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COORDINATION COMPLEXES CONTAINING MULTIDENTATE LIGANDS

V*. THE REACTIONS BETWEEN *trans*-CARBONYLCHLOROBIS-(TRIPHENYLPHOSPHINE)IRIDIUM AND *trans*-CARBONYLCHLORO(TRIPHENYLARSINE)IRIDIUM AND SOME TRIDENTATE GROUP VB LIGANDS

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Summary

Bis[3-(dimethylarsino)propyl] phenylarsine, (tas), reacts with *trans*-$Ir(CO)(EPh_3)_2X$ (E = P, As; X = F, Cl, Br, I) to yield the [Ir(CO)(tas)] X complexes. In contrast, the similar ligand bis[3-(dimethylarsino)propyl] phenylphosphine, (dap), reacts with *trans*-$Ir(CO)(EPh_3)_2X$ (E = P, As; X = Cl, Br, I) to yield a mixture of [Ir(CO)(dap)X] and [Ir(CO)(dap)] X, and with *trans*-$Ir(CO)(EPh_3)_2F$ (E = P, As) to yield solely [Ir(CO)(dap)F]. The cations $[Ir(CO)(L)]^+$ (L = tas, dap) readily yield tetraphenylborate derivatives, $[Ir(CO)(L)]BPh_4$. The oxygenation of $[Ir(CO)(tas)]^+$ in solution proceeds almost to completion after 15 h, whereas $[Ir(CO)(dap)]^+$ does not appear to undergo oxygenation.

Introduction

There is little documented work on the reaction of tridentate ligands with *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) or its analogues. Siegl, Lapporte and Collman [2] made a study of the reaction of the tripodal tridentate 1,1,1-tris[(diphenylphosphino)methyl] ethane (TDPME) with *trans*-$Ir(CO)Cl(PPh_3)_2$. The product was the five-coordinate Ir(CO)Cl(TDPME) which underwent dissociation of one phosphine group in solution and the resulting four-coordinate moeity reacted with oxygen to yield the carbonate derivative.

Since Vaska [3] showed that *trans*-$Ir(CO)Cl(PPh_3)_2$ reversibly binds oxygen, interest in synthetic oxygen carriers has grown rapidly and recent work has examined the O—O distance in the complexes [4], dioxygen uptake as a func-

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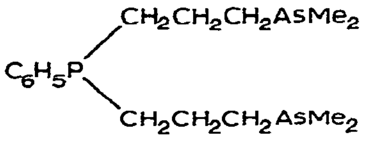
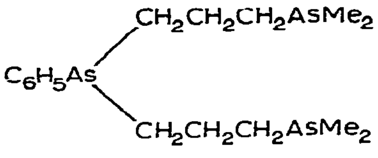
* For Parts III and IV see refs 1a and 1b.

tion of ligand [5], and the effect of changing the central d^8 metal ion [6]. In an effort to synthesize new dioxygen carriers containing multidentate ligands, which may relate to natural oxygen carriers more so than previously reported complexes, we have already studied the reaction of a series of bidentate Group Vb ligands with *trans*-Ir(CO)Cl(PPh$_3$)$_2$ [7], and we have extended this work to include the reactions of the potentially tridentate ligands bis[3-(dimethylarsino)propyl]phenylphosphine (dap), I, bis[3-(dimethylarsino)propyl]phenylarsine (tas), II, and bis [*o*-(diphenylarsino)phenyl] phenylphosphine (dap), III, with the iridium(I) complexes IV.


(I)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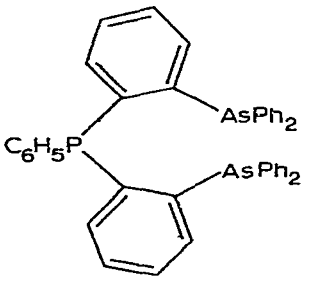
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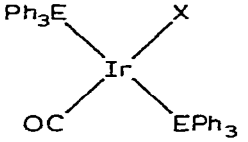

(IV)

E = P or As
X = F, Cl,
Br, or I

Reaction of Ir(CO)X(EPh$_3$)$_2$ with tas

When a benzene solution of *trans*-Ir(CO)X(EPh$_3$)$_2$ (X = F, Cl, Br, I; E = P, As) was treated with a 10% excess molar equivalent of tas in benzene at room temperature immediate precipitation occurred to yield the corresponding carbonylbis[3-(dimethylarsino)propyl]phenylarsineiridium(I) halide species. The analyses are consistent with the replacement of two triphenylphosphine or triphenylarsine ligands by tas. The complexes have similar colours and have conductance values in nitromethane consistent with assignments as 1/1 electrolytes [8], [Ir(CO)(tas)]X (X = F, Cl, Br, I), (see Table 1).

The carbonyl absorptions of these complexes in Nujol mulls consist of a single band in the range 2030—2040 cm^{-1} and are significantly different from the carbonyl absorptions of the starting materials, which are in the range 1945—1960 cm^{-1}, and this is indicative of a major structural change (Scheme 1).

SCHEME 1

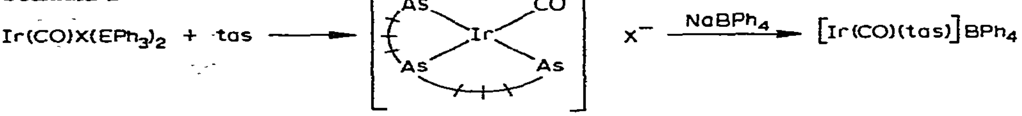


TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF THE COMPLEXES

Complex	Colour	M.P. (°C)	ν(CO) (cm^{-1})	Λ_M[a]	Analysis found (calcd.) (%)		
					C	H	Cl
[Ir(CO)(tas)]F	Fawn	251—258	2038	62[b]	29.2 (29.8)	4.7 (4.7)	
[Ir(CO)(tas)]Cl	Pale yellow	247—250	2045	59[b]	28.8 (29.1)	3.4 (4.1)	4.5 (5.0)
[Ir(CO)(tas)]Br	Pale yellow	242—248	2027	58[b]	27.0 (27.4)	3.8 (3.9)	
[Ir(CO)(tas)]I	Yellow	250—256	2045	59[b]	25.8 (25.7)	3.5 (3.7)	
Ir(CO)F(dap)	Fawn	210—214	1907	4[c]	31.3 (31.8)	4.2 (4.5)	
Ir(CO)Cl(dap)	Pale yellow	252—258	2035, 1915	35[c]	31.7 (31.0)	4.8 (4.4)	5.3 (5.4)
Ir(CO)Br(dap)	Pale yellow	242—250	2037, 1925	36[b]	28.8 (29.1)	4.3 (4.1)	
Ir(CO)I(dap)	Yellow	250—256	2030, 1913	41[b]	28.0 (27.3)	4.4 (3.9)	
[Ir(CO)(tas)]BPh$_4$	*d*		2034		47.4 (48.3)	3.1 (3.0)	
	e		2037		47.1	2.5	
	f		2036		48.1	3.0	
[Ir(CO)(dap)]BPh$_4$	*g*		2037		50.1 (52.3)	5.1 (5.2)	
	e		2040		50.0	5.5	
	f		2042		49.3	4.9	

[a] ohm^{-1} cm^2 M^{-1}. [b] In dimethylformamide. [c] In nitromethane. [d] Synthesised from the fluoride [e] Synthesised from the bromide. [f] Synthesised from the iodide. [g] Synthesised by in situ reaction of *trans*-Ir(CO)Cl(PPh$_3$)$_2$ and dap in presence of NaBPh$_4$.

The rather high carbonyl absorptions are consistent with the formation of a cation [2, 9]. The ionic halides can be replaced by tetraphenylborate (Scheme 1, see Table 1), confirming the ionic structure. The tetraphenylborate derivatives have almost identical carbonyl absorptions to those of the halide precursors. The ^{1}H NMR spectrum of the free ligand contains a strong sharp peak at 8.47 τ which is assigned to the methyl protons of the —AsMe$_2$ groups. In the complexes a broader signal is observed at 8.01 τ, and the disappearance of the 8.47 τ signal indicates that the terminal —AsMe$_2$ groups are coordinated.

Reaction of [Ir(CO)(tas)]X with dioxygen

The ability of a four-coordinate iridium(I) complex to coordinate dioxygen depends on the electron density at the metal and on steric factors [5]. A cationic complex should, due to electronic factors, be less effective in oxygenation than an uncharged complex. The high ν(CO) values of the [Ir(CO)(tas)]$^+$ complexes suggested that they would be poorer coordinators of dioxygen than Vaska's complex.

Oxygenation was followed by monitoring the ν(CO) absorption in dichloromethane solution. The original carbonyl absorption was progressively replaced by a new carbonyl peak as oxygenation proceeded, but even after 15 h

$$[Ir(CO)(tas)]^+ + O_2 \rightarrow [Ir(CO)(tas)(O_2)]^+$$

$$\nu(CO)\ 2035\ cm^{-1} \qquad \nu(CO)\ 2050\ cm^{-1}$$

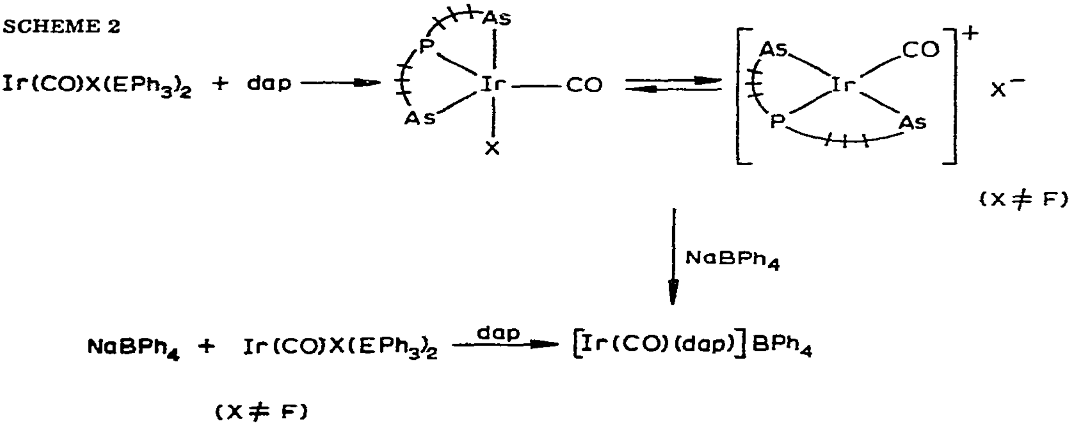
of bubbling O_2 through the solutions the original carbonyl absorption had not been replaced altogether. Solids could be obtained from these solutions but it did not prove possible to separate the oxygenated species from the starting materials. Analytical figures on the solids are not sensitive enough to give any clear idea on percentage conversion, though a qualitative estimate from IR spectra suggests 70—80% after 15 h. Ligand absorptions in the 800—900 cm^{-1} region precluded the identification of bands in this region assignable to coordinated dioxygen [4].

Reaction of $Ir(CO)X(EPh_3)_2$ with dap

Benzene solutions of *trans*-$[Ir(CO)X(EPh_3)_2]$ (X = F, Cl, Br, I; E = P, As) react with dap with the immediate precipitation of solid Ir(CO)X(dap). Table 1 lists the analytical values, melting points, colours, ν(CO) absorptions, and conductivities of the complexes. Except when X = F the compounds exhibit two carbonyl bands in the regions 1910—1925 and 2030—2040 cm^{-1}, both of strong intensity. Analytical data are indicative of a reaction involving the replacement of both EPh_3 groups by the dap ligand (Scheme 2).

The magnitude of the conductivity values for the complexes measured in nitromethane are well below those expected for a 1/1 electrolyte. Furthermore, the two carbonyl absorptions can be explained by a mixture of ionic and cocalent forms. The higher frequency absorption is assignable to the ionic form.

SCHEME 2



The covalent form exhibits ν(CO) at 1910 cm^{-1}; which is rather low compared to ν(CO) in the starting materials, and is probably due to the higher electron density at the iridium afforded by the simultaneous coordination of the two arsenic and one phosphorus groupings resulting in increased back-donation to CO from the iridium.

In order to characterise the system further an attempt was made to isolate the ionic and covalent forms by means of ion-exchange chromatography using Dowex 50 X8, 20—50 cation resin, and gradient elution. Difficulty was experienced in recovering the applied complex in the effluent and lack of conclusive results forced this approach to be abandoned. The problem was approached indirectly by isolation of the tetraphenylborate salts, [Ir(CO)(dap)]BPh_4, by displacement of the proposed solution equilibrium (Scheme 2). The analytical data for complexes so prepared are listed in Table 1. Alternatively, the totally ionic form is readily preparable by adding dap to a benzene solution of Ir(CO)X(EPh_3) ($X \neq F$) and $NaBPh_4$, resulting in the immediate precipitation of [Ir(CO)(dap)]BPh_4, ν(CO) 2037 cm^{-1}.

In the case of the reaction between Ir(CO)F$(EPh_3)_2$ (E = P, As) and dap, a fawn-coloured complex, [Ir(CO)F(dap)], is obtained, which is a non-conductor in nitromethane, and exhibits a single ν(CO) absorption at 1910 cm^{-1}. That no ionic species exist in equilibrium with this covalent form and, moreover, that the fluorine is tightly covalently bound to the iridium, is shown by the fact that addition of $NaBPh_4$ to a solution of [Ir(CO)F(dap)] does not yield any tetraphenylborate derivative. We can offer no explanation for the anomalous behaviour of the fluoro derivative, but we point out that other workers have noted similar anomalies [10].

Infrared monitoring of the carbonyl absorption of the Ir(CO)X(dap) complexes in dichloromethane in an oxygen atmosphere failed to show any oxygenation even after two days. Thus the dap complexes show less affinity for dioxygen than do the tas derivatives. Vaska and Chen [5] have shown that complexes of type *trans*-[Ir(CO)Cl$(L)_2$] undergo oxygenation at a slower rate when L is a phosphine than when L is an arsine group. Thus we might extrapolate this to the situation we find here where $[Ir(CO)(dap)]^+$ complexes are more reluctant to oxygenate than $[Ir(CO)(tas)]^+$ species. That the covalent [Ir(CO)X(dap)] did not oxygenate is probably due to the reluctance of pentacoordinate complexes to expand their coordination number to seven (if dioxygen is considered as a bidentate species). Adverse steric factors may still operate in the four-coordinate $[Ir(CO)(L)]^+$ (L = tas, dap) complexes, however, as molecular models of these complexes do indicate that the central iridium atom is protected to some extent by the protons of the trimethylene groups in the chelate.

A benzene solution of dap failed to show any reaction with *trans*-Ir(CO)$(EPh_3)_2$Cl (E = P or As), even after long reflux times. It is somewhat surprising to find that dap will not even replace the $AsPh_3$ groups in *trans*-Ir(CO)$(AsPh_3)_2$Cl.

Conclusion

This work has shown that *trans*-Ir(CO)$(EPh_3)_2$X (E = P, As) complexes readily react with tas to produce the $[Ir(CO)(tas)]^+$ species, but with dap reacts to produce a mixture of [Ir(CO)(dap)]X and [Ir(CO)(dap)X] (X = Cl, Br, I), or exclusively [Ir(CO)(dap)F]. Further differences are seen in the oxygenation reactions of these complexes. In dichloromethane solution oxygenation of the majority of $[Ir(CO)(tas)]^+$ species is complete after 15 h, whereas the Ir(CO)(dap)X complexes exhibit no tendency whatsoever to oxygenate.

Experimental

All reactions were performed under nitrogen using Schlenk-tube technique and solvents deaerated by refluxing under nitrogen. Elemental analyses were performed by the Microanalytical Service of this Department. Infrared spectra were recorded on a Perkin—Elmer 625 spectrophotometer. NMR spectra were obtained on a Hitachi—Perkin—Elmer R-20A High Resolution NMR Spectrometer. Melting points, determined on a Gallenkamp apparatus, are uncorrected. Conductivity measurements were performed on a Cambridge conductivity Bridge. Ligands were prepared by published methods [11—13]. The dap is a crystalline solid, but tas and dap were characterised by complexation with Na_2PtCl_4 in ethanol to yield the yellow complexes $PtLCl_2$. Found, C, 28.3; H, 4.0; Cl, 11.1%. Pt(dap)Cl_2 calcd.: C, 29.0; H, 4.3; Cl, 10.6%. Found: C, 26.3; H, 3.7; Cl, 10.9. Pt(tas)Cl_2 calcd.: C, 27.2; H, 4.1; Cl, 10.0%.

Complexes

trans-Chlorocarbonylbis(triphenylphosphine)iridium(I) was prepared by the method of Collman and Kang [14]. M.p. 257—260°.

trans-Chlorocarbonylbis(triphenylarsine)iridium(I) was prepared by an adaptation of the method used by Yagupsky and Wilkinson [15] and has been found to give improved yields. Carbon monoxide was bubbled through refluxing sodium chloroiridite (2.7 g, 5.7 mmol) in 2-methoxyethanol (105 ml) for 3—4 h after which the solution was pale yellow. After cooling to room temperature triphenylarsine (2.4 g, 7.85 mmol) was added, the mixture was refluxed for 10 min and on cooling yielded a yellow solid, which was filtered from the dark brown solution. The precipitate was dried in vacuo to give a mixture of *trans*-Ir(CO)Cl$(AsPh_3)_2$ and various impurities with IR absorptions in the carbonyl region. Recrystallisation was performed by dissolving the mixture in warm deaerated benzene under nitrogen and filtering off the impurities via a No. 3 Schlenk filter stick. The volume of the filtrate was reduced under a stream of nitrogen and an equal volume of deaerated n-hexane was added to yield a yellow precipitate. This was filtered and dried in vacuo. Yield 0.85 g (25%). The original impure fraction can again be extracted to yield further quantities of *trans*-Ir(CO)Cl$(AsPh_3)_2$. Total yield ≈38%. (Found, C, 51.4; H, 3.6; Cl, 4.7. $C_{37}H_{30}OClAs_2Ir$ calcd.: C, 51.3; H, 3.5; Cl, 4.1%.) M.P. 253—255°.

Analogous Ir(CO)$(EPh_3)_2$X complexes were prepared by methods reported in the literature [6, 16, 17].

Reaction of the complexes with dioxygen

A 1.43×10^{-4} *M* solution in dichloromethane was contained in a 5 ml volumetric flask fitted with a suba-seal stopper. Three syringe needles in the stopper allowed for the entry of dioxygen below the surface of the liquid, its subsequent passage to a flowmeter, and access for sampling the solution. Oxygenation was performed at room temperature by bubbling oxygen through the solution at a standard rate as measured by the flowmeter.

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