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THE REACTION OF TRIHYDROBISTRIPHENYLPHOSPHINE IRIDIUM $IrH_3(PPh_3)_2$ WITH DIAZONIUM SALTS

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Summary

The reaction of $IrH_3(PPh_3)_2$ with *p*-substituted aryldiazonium salts gives the compounds $[IrH_2(NH{=}NC_6H_4R)(PPh_3)_2]^+BF_4^-$ at low temperature (−10°C) and the *o*-metalated complexes $[\overline{IrH(NH{=}N}C_6H_3R)(PPh_3)_2]^+BF_4^-$ (R = F, OCH_3) at 40—50°C. The reactions of the *o*-metalated complexes with CO, PPh_3, NaI and HCl have been studied.

Introduction

The reactions of $IrH_3(PPh_3)_3$ [1,2], $Ir_2(CO)_6(PPh_3)_2$ [3] and $[Ir(CO)_2(PPh_3)\text{-}\mu(SO_2)]_2$ [4] with aryldiazonium salts have been reported. We now describe the reaction of the coordinatively unsaturated hydride $IrH_3(PPh_3)_2$ with the tetrafluoroborates of *p*-substituted aryldiazonium ions, $[p\text{-}RC_6H_4N_2]^+BF_4^-$ (R = F, OCH_3).

Results and discussion

The hydride $IrH_3(PPh_3)_2$ (I) reacts (see Scheme 1) with *p*-substituted aryldiazonium tetrafluoroborates to give one of two compounds, depending upon the reaction conditions. When the reaction takes place in methylene chloride under nitrogen for 1 h at −10°C, a yellow compound is obtained and separates upon addition of hexane: $[IrH_2(NH{=}NC_6H_4R)(PPh_3)_2]^+BF_4^-$ (IIa, IIb) a formula supported by analytical (Table 1) and spectral data (Table 2); the IR spectrum shows a weak band at 3170 cm^{-1} due to N—H stretching and two other very weak bands at 2050, 2150 cm^{-1} assigned to Ir—H stretching. In the

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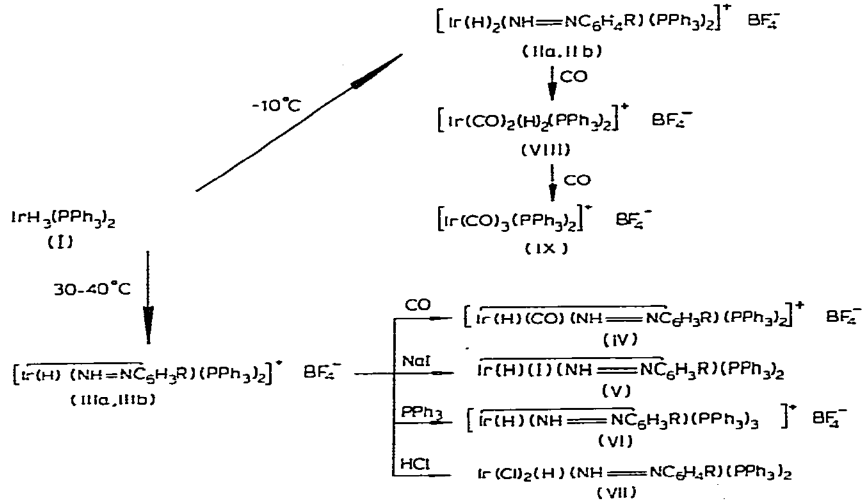

SCHEME 1

p-methoxyphenyldiazonium tetrafluoroborate derivative a strong band at 1270 cm^{-1} is assigned to C—O—C frequency. The N=N stretching mode is expected at values around 1400—1500 cm^{-1} and a band is, in fact, observed at 1500 cm^{-1}, but in the absence of isotopic labelling the assignment is only tentative. The NMR spectrum in $CDCl_3$ shows signals at τ —3.5 due to NH presence, at τ 6.1 due to CH_3 group and a triplet at τ 34.6 due to hydridic hydrogen (see Table 2).

TABLE 1

ANALYTICAL DATA FOR COMPOUNDS II—X

	Compound	Color	Analysis (Found (calcd.) (%))			
			C	H	N	Cl
II ^{a}	$[IrH_2(NH{=}NC_6H_4OCH_3)(PPh_3)_2]^+ BF_4^-$	yellow	53.96 (54.80)	4.17 (4.25)	2.87 (2.99)	
II ^{b}	$[IrH_2(NH{=}NC_6H_4F)(PPh_3)_2]^+ BF_4^-$	yellow	54.10 (54.4)	3.95 (3.8)	2.85 (3.02)	
III ^{a}	$[IrH(NH{=}NC_6H_3OCH_3)(PPh_3)_2]^+ BF_4^-$	yellow-green	54.2 (54.80)	4.2 (4.25)	2.85 (2.99)	
III ^{b}	$[IrH(NH{=}NC_6H_3F)(PPh_3)_2]^+ BF_4^-$	yellow-green	54.3 (54.4)	3.95 (3.8)	2.9 (3.08)	
IV	$[Ir(H)(CO)(NH{=}NC_6H_3OCH_3)(PPh_3)_2]^+ BF_4^-$	orange	54.1 (54.3)	4.14 (3.94)	2.75 (2.89)	
V	$Ir(H)(I)(NH{=}NC_6H_3OCH_3)(PPh_3)_2$	orange	52.2 (52.8)	3.8 (3.88)	2.75 (2.86)	
VI	$[Ir(H)(NH{=}NC_6H_3OCH_3)(PPh_3)_3]^+ BF_4^-$	yellow	60.5 (61.0)	4.20 (4.41)	2.25 (2.34)	
VII	$Ir(Cl)_2(H)(NH{=}NC_6H_4OCH_3)(PPh_3)_2$	yellow	54.8 (55.6)	4.14 (4.2)	2.83 (3.1)	7.4 (7.64)
VIII	$[Ir(CO)_2H_2(PPh_3)_2]^+ BF_4^-$	white	52.6 (52.9)	3.5 (3.7)		
IX	$[Ir(CO)_3(PPh_3)_2]^+ BF_4^-$	white	53.04 (52.6)	3.56 (3.7)		
X	$[Ir(CO)_3(PPh_3)_2]^+ B(C_6H_5)_4^-$	white	66.9 (67.6)	4.38 (4.56)		

The presence of only one triplet in the NMR spectrum indicates that the two hydrogen atoms are equivalent.

If the reaction is carried out at 0° C, a mixture of isomers is obtained which cannot be easily separated while at 30—40° C a yellowish green compound, $[\overline{IrH(NH{=}N}C_6H_3R)(PPh_3)_2]^+BF_4^-$ (IIIa, IIIb), is formed. *ortho*-Metallation involving diazonium salts and iridium was observed for derivatives of $IrCO(PPh_3)_2Cl$ [5], $IrH_3(PPh_3)_3$ [1], $IrHCO(PPh_3)_3$ [6], so it seemed likely that in this reaction there is also *ortho*-metallation, to give compounds IIIa and IIIb. The IR spectrum shows a medium strong band at 3260 cm^{-1} assignable to N—H stretching mode and a very weak band at 2150 cm^{-1} due to Ir—H frequency. When *p*-methoxyphenyldiazonium tetrafluoroborate is used, in addition to the C—O—C stretching frequency a strong band is noticed at 1230 cm^{-1}, and we have always observed the presence of this band in an *ortho*-metallated species. The NMR spectrum shows a triplet (τ 23.8; J(PH) 18 Hz) further split into a doublet due to coupling of the hydride with the NH group (^3J(HH) 4 Hz); upon irradiation of the doublet at τ —4.8 due to NH group (^3J(HH) 4 Hz) the doublet disappears. The same doublet disappears when the NMR spectrum is recorded in $D_3C{-}CO{-}CD_3$ because of deuterium exchange with the NH group. We have previously observed H—Ir—N—H coupling in the compounds $[IrH_2(NH{=}NC_6H_4OCH_3)(PPh_3)_3]^+BF_4^-$ [1] and $\overline{Ir(H)(I)(NH{=}N}C_6H_3OCH_3)(PPh_3)_2$ [2], although it has never been observed in other analogous compounds [7]. In the NMR spectrum of compound IIIa the signal due to the protons of the CH_3 group is at τ 6.8. This is higher than the value for compound IIa (τ 6.1). Probably when *ortho*-metallation occurs a CH_3 group enters the shielding zone of a phenyl ring and the τ value increases due to the anisotropic effect. The *o*-metallated compounds IIIa and IIIb were also obtained by heating IIa and IIb. Compounds IIIa and IIIb were deprotonated with a dilute ethanol solution of potassium hydroxide; the products are non-electrolytes and their IR spectra no longer show a band due to N—H (nor, of course, a band due to the BF_4 ion), but they have not completely characterised because an analytically pure sample has not been obtained.

Compounds IIa and IIb react with carbon monoxide with loss of the arylazo group, yielding $[Ir(H_2)(CO)_2(PPh_3)_2]^+BF_4^-$ (VIII). Further action of CO leads to $[Ir(CO)_3(PPh_3)_2]^+BF_4^-$ (IX), previously obtained as perchlorate salt [8]. The IR spectrum of IX shows three bands at 2100, 2030, 1990 cm^{-1} in Nujol, while in chloroform solution there is only one band at 2010 cm^{-1}. Only one band was observed in the IR spectra, in Nujol and in solution, for the corresponding perchlorate or tetraphenylborate salts, in agreement with the D_{3h} symmetry of a bipyramidal structure having the two phosphine ligands in *trans* to each other. The presence of three bands in the IR spectrum in Nujol of IX is probably due to a symmetry distortion caused by strong ionic interaction. The compound IIIa adds one CO molecule to give $[\overline{Ir(H)(CO)(NH{=}N}C_6H_3OCH_3)(PPh_3)_2]^+BF_4^-$ (IV), which is not affected by further CO. The IR spectrum shows the bands due to N—H (3240 cm^{-1}) Ir—H (2150 cm^{-1}) and C—O—C (1270, 1230 cm^{-1}) frequencies; in addition the presence of a band at 1230 cm^{-1} indicates the presence of an *ortho*-metallated species. In the NMR spectrum, the hydride signal appears as a triplet centred at τ 24.9 (J(P—H) 16 Hz) split into doublets (^3J(H—H) 4 Hz), and the NH protons appears also as a doublet at τ —5

TABLE 2

SPECTRAL DATA FOR COMPOUNDS II—X

s = singlet, d = doublet, t = triplet, m = multiplet.

Compound	Infrared data (Nujol)(cm^{-1})				NMR data (ppm) J(Hz)	
	NH	IrH	CO	C—O—C	solvent	
IIa	3170w	2050vw 2150 vw		1270s	$CDCl_3$	NH —3.5(s) CH_3 6.1(s) IrH 34.6(t) $J_{(PH)}$ 14
IIb	3170w	2050vw 2150 vw)			$CDCl_3$	NH —4(s) IrH 34.5(t) $J_{(PH)}$ 12.4
IIIa	3260ms	2150vw		1270w 1230ms	$CDCl_3$	NH —4.8(d) CH_3 6.8(s) IrH 23.8(t) $J_{(PH)}$ 18 $^3J_{(HH)}$ 4
IIIb	3260ms	2150vw			$CDCl_3$	NH —5.2(d) IrH 23.83(t) $J_{(PH)}$ 16 $^3J_{(HH)}$ 2
					CD_3COCD_3	IrH 23.7(t) $J_{(PH)}$ 18
IV	3240ms	2150w	2050s	1270w 1230ms	$CDCl_3$	NH —5.5(d) CH_3 6.6(s) IrH 24.7(t) $J_{(PH)}$ 16 $^3J_{(HH)}$ 4
V	3170ms	2100w		1270w 1230ms	$CHCl_3$	NH 4.71(d) CH_3 7.08(s) IrH 24.9(t) $J_{(PH)}$ 14 $^3J_{(HH)}$ 4 [2]
VI	3240ms	2100wv		1270w 1230ms	$CHCl_3$	NH 4.2(d) CH_3 7.8(s) IrH 25.0(m) [2]
VII	3120w	2070vw		1270s	$CDCl_3$	NH —2.5(d) CH_3 6.1(s) IrH 24.7(t) $J_{(PH)}$ 18 $^3J_{(HH)}$ 4
VIII		2150m	2080sh 2050s			
IX			2100m 2030vs 1990vs (solv,CH_2Cl_2) 2020vs			
X			2000vs			

(^3J(H—H) 4 Hz). Again irradiation of the NH group eliminates the ^3J(H—H) coupling. The reaction of the compound IIIa with NaI leads to $\overline{\mathrm{Ir(H)(I)(NH{=}NC}}\mathrm{_6H_3OCH_3)(PPH_3)_2}$ [4] (V) the structure of which has been determined crystallographically [9]. Complex IIIa adds a molecule of PPh_3 to give $[\overline{\mathrm{Ir(H)(NH{=}NC}}\mathrm{_6H_3OCH_3)(PPh_3)_3]^+BF_4^-}$ (VI) [1]. Analysis of the product obtained by treatment of IIIa with HCl indicates that the product is $Ir(Cl)_2(H)(NH{=}NC_6H_4OCH_3)(PPh_3)_2$ (VII); it is a non-electrolyte and contains two chloro atoms for each iridium atom; the IR (Ir—H 2070 cm^{-1}) and NMR spectra (τ 24.7 J(PH) 18 Hz) show the presence of a hydride. There is no bond in the IR spectrum assignable to the BF_4^- group, and in the C—O—C frequency region there is only one band at 1270 cm^{-1}. On this evidence, it is reasonable to conclude compound VII is not an *ortho*-metallated species.

The reaction of I with aryldiazonium ions having substituents in the 2 and 6 positions were studied in order to see what happens when *ortho*-metallation is impossible. The ions derived from the slightly basic 2,6-dichloroaniline derivative and the more basic 2,6-dimethylaniline derivative were used, but it was not possible to isolate crystalline material. The IR and NMR spectra show no signal assignable to NH group and the nitrogen and the carbon analyses are not reproducible. We assume that the arylazo group initially coordinates without entering in the Ir—H bond, and since it is not stable in the coordination sphere, it leaves and probably forms $[Ir(H)_2(PPh_3)_2]^+BF_4^-$. (The perchlorate of this compound was previously reported [8] and is known to react with carbon monoxide to yield $[Ir(CO)_3(PPh_3)_2]^+ClO_4^-$.) By treatment of the product solution with carbon monoxide we isolated $[Ir(CO)_3(PPh_3)_2]^+BF_4^-$ (IX).

Experimental

[Dihydro(p-methoxyphenyldiazene)bis(triphenylphosphine)iridium] tetrafluoroborate, $[IrH_2(NH{=}NC_6H_4OCH_3)(PPh_3)_2]^+BF_4^-$ *(IIa)*

Compound I (0.2 g) in methylene chloride (40 ml) was treated with $(N_2C_6H_4OCH_3)^+BF_4^-$ (0.065 g) at —10°C under nitrogen. The mixture was stirred for 1 h. The yellow solution was filtered, and concentrated below 0°C. Addition of hexane gave IIa as a yellow precipitate (yield 0.157 g; 60%).

[Dihydro(p-fluorophenyldiazene)bis(triphenylphosphine)iridium] tetrafluoroborate, $[IrH_2(NH{=}NC_6H_4F)(PPh_3)_2]^+BF_4^-$ *(IIb)*

By the same procedure from compound I (0.2 g) and $(N_2C_6H_4F)^+BF_4^-$ (0.06 g) the yellow compound IIb (yield 0.145 g; 55%) was obtained.

[Hydro(p-methoxyphenyldiazene-C^2,N^1)bis(triphenylphosphine)iridium] tetrafluorobarate, $[\overline{\mathrm{IrH(NH{=}NC}}\mathrm{_6H_4OCH_3)(PPh_3)_2]^+BF_4^-}$ *(IIIa)*

Compound I (0.2 g) in benzene (20 ml) and methylene chloride (20 ml) was treated with $(N_2C_6H_4OCH_3)^+BF_4^-$ (0.065 g) and the mixture was refluxed for 3 h under nitrogen. The yellow solution was cooled, and dropwise addition of hexane led to separation of a yellow green compound (yield 0.130 g; 50%).

[Hydro(p-fluorophenyldiazene-C^2,N^1)bis(triphenylphosphine)iridium] tetrafluoroborate, $[\overline{\mathrm{IrH(NH{=}NC}}\mathrm{_6H_3F)(PPh_3)_2]^+BF_4^-}$ *(IIIb)*

Similarly, from compound I (0.2 g) and $(N_2C_6H_4F)^+BF_4^-$ (0.065 g), the yellow green IIIb (yield 0.175 g; 65%) was obtained.

[Hydro(carbonyl)(p-methoxyphenyldiazene-C^2,N^1)bis(triphenylphosphine)iridium] tetrafluoroborate, $[\overline{Ir(H)(CO)(NH{=}NC}_6H_3OCH_3)(PPh_3)_2]^+BF_4^-$ *(IV)*

Carbon monoxide was bubbled through a solution of IIIa (0.150 g) in benzene (40 ml) for 1 h at room temperature. The deep red solution yielded an orange crystalline compound, which was recrystallized from chloroform and benzene (yield 0.104 g; 68%).

Hydroiodo(p-methoxyphenyldiazene-C^2,N^1)bis(triphenylphosphine)iridium, $\overline{Ir(H)(I)(NH{=}NC}_6H_3OCH_3)(PPh_3)_2$ *(V)*

To a solution of IIIa (0.150 g) in benzene (30 ml) was added a saturated ethanolic solution of NaI (20 ml). The solution was refluxed for 6 h. The mixture was cooled, then filtered, and evaporated to dryness under vacuum. The residue was extracted with cold benzene (20 ml) and hexane (40 ml) was added to precipitate the orange complex V (yield 0.062 g; 40%).

[Hydro(p-methoxyphenyldiazene-C^2,N^1)tris(triphenylphosphine)iridium] tetrafluoroborate, $[\overline{Ir(H)(NH{=}NC}_6H_3OCH_3)(PPh_3)_3]^+BF_4^-$ *(VI)*

Compound IIIa (0.150 g) in benzene (25 ml) was treated with $P(C_6H_5)_3$ (0.04 g) at room temperature under nitrogen. The mixture was stirred for 7—8 h. The red solution was concentrated, and addition of hexane gave a yellow precipitate which was washed several times with hexane (yield 0.1 g; 52%).

Dichlorohydro(p-methoxyphenyldiazene)bis(triphenylphosphine)iridium, $Ir(Cl)_2(H)(NH{=}NC_6H_4OCH_3)(PPh_3)_2$ *(VII)*

Hydrogen chloride was bubbled through a solution of compound IIIa (0.150 g) in benzene (40 ml) for about 1 h at room temperature. From the brown solution a yellow compound was precipitated by addition of hexane (yield 0.08 g; 55%).

[Dihydro(dicarbonyl)bis(triphenylphosphine)iridium] tetrafluoroborate, $[Ir(CO)_2H_2(PPh_3)_2]^+BF_4^-$ *(VIII)*

Carbon monoxide was bubbled through a solution of IIa (0.150 g) in benzene (40 ml) for 1 h at 70—80° C. A white crystalline compound was formed (yield 0.1 g; 80%).

[Tricarbonylbis(triphenylphosphine)iridium] tetrafluoroborate, $[Ir(CO)_3(PPh_3)_2]^+BF_4^-$ *(IX)*

Carbon monoxide was bubbled through a solution of VIII (0.1 g) in benzene (30 ml) for 2—3 h at 70—80° C. A white crystalline compound is formed (yield 0.96 g; 92%).

[Tricarbonylbis(triphenylphosphine)iridium] tetraphenylborate, $[Ir(CO)_3(PPh_3)]^+B(C_6H_5)_4$ *(X)*

A solution of IX (0.1 g) in ethanol (20 ml) was treated with $NaB(C_6H_5)_4$ in ethanol. A white precipitate was immediately obtained.

References

1 G. Caglio and M. Angoletta, Gazz. Chim. Ital., 102 (1972) 402.
2 M. Angoletta, L. Malatesta, P.L. Bellon and G. Caglio, J. Organometal. Chem., 114 (1976) 219.
3 M. Angoletta and G. Caglio, J. Organometal. Chem., 182 (1979) 425.
4 M. Angoletta and G. Caglio, J. Organometal. Chem., 185 (1980) 105.
5 F.W.B. Einstein, A.B. Gilchrist, G.W. Bayner Canham and D. Sutton, J. Am. Chem. Soc., 94 (1972) 645.
6 M. Angoletta, P.L. Bellon, M. Manassero and M. Sansoni, Gazz. Chim. Ital., 107 (1977) 441.
7 K.R. Laing, S.D. Robinson and M.F. Uttley, J. Chem. Soc., (1973) 2713.
8 L. Malatesta, G. Caglio and M. Angoletta, J. Chem. Soc., (1965) 6974.
9 P.L. Bellon, F. DeMartinn, M. Manassero, M. Sansoni and G. Caglio, J. Organometal. Chem., 157 (1978) 209.