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THE REACTION OF BIS[TRICARBONYL(TRIPHENYLPHOSPHINE)IRIDIUM], $Ir_2(CO)_6(PPh_3)_2$, WITH DIAZONIUM SALTS

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Summary

The reaction of $Ir_2(CO)_6(PPh_3)_2$ with *p*-substituted aryldiazonium salts gives the *o*-metalated complexes $[\overline{Ir(CO)_2(NH{=}NC}_6H_3R)(PPh_3)]_2^{2+}\ 2BF_4^-$. These react with KOH in ethanol to give the deprotonated derivatives, and with halogens to give halogenated derivatives by cleavage of the carbon—metal bond.

Introduction

Continuing our work on the chemistry of $Ir_2(CO)_6(PPh_3)_2$ we have investigated its reaction with diazonium salts. These are known to react with phosphine-transition metal complexes to give a variety of products containing arylazo and related nitrogen ligands, but their reactions with compounds containing metal—metal bonds have never been investigated, and so we examined then the reaction with the dimeric compound $Ir_2(CO)_6(PPh_3)_2$.

Results and discussion

The tetrafluoroborates of *para*-substituted aryldiazonium ions $[p\text{-}XC_6H_4N_2]^+$ BF_4^- (X = Me, OMe, F, NO_2) react with $Ir_2(CO)_6(PPh_3)_2$ (I) suspended in benzene to give salts, II, with evolution of two moles of carbon monoxide. The salts are dark red to brown in colour, and their solubilities in common organic solvents depend on the substituent X. These salts are not simple substitution products (as might have been deduced from the elemental analyses alone). In their IR spectra a band is present at 3200 cm^{-1}, attributable to a NH stretching mode, and the NMR spectra show signals at τ —5 to —6 ppm, which disappear

TABLE 1

FORMULAE AND ANALYTICAL DATA OF COMPOUNDS II—IV

	Compound	Color	Analysis (found (calcd.) (%))			
			C	H	N	Halogen
IIa	$[Ir(CO)_2(NH{=}NC_6H_3CH_3)(PPh_3)]_2^{2+}\ 2\ BF_4^-$	deep red	43.41 (45.3)	3.22 (3.35)	4.22 (3.98)	
IIb	$[Ir(CO)_2(NH{=}NC_6H_3OCH_3)(PPh_3)]_2^{2+}\ 2\ BF_4^-$	deep red	43.81 (44.2)	3.25 (3.0)	4.08 (3.80)	F 9.97 (10.4)
IIc	$[Ir(CO)_2(NH{=}NC_6H_3F)(PPh_3)]_2^{2+}\ 2\ BF_4^-$	deep red	43.40 (43.40)	2.64 (2.63)	4.05 (3.88)	
IId	$[Ir(CO)_2(NH{=}NC_6H_3NO_2)(PPh_3)]_2^{2+}\ 2\ BF_4^-$	deep red	44.45 (44.12)	2.98 (2.88)	5.00 (5.35)	
IIIb	$[Ir(CO)_2(N{=}NC_6H_3OCH_3)(PPh_3)]_2$	brown	49.50 (50.40)	3.47 (3.42)	4.30 (4.35)	
IIIc	$[Ir(CO)_2(N{=}NC_6H_3F)(PPh_3)]_2$	brown	48.00 (49.00)	3.04 (2.98)	4.65 (4.42)	
IVa	$[Ir(CO)_2(I)(N{=}NC_6H_4CH_3)(PPh_3)]_2$	red	42.31 (42.8)	2.92 (3.02)	3.99 (3.70)	I 16.20 (16.80) [a]
IVb	$[Ir(Cl)(CO)_2(N{=}NC_6H_4OCH_3)(PPh_3)]_2$	orange	47.10 (47.40)	3.25 (3.36)	4.12 (4.27)	Cl 5.08 (5.20)
IVc′	$[Ir(Cl)(CO)_2(N{=}NC_6H_4F)(PPh_3)]_2$	yellow	46.10 (46.70)	2.83 (3.00)	4.20 (4.07)	Cl 5.03 (5.07)
IVc″	$[Ir(Br)(CO)_2(N{=}NC_6H_4F)(PPh_3)]_2$	light brown	43.20 (43.80)	2.67 (2.67)	3.74 (3.93)	Br 11.22 (11.40)
IVc‴	$[Ir(CO)_2(I)(N{=}NC_6H_4F)(PPh_3)]_2$	orange	40.82 (41.00)	2.66 (2.50)	3.63 (3.69)	I 16.20 (16.65)
IVd	$[Ir(Br)(CO)_2(N{=}NC_6H_4NO_2)(PPh_3)]_2$	light brown	41;40 (41.80)	2.53 (2.57)	5.64 (5.68)	

[a] O 4.50 (4.20).

on treating the compound with D_2O; these signals are again attributable to an NH group. The presence of an imine hydrogen, as revealed by the IR and NMR spectra, cannot be ascribed for example, to protonation of the nitrogen by HBF_4 formed by decomposition of the diazonium salt for in this case the elemental analyses would have been considerably different. The most obvious rationalisation of the results is that the compounds $[\overline{Ir(CO)_2PPh_3(NH{=}NC_6}H_3R)]_2^{2+}\ 2BF_4^-$ (II) are formed. These compounds have an *ortho*-metalated bond between iridium and the carbon at the *ortho* position of the phenyldiazonium molecule, the hydrogen having migrated to the nitrogen atom coordinated to the metal. This type of *ortho*-metalation has been observed previously in the reaction between the compound $Ir(CO)(PPh_3)_2Cl$ and aryldiazonium salts [2], and is also present in $\overline{IrCl_2(NH{=}NC_6}H_3OMe)(PPh_3)_2$ [3]. The salts II appear to retain the intermetallic bond, as shown by the fact that the iridium atom is still diamagnetic, despite the change in oxidation state to 2+. A very broad band appearing in the NMR spectra at τ 6—7 ppm may be attributed to water bonded to the anion or to partial hydrolysis of the anion itself. A broad band at 3500 cm^{-1} in the IR spectra is again attributable to the presence of water. These characteristic IR and NMR features disappear when the tetrafluoroborate is replaced by tetraphenylborate. As mentioned above, the oxidation state of iridium in the derivatives II is 2+, while in compound I it is zero; the reaction may thus be considered to be an oxidative addition. The increase in oxidation state of iridium is conformed by on increase in the stretching frequencies of the carbonyl groups. Compounds II show a broad band above 2000 cm^{-1} (with three shoulders), while the starting compound I gives a broad band at 1940 cm^{-1}. The IR spectra of acetone solutions of compounds II are little different from those in Nujol, indicating that the same structure is retained in solution.

The IR spectra confirm that an *ortho*-metallic bond is present. We previously reported [3] that in some iridium derivatives of *o*-methoxyphenyldiazonium tetrafluoroborate, in which the presence of an *ortho*-metalated bond was proved by X-ray crystallography, the C—O—C frequency, which usually appears at 1270 cm^{-1}, shifts to ca. 1230 cm^{-1}. In compounds IIb there is indeed an intense band at 1230 cm^{-1}; in addition a band is present at 810 cm^{-1}, which may be attributed to the 1,2,4-trisubstituted phenyl group.

The NMR spectrum shows signals due to the CH_3 group at τ 7.68 and 6.2 ppm for the methyl and methoxy derivatives, respectively. In the IR spectra measured in Nujol, in KBr discs and in Voltalef, it was impossible to identify the $\nu(N{=}N)$ frequency. According to Ibers [4], the N=N stretching mode may be expected to give a band at 1400 cm^{-1} since the coordinated aryldiazene group contains two nitrogen atoms with sp^2 hybridisation. However, the absorption bands of the aromatic rings lie between 1500—1600 cm^{-1}, and these may interfere. Further evidence that *ortho*-metalation has occurred, was obtained by repeating the reactions using diazonium salts having the 2,6 positions occupied. Using both the only slightly basic 2,6-dichloroaniline derivative and the more basic 2,6-dimethylaniline derivative, compounds were obtained having properties entirely different from those of II. The IR and NMR spectra of these compounds, presently under further study, do not have bands due to NH groups and the elemental analyses for nitrogen give low, irreproducible, values.

TABLE 2

SPECTRAL DATA FOR COMPOUNDS II—IV

Compound	Infrared data (Voltalef) (cm^{-1})			NMR data (τ(ppm))		
	ν(CO)	ν(NH)	ν(COC)	solvent		
IIa	2110(sh)2080(sh) 2060vs, 2000(sh)	3220ms		CD_3COCD_3	NH —5.4	CH_3 7.68
IIb	2120(sh)2099(sh) 2068vs, 2016(sh)	3242ms	1270w, 1230vs	CD_3COCD_3	NH —5.0	OCH_3 6.20
IIc	2120(sh)2100(sh) 2075vs, 2020(sh)	3220ms		CD_3COCD_3	NH —5	
IId	2100(sh)2060(sh) 2050vs, 2000(sh)	3170				
IIIb	2000vs		1270w, 1230vs			
IIIc	2020vs					
IVa	2040vs					
IVb	2050vs		1270vs			
IVc'	2040vs					
IVc''	2040vs					
IVc'''	2060vs					
IVd	2050vs					

The compounds II are very stable to heat and also to the action of carbon monoxide. Conductances in nitrobenzene solution are as expected for bi-univalent electrolytes: *p*-fluoro: Λ_m 45.4; *p*-methoxy: Λ_m 40.4; *p*-tolyl: Λ_m 42.4 ohm^{-1} cm^2 mol^{-1}.

Experimental confirmation of the dimeric structure was obtained by deprotonation of the compounds II using diluted potassium hydroxide or sodium carbonate in water/ethanol mixture. This treatment gave compounds which were no longer ionic and had molecolar weights corresponding to the formula $[Ir(CO)_2PPh_3(N{=}NC_6H_3R)]_2$ (III). The IR spectra of III no longer show a band at 3200 cm^{-1} due to ν(NH) nor, of course, that due to the BF_4^- ion. The stretching modes of the carbonyl groups are at slightly lower frequency, as predicted for a change from a cationic species, in which the metal ion has a greater electron density. Addition of tetrafluoboric acid to this deprotonated products reformed the compounds II.

Independent of the nature of the substituent X, the salts II underwent an interesting reaction with alkali halides. Unlike most other reactions of this type, the substitution of the uncoordinated BF_4^- anion by the halide ion which coordinates to the metal, is not accompanied by elimination of a carbonyl group. This conclusion follows from the elemental analysis for oxygen and from the IR spectrum, which in the CO stretching region is virtually identical to that of the starting compound. It is thus probable that the iridium—carbon bond is broken, and the aryldiazene group, PhN=NH, is transformed into the aryldiazenate ion, $PhN{=}N^-$, with formation of compound IV. In agreement with this interpretation, in compounds IV the NH band is no longer present in the IR spectrum and the NMR spectrum also shows no NH signal. Furthermore if the *ortho*-metalated bond were still present, the coordination of the halide without any elimination of carbon monoxide would bring the coordination of the iridium to 7, which is highly improbable. The scission of the *ortho*-metalated bond in this compound may be attributed to an increase in the electron density on the metal caused by the coordination of a halogen.

Experimental

Bis[dicarbonyl(*p*-tolyldiazene-*C*^{2}, *N*^{1})triphenylphosphineiridium] bis(tetrafluoroborate), $[\overline{\text{Ir}(\text{CO})_2(\text{NH=NC}}_6\text{H}_3\text{CH}_3)\ (\text{PPh}_3)]_2^{2+}\ 2\text{BF}_4^-$ (IIa). A stirred suspension of compound I (0.2 g) in benzene (60 ml) and methylene chloride (2 ml) under nitrogen at room temperature was treated with $[p\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2]^+\cdot$ BF_4^- (0.120 g). After 5 h the deep red solution was filtered and concentrated. On addition of hexane a deep red compound was precipitated and this was recrystallized from benzene and hexane (yield 0.115 g; 43%); Λ_m (10^{-3} *M*, nitrobenzene) 42.4 ohm^{-1} cm^2 mol^{-1}.

Bis[dicarbonyl(*p*-methoxyphenyldiazene-*C*^{2}, *N*^{1})triphenylphosphineiridium] bis(tetrafluoroborate), $[\overline{\text{Ir}(\text{CO})_2(\text{NH=NC}}_6\text{H}_3\text{OCH}_3)\ (\text{PPh}_3)]_2^{2+}\ 2\text{BF}_4^-$ (IIb). This compound was prepared as above from I (0.2 g) and $[p\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2]^+\ \text{BF}_4^-$ (0.120 g). Deep red compound (yield 0.129 g; 47%; m.p. 208°C; Λ_m (10^{-3} *M*, nitrobenzene) 40.4 ohm^{-1} cm^2 mol^{-1}.

Bis[dicarbonyl(*p*-fluorophenyldiazene-*C*^{2}, *N*^{1})triphenylphosphineiridium] bis(tetrafluoroborate). $[\overline{\text{Ir}(\text{CO})_2(\text{NH=NC}}_6\text{H}_3\text{F})\ (\text{PPh}_3)]_2^{2+}\ 2\text{BF}_4^-$ (IIc). Prepared as above from I (0.2 g) and $[p\text{-FC}_6\text{H}_4\text{N}_2]^+\ \text{BF}_4^-$ (0.120 g). Deep red compound (yield 0.17 g; 63%); m.p. 240°C; Λ_m (10^{-3} *M*, nitrobenzene) 45.4 ohm^{-1} cm^2 mol^{-1}.

Bis[dicarbonyl(*p*-nitrophenyldiazene-*C*^{2}, *N*^{1})triphenylphosphineiridium) bis(tetrafluoroborate), $[\overline{\text{Ir}(\text{CO})_2(\text{NH=NC}}_6\text{H}_3\text{NO}_2)\ (\text{PPh}_3)]^{2+}\ 2\text{BF}_4^-$ (IId). Prepared as above from I (0.2 g) and $[p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2]^+\ \text{BF}_4^-$ (0.18 g) (yield 0.12 g; 43%).

Bis[dicarbonyl(*p*-methoxyphenyldiazenato-*C*^{2}, *N*^{1}) triphenylphosphineiridium], $[\overline{\text{Ir}(\text{CO})_2(\text{N=NC}}_6\text{H}_3\text{OCH}_3)\ (\text{PPh}_3)]_2$ (IIIb). Compound IIb (0.1) was treated with one mole of KOH in ethanol and the mixture was stirred at room temperature for 24 h. The solution was filtered and evaporated in vacuo. The brown residue was washed with H_2O, dissolved in benzene and precipitated with hexane. Mol. wt. (in C_6H_6) found 1320; calcd. 1290.

Bis[dicarbonyl(*p*-fluorophenyldiazenato-*C*^{2}, *N*^{1})triphenylphosphine)iridium], $[\overline{\text{Ir}(\text{CO})_2(\text{N=NC}}_6\text{H}_3\text{F})\ (\text{PPh}_3)]_2$ (IIIc). As above, mol. wt. (in C_6H_6) found 1345; calcd. 1266.

Bis[dicarbonyl(iodo) (*p*-tolyldiazenato)triphenylphosphineiridium], $[\text{Ir}(\text{CO})_2(\text{I})\ (\text{N=NC}_6\text{H}_4\text{CH}_3)\ (\text{PPh}_3)]_2$ (IVa). A solution of compound IIa (0.05 g) in deaerated EtOH (10 ml) under nitrogen was treated at room temperature with excess NaI (0.015 g). The mixture was stirred for 1.5 h. The solution was concentrated as a red compound. Recrystallization was from benzene and hexane (yield 0.033 g; 62%); mol. wt. (in C_6H_6) found 1498; calcd. 1512).

Bis[(chloro)dicarbonyl(*p*-tolyldiazenato)triphenylphosphineiridium], $[\text{Ir}(\text{Cl})\ (\text{CO})_2(\text{N=NC}_6\text{H}_4\text{OCH}_3)\ (\text{PPh}_3)]_2$ (IVb). As above, from compound IIb (0.05 g) and excess LiCl (0.005 g). The orange red compound was recrystallized from a mixture of C_6H_6 and CH_2Cl_2 (10/1) by addition of hexane (yield

0.0223 g; 48%); mol. wt. (in C_6H_6) found 1385; calcd. 1361).

Bis[(chloro)dicarbonyl(*p*-fluorophenyldiazenato)triphenylphosphineiridium], $[Ir(Cl)(CO)_2(N{=}NC_6H_4F)(PPh_3)]_2$ (IVc′). As above from IIc (0.1 g) in benzene (20 ml) and excess LiCl (0.008 g) in EtOH (5 ml). The yellow compound was precipitated from hexane, and recrystallized from benzene by addition of hexane (yield 0.052 g; 56%); mol. wt. (in C_6H_6) found 1308; calcd. 1337.

Bis[(bromo)dicarbonyl(*p*-fluorophenyldiazenato)triphenylphosphineiridium], $[Ir(Br)(CO)_2(N{=}NC_6H_4F)(PPh_3)]_2$ (IVc″). As above, from compound IIc (0.10 g) in benzene (30 ml) and methylene chloride (2 ml) and excess LiBr (0.018 g) for 4 h. The light brown compound precipitated with hexane was recrystallized from benzene by addition of hexane (yield 0.063 g; 64%); mol. wt. (in C_6H_6) found 1415; calcd. 1426.

Bis[dicarbonyl(iodo) (*p*-fluorophenyldiazenato)triphenylphosphineiridium], $[Ir(CO)_2(I)(N{=}NC_6H_4F)(PPh_3)]_2$ (IVc‴). As above, from IIc (0.1 g) in benzene (30 ml) and excess NaI (0.03 g) for 2 h. The orange compound precipitated from hexane was recrystallized from benzene by addition of hexane (yield 0.075 g; 72%); mol. wt. (in C_6H_6) found 1498; calcd. 1520.

Bis[(bromo)dicarbonyl(*p*-nitrophenyldiazenato)triphenylphosphineiridium], $[Ir(Br)(CO)_2(N{=}NC_6H_4NO_2)(PPh_3)]_2$ (IVd). As above, from IId (0.1 g) in benzene (25 ml) and methylene chloride (2 ml) and excess LiBr (0.015 g) for 4 h. The light brown compound precipitated with hexane was recrystallized from benzene by addition of hexane.

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