negligible influence of charge on the latter band was previously observed in $Ph{-}N{=}N{-}p\text{-}C_6H_4OMe$ and  $(Ph{-}\overset{H}{N{=}N}{-}p\text{-}C_6H_4OMe)^+$ [5]. The frequencies of the N—H and Ir—H stretching modes of the chloride-, bromide- and iodide-substituted compounds decrease with the electronegativity of the halogen.

The NMR spectra of the three compounds are practically identical, which allows the same structure to be assigned to the chloro compound VI. In these spectra, the hydride signal appears as a 1 : 2 : 1 triplet centred at $\tau = 24.9$, split into doublets (J(H(N),H) ≃ 4 Hz). The methoxy protons give a singlet at $\tau = 7.08$, while the NH proton appears as a doublet at $\tau = 4.71$ (J = 4 Hz).

When the halogen is chloride, we also isolated a second form, VIb. As far as the structure of this compound is concerned, we can say only that the hydride hydrogen is probably *trans* to the *o*-phenyl carbon atom for the following reasons. For compounds IX, X and XI (see below) it turns out that the chlorine *trans* to the carbon atom undergoes a much greater *trans* influence than that *trans* to the nitrogen atom. If this also holds good for the hydrogen atom, this influence would explain the decrease in ν(Ir—H) of VIb (2055 cm^{-1}), in which the hydride hydrogen is *trans* to the nitrogen atom, as compared to that of isomer VIa (2120 cm^{-1}). From the NMR spectrum of VIb, which is virtually identical to that of VIa, we can deduce only that the triphenylphosphines are



(VI a)



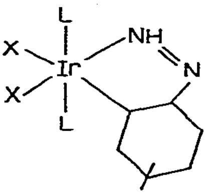
(VI b)

cis to the hydride hydrogen atom. We propose therefore for these isomers the structures VIa and VIb.

Compounds VII and VIII, in which X = Br or I, react with the corresponding halogen as in reaction 2:

$$\underline{IrHXL_2NHNC}_6H_3OMe + \tfrac{1}{2} X_2 \rightarrow \underline{IrX_2L_2NHNC}_6H_3OMe + HX \qquad (2)$$

The substitution of the hydrogen by the halogen is quantitative and gives slightly-soluble, red, crystalline compounds having IR spectra (in nujol) in agreement with the structure:



The same reaction using chlorine, even if quantities equal to or lower than the stoichiometric amount of chlorine are used, gives very low yields. However, high yields of $\underline{IrCl_2L_2NHNC}_6H_3OMe$ (IX) were obtained on leaving a chloroform solution of I to stand for 15—20 days. Attempts to repeat this reaction, by treating I with Cl_2, $COCl_2$ or HCl in the same solvent, were unsuccessful. Evidently, slow equilibria are set up, which permit the formation of the *ortho*-metalated ring, the elimination of a triphenylphosphine ligand and the substitution of the hydride hydrogen by the chlorine atom.

The structure of one of these hexa-coordinated compounds IX has been determined crystallographically [6]. The two triphenylphosphines are *trans* to one another and the halogens in positions *trans* to the NH group with the *o*-metalated carbon atom lie in the plane orthogonal to the two phosphines. As has previously been observed, the chlorine *trans* to the *o*-metalated carbon atom gives an Ir—Cl bond length of 2.494(3) Å, while that *trans* to the NH an Ir—Cl bond length of 2.393(3) Å.

Complexes IX, X and XI are chemically very stable. They are not reduced by $NaBH_4$ and are recovered unaltered after boiling in alcoholic potassium hydroxide.

Experimental

Ia (*mer* form) was prepared from $IrH_3(PPh_3)_3$ (3.53 g) in CH_2Cl_2 (20 ml) at 0°C and $[p\text{-}C_6H_4(OCH_3)N_2]BF_4$ (1.2 g, 50% excess) by stirring at room temperature for 1 h. The brown solution was evaporated in vacuo at room temperature, and the solid residue was extracted with cold benzene (20 ml). On pouring the filtered solution dropwise into hexane (150 ml) a yellow powder separated (yield 3.55 g, 81%). Ib (*fac* form) was prepared by dissolving Ia (2.5 g) in warm ethanol (20 ml) and cooling. The isomeric form separated in yellow crystals (2 g). II, III and IV were obtained as Ia from the corresponding diazocompounds. V was obtained from I (4.7 g) in benzene (30 ml), by refluxing for 20 h. After cooling, the solution was poured dropwise into hexane (250 ml) and gave a golden yellow precipitate (yield 4.25 g, 90%) as an isomeric mixture. The isomeric form Va was obtained by chromatography on Al_2O_3; 10% H_2O, by elution with CH_2Cl_2, as the last fraction. VIa was obtained from V (2.8 g) in ethanol (30 ml) at room temperature with LiCl (0.6 g) in ethanol. After 6 h the orange precipitate was filtered off (yield 1.5 g, 72%). VIb was obtained from a suspension of V (3.2 g) and LiCl (0.7 g) in $CHCl_3$ at room temperature by stirring for 6 h. The orange precipitate was filtered off and washed with water, ethanol and hexane (yield 1.8 g, 67%). VII and VIII were prepared as VIa or VIb with NaBr and NaI respectively. IX was obtained as red crystals by allowing a solution of I (2.7 g) in $CHCl_3$ (20 ml) to stand for 3 weeks at room temperature (yield 1.22 g, 53%). X was obtained from VII (2.4 g) in $CHCl_3$ (20 ml) and a solution of Br_2 (0.3 g) in $CHCl_3$ (10 ml) by subsequent addition of ethanol (30 ml). This gave orange crystals. (yield 2.2 g, 76%). XI was obtained from VIII (2.4 g) with I_2 (0.9 g). (yield 2.4 g, 80%).

References

1 D. Sutton, Chem. Soc. Rev., 1975, 4, 3, 443.
2 G. Caglio and M. Angoletta, Gazz. Chim. Ital., 102 (1972) 462.
3 L.J. Bellamy, The infrared spectra of complex molecules, Methuen, London, 1957, p. 64 ff.
4 P.L. Bellon, G. Caglio, M. Manassero and M. Sansoni, in press.
5 Si-Jung Yeh and H.H. Jaffé, J. Org. Chem., 24 (1959) 717.
6 P.L. Bellon, G. Caglio, M. Manassero and M. Sansoni, J. Chem. Soc. Dalton, 1974, 897.