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THE REACTION OF DI((μ-SULPHUR DIOXIDE) BIS(DICARBONYL-(TRIPHENYLPHOSPHINE)IRIDIUM) $[Ir(CO)_2(PPh_3)\mu(SO_2)]_2$ WITH ARYLDIAZONIUM SALTS

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Summary

The reaction of $[Ir(CO)_2(PPh_3)\mu(SO_2)]_2$ with *p*-substituted aryldiazonium salts gave the compounds $\{[Ir(CO)_2(PPh_3)]_2\mu(N_2C_6H_4R)\mu(SO_2)\}^+BF_4^-$, in which a molecule of sulphur dioxide has been replaced by a molecule of aryldiazenate. Treatment of these products with HBF_4 gave the protonated derivatives $\{[Ir(CO)_2(PPh_3)]_2\mu(N{=}NHC_6H_4R)\mu(SO_2)\}^{2+}2\ BF_4^-$, while alkali halides gave the non electrolytes $[Ir(CO)(PPh_3)]_2\mu(X)\mu(N_2C_6H_4R)\mu(SO_2)$, which have halogen bridging two iridium atoms.

Introduction

In a previous communication [1] the reactions of $Ir_2(CO)_6(PPh_3)_2$ with aryldiazonium salts were reported. We have now extended the study to $[Ir(CO)_2(PPh_3)\mu(SO_2)]_2$ [2], obtained from $Ir_2(CO)_6(PPh_3)_2$ and sulphur dioxide, which had shown a remarkable and interesting reactivity.

Results and discussion

The reactions of $[Ir(CO)_2(PPh_3)\mu(SO_2)]_2$ (I) with *p*-tolyl, *p*-methoxy and *p*-fluoro phenyldiazonium tetrafluoroborate lead to the compounds $\{[Ir(CO)_2(PPh_3)]_2\mu(N_2C_6H_4R)\mu(SO_2)\}^+BF_4^-$ (II) in which an RN_2 group has replaced one of the two SO_2 groups. The reaction can be formally represented as a reduction of the entering diazonium cation RN_2^+ to diazenate anion by the SO_2^{2-} species, which is oxidised to sulphur dioxide. This explains why the entry of the RN_2

TABLE 1

ANALYTICAL DATA

No	Compound	Color	Analysis found (calcd.) (%)					
			C	H	N	Other		
IIa	$\{[\mathrm{Ir(C}$[illegible]$\mathrm{(P}$[illegible]$_3)]_2\mu(N_2C_6H_4CH_3)\mu(SO_2)\}^+BF_4^-$	red	44.0	3.24	2.37	2.36		
			(43.7)	(2.87)	(2.17)	(2.48) S		
IIb	$\{[Ir(CO)_2(PPh_3)]_2\mu(N_2C_6H_4OCH_3)\mu(SO_2)\}^+BF_4^-$	red	42.34	2.68	2.41	2.32		
			(43.0)	(2.87)	(2.14)	(2.45) S		
IIc	$\{[Ir(CO)_2(PPh_3)]_2\mu(N_2C_6H_4F)\mu(SO_2)\}^+BF_{4_2}$	deep pink	43.0	2.81	2.28			
			(42.7)	(2.62)	(2.16)			
III	$\{[Ir(CO)_2(PPh_3)]_2\mu(N{=}NHC_6H_4OCH_3)\mu(SO_2)\}^{2+}BF_4^-$	light brown	40.9	2.70	2.10			
			(40.5)	(2.64)	(2.02)			
IV	$[Ir(CO)(PPh_3)]_2\mu(Br)\mu(N_2C_6H_4CH_3)\mu(SO_2)$	orange	43.5	3.07	2.23			
			(44.0)	(3.0)	(2.28)			
V	$[Ir(CO)(PPh_3)]_2\mu(Cl)\mu(N_2C_6H_4OCH_3)\mu(SO_2)$	orange	44.65	3.04	2.23	2.46		
			(45.0)	(3.08)	(2.33)	(2.90) Cl		
VI	$[Ir(CO)(PPh_3)]_2\mu(I)\mu(N_2C_6H_4OCH_3)\mu(SO_2)$	orange	40.8	2.58	2.07	2.46	10.10	6.4
			(41.8)	(2.86)	(2.17)	(2.48) S	(9.84) I	(6.2) O

groups into a bridging position is rare, and in fact only example is known [3]; in the other cases reported, [4,5] the bridging aryldiazenate group was obtained indirectly by rearrangement.

Conductivity measurements on the compounds II in 10^{-3} M nitrobenzene solution gives Λ_m 12—14 ohm^{-1} cm^2 mol^{-1}, showing that they are electrolytes, but the values are very low for uni-univalent electrolytes (normally in the range 20—30 ohm^{-1} cm^2 mol^{-1}) even allowing for the large volume of the cation. The aryldiazenate moiety in the cation II would have a bent structure, i.e. with two angles of 120° to two sp^2 hybridised nitrogen atoms. The ligand RN_2, thus behaves as a Lewis acid, withdrawing electrons from the iridium atom so that positive charge is transferred to the metal ion. The NMR spectra showed no evidence for the presence of hydrogen atoms other than those of the organic moiety. In the IR spectra (Nujol and KBr discs) there is broad band at 2080 cm^{-1} with shoulders at 2100 and 2030 cm^{-1}, due to the carbonyl stretching modes (Table 2). This stretching frequency is virtually the same as that for the starting compound I, confirming an unchanged distribution of charge.

The broad band in the IR spectrum of compound II is considered to be the sum of four overlapping bands. These four bands show up separately in compound I, for which a structure with two pairs of CO in *cis* positions is suggested. Indeed, a *cis* configuration seems the only one possible if the two SO_2 molecules bridge two iridium atoms bonded by an intermetallic bond. This structure is confirmed by the fact that treatment of compound I with hydrogen under mild conditions gives the hydride derivative $[Ir(CO)_2(PPh_3)(H)]_2\mu(SO_2)$. The structure [6] of this compound, determined by X-ray crystallography, contains an SO_2 bridge, an intermetallic bond and the four CO groups in *cis* position in pairs. The fact that in II the replacement of an SO_2 by an aryldiazenate group does not influence the carbonyl stretching frequencies argues in favour of a bridging position for the azo group, with no other change in the structure. The nature of the substituents X has no influence on the frequencies of the carbonyl bands. The $\nu(N{=}N)$ frequency could not be observed; it should lie in the range 1500—1400 cm^{-1}, the same as those of aromatic rings. The $\nu(SO)$ frequencies are, in turn, hidden by the BF_4^- bands.

Compounds II are very stable, both thermally and towards addition of sulphur dioxide, which does not re-form the starting compound neither do they re-form $Ir_2(CO)_6(PPh_3)_2$ on reaction with carbon monoxide, unlike I, demonstrating that replacement of an SO_2 group by RN_2 increases the stability. Reaction with HBF_4 gives a protonated derivative III showing an NH band in the IR spectrum. The protonation must be considered to take place at the nitrogen which is not coordinated to the metal. On reaction with iodine, compounds II eliminate the diazenate moiety to give a previously reported compound [2]; this is dimeric, with an SO_2 molecule and two iodine atoms bridging and two terminal iodine ligands. The structure has been confirmed by X-ray studies [7].

On reaction of compounds II with lithium chloride, bromide and sodium iodide, replacement of the tetrafluoroborate by a halide ion and elimination of two moles of carbon monoxide occur, with formation of the non ionic compounds IV, V, VI. The far IR spectra of the chloro-derivatives V, show a band at 250 cm^{-1} which is not present for the compounds II, or for the bromo and iodo derivatives, and which must be attributed to a bridging chloride ligand.

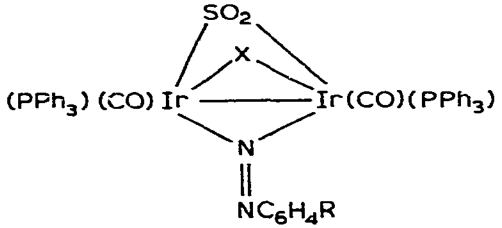
TABLE 2

INFRARED DATA [a]

Compound	ν(CO) (cm^{-1})	ν(SO) asym	(cm^{-1}) sym	Other frequencies (cm^{-1})
IIa	2100(sh), 2080s, 2030(sh)			
IIb	2100(sh), 2080s, 2030(sh)			
IIc	2100(sh), 2080s, 2030(sh)			
III	2100(sh), 2080s, 2030(sh)			ν(NH) 3250m
IV	2050s	1200w	1070m	
V	2040s	1200w	1070m	ν(Ir—Cl—Ir) 250m
VI	2040s	1200w	1070m	

[a] Determined as KBr discs.

This and the diamagnetism of these dimeric neutral compounds, suggests the following structure:



Experimental

Bis[dicarbonyl(triphenylphosphine)iridium] μ-(p-tolyldiazenato)μ-(sulphur dioxide) tetrafluoroborate. $\{[Ir(CO)_2(PPh_3)]_2\mu(N_2C_6H_4CH_3)\mu(SO_2)\}^+BF_4^-$ *(IIA)*

Compound I (0.2 g) in benzene (40 ml) under nitrogen at room temperature was treated with p-$CH_3C_6H_4N_2^+BF_4^-$ with stirring. After 4 h the red solution was filtered and concentrated. A red compound was precipitated by addition of hexane and recrystallized from benzene and dichloromethane (10/1) with hexane (0.157 g, 70%). M.p. 245°C. Λ_m (10^{-3} M, nitrobenzene) 14.7 ohm^{-1} cm^2 mol^{-1}.

Bis[dicarbonyl(triphenylphosphine)iridium] μ-(p-methoxyphenyldiazonato)-μ-(sulphur dioxide) tetrafluoroborate $\{[Ir(CO)_2(PPh_3)]_2\mu(N_2C_6H_4OCH_3)\text{-}\mu(SO_2)\}^+BF_4^-$ *(IIB)*

As above from I (0.110 g) and p-$CH_3OC_6H_4N_2^+BF_4^-$ (0.04 g) (ratio 1/2). A red compound was obtained (0.092 g, 75%). M.p. >>245°C. Λ_m (10^{-3} M, nitrobenzene) 13.6 ohm^{-1} cm^2 mol^{-1}.

Bis[dicarbonyl(triphenylphosphine)iridium] μ-(p-fluorophenyldiazenato) μ-(sulphur dioxide) tetrafluoroborate $\{[Ir(CO)_2(PPh_3)]_2\mu(N_2C_6H_4F)\mu(SO_2)\}^+\text{-}BF_4^-$ *(IIC)*

As above from I (0.194 g) and p-$FC_6H_4N_2^+BF_4^-$ (0.08 g) (ratio 1/2). A deep pink compound was obtained. (0.124 g, 56.5%). M.p. >>245°C. Λ_m (10^{-3} M, nitrobenzene) 14.3 ohm^{-1} cm^2 mol^{-1}.

Bis[dicarbonyl(triphenylphosphine)iridium] μ-(protonated p-methoxyphenyldiazenato)μ-(sulphur dioxide) bis tetrafluoroborate $\{[Ir(CO)_2(PPh_3)]_2\mu(N{=}NHC_6H_4OCH_3)\mu(SO_2)\}^{2+}2\ BF_4^-$ *(III)*

From IIb (0.1 g) in ethanol (15 ml) and benzene (15 ml) + HBF_4 40% (0.1 ml). After 1 h the solution was filtered concentrated to a small volume, and the light brown complex was precipitated with H_2O, and washed with H_2O. (0.085 g, 79%).

Bis[carbonyl(triphenylphosphine)iridium] μ-(bromo)μ-(p-tolylphenyldiazenato) μ-(sulphur dioxide) $[Ir(CO)(PPh_3)]_2\mu(Br)\mu(N_2C_6H_4CH_3)\mu(SO_2)$ *(IV)*

From IIa (0.1 g) in deaerated ethanol (15 ml) and excess LiBr (0.012 g) with stirring under nitrogen at room temperature. After 1 h the solution was filtered and concentrated to small volume, and an orange complex precipitated by addition of water. It was recrystallized from benzene by addition of hexane (0.057 g, 60%). Mol.Wt. (in $CHCl_3$) 1240 (calcd. 1227).

Bis[carbonyl(triphenylphosphine)iridium] μ-(chloro)μ-(p-methoxyphenyldiazenato)μ-(sulphur dioxide) $[Ir(CO)(PPh_3)]_2\mu(Cl)\mu(N_2C_6H_4OCH_3)\mu(SO_2)$ *(V)*

As above from IIb (0.1 g) and excess LiCl (0.08 g). An orange compound was obtained (0.051 g, 56%). Mol.Wt. (in $CHCl_3$) 1210 (calcd. 1198.5).

Bis[carbonyl(triphenylphosphine)iridium] μ-(iodo)μ-(p-methoxyphenyldiazenato)μ-(sulphur dioxide) $[Ir(CO)(PPh_3)]_2\mu(I)\mu(N_2C_6H_4OCH_3)\mu(SO_2)$ *(VI)*

From IIb (0.1 g) in benzene (25 ml) and an excess of NaI (0.02 g) with stirring at room temperature under nitrogen for 1.5 h. The orange solutions was filtered and concentrated, and addition of hexane gave an orange precipitate, which was recrystallized from benzene by addition of hexane (0.05 g, 50%). Mol.Wt. (in $CHCl_3$) 1306 (calcd. 1291).

References

1 M. Angoletta, Proceedings VIII Convegno Chimica Inorganica, Jesolo, (1975) A29.
2 M. Angoletta, L. Malatesta, G. Caglio, J. Chem. Soc. Dalton, (1977) 2131.
3 F.W.B. Einstein, D. Sutton, P.L. Vogel, Inorg. Nucl. Chem. Lett., 12 (1976) 671.
4 E.W. Abel, C.A. Burton, J. Chem. Soc. Chem. Commun., (1974) 268.
5 M.E. Deane, F.J. Labor, J. Organometal. Chem., 67 (1974) C19.
6 M. Angoletta, P.L. Bellon, M. Manassero, M. Sansoni, J. Organometal. Chem., 81 (1974) C40.
7 P.L. Bellon, M. Manassero, M. Sansoni, Abstracts of second Yugoslav-Italian Crystallographic Conference, Dubrovnik, 1976, Proceedings of the Yugoslav Centre of Crystallography, Supplement to Vol. 11 (1976), A.61.