

Preliminary communication

Cationic oxygen adducts from rhodium and iridium carbonyl salts

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The reactions of $[\text{IrCl}(\text{CO})\text{L}_2]$ [$\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ and $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$] with the ligands, L, in methanol in the presence of the anions, ClO_4^- or $\text{B}(\text{C}_6\text{H}_5)_4^-$, have been reported to give ionic derivatives of the type, $[\text{Ir}(\text{CO})\text{L}_4]$ [anion]¹. The five-coordinate di- and tricarbonyl salts, $[\text{Ir}(\text{CO})_2\text{L}_3]$ [anion] and $[\text{Ir}(\text{CO})_3\text{L}_2]$ [anion] respectively, have also been prepared by similar reactions involving carbon monoxide^{1,2}.

We now find that warming a suspension of $[\text{RhCl}(\text{CO})\text{L}_2]$ [$\text{L} = \text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$ and $\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$] in hot methanol with the ligand L followed by addition of the anions PF_6^- or $\text{B}(\text{C}_6\text{H}_5)_4^-$, gives the four-coordinate salts, $[\text{Rh}(\text{CO})\text{L}_3]$ [anion]. In contrast, the corresponding reactions involving $[\text{RhCl}(\text{CO})\text{L}_2]$ [$\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ and $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$] give the five-coordinate cationic derivatives, $[\text{Rh}(\text{CO})\text{L}_4]$ [anion]. It is probable that steric repulsions between the ligands, L, constitutes the governing factor in determining whether four- or five-coordinate cations form in the above reactions.

The iridium(III) hydride $\{\text{IrHCl}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3\} \text{B}(\text{C}_6\text{H}_5)_4$, has previously been obtained by the addition of HCl to $\{\text{Ir}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$ ¹. We find that the salts $[\text{IrHCl}(\text{CO})\text{L}_3]$ [anion] [$\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ and $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$; anion = $\text{B}(\text{C}_6\text{H}_5)_4^-$ or PF_6^-], of configuration I, are more readily prepared by treating $[\text{IrHCl}_2(\text{CO})\text{L}_2]$ (configuration II)¹ or $[\text{IrHCl}_2(\text{CO})_2]_x \cdot \text{H}_2\text{O}$ (x probably = 2) with one or three moles of the ligand, L, per iridium atom respectively, in hot methanol in the presence of suitable large anions.

The complexes $[\text{Ir}(\text{CO})\text{L}_4] \text{B}(\text{C}_6\text{H}_5)_4$ [$\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ or $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$] are formed¹ in the same way as the rhodium analogues. They also form readily in ca. 40% yield, however, by the dehydrohalogenation of the hydrocarbonyl salts $[\text{IrHCl}(\text{CO})\text{L}_3]$ [anion] [anion = PF_6^- or $\text{B}(\text{C}_6\text{H}_5)_4^-$] with triethylamine in cold oxygen-free acetone solution. The isolation of these salts is effected by adding degassed [with N_2] ethanol to the acetone solution and bubbling off the acetone with a stream of nitrogen. The yield of the five-coordinate monocarbonyls can be increased to ca. 70% by performing the above reactions in the presence of excess ligand, L.

Corresponding salts of formula $[\text{Ir}(\text{CO})\text{L}_3] \text{PF}_6$ ($\text{L} = \text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$ or $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$) are obtained by the addition of three moles of L, per iridium atom, to a suspension of the cyclooctene complex $[\text{IrCl}(\text{CO})(\text{C}_8\text{H}_{14})_2]_2$ in hot methanol, in the presence of PF_6^- ions.

TABLE I
IR DATA ON SOME RHODIUM AND IRIIDIUM SALTS ^a

Compound	$\nu(\text{M-H}) \text{ cm}^{-1}$	$\nu(\text{CO}) \text{ cm}^{-1}$	$\nu(\text{O-O}) \text{ cm}^{-1}$
$\{\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_5]_3\} \text{PF}_6$		1990	
$\{\text{Ir}(\text{CO})[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_3\} \text{PF}_6$		1998	
$\{\text{Rh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_5]_3\} \text{B}(\text{C}_6\text{H}_5)_4$		1992	
$\{\text{Rh}(\text{CO})[\text{PCH}_3(\text{C}_6\text{H}_5)_2]_3\} \text{PF}_6$		2015	
$\{\text{Rh}(\text{CO})[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$		1922	
$\{\text{Rh}(\text{CO})[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{PF}_6$		1938	
$\{\text{IrHCl}(\text{CO})[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3\} \text{B}(\text{C}_6\text{H}_5)_4$	2125	2039	
$\{\text{Ir}(\text{O}_2)[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$			observed ^b
$\{\text{Ir}(\text{O}_2)[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$			838
$\{\text{Rh}(\text{O}_2)[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$			852
$\{\text{Rh}(\text{O}_2)[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$			856

^a Measured in nujol mulls. ^b Overlapping anion resonances.

A solution of the complexes $[\text{M}(\text{CO})\text{L}_4] \text{B}(\text{C}_6\text{H}_5)_4$ [$\text{M} = \text{Rh}$ or Ir ; $\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ or $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$], in acetone reacts rapidly with air to give stable oxygen adducts, $[\text{M}(\text{O}_2)\text{L}_4] \text{B}(\text{C}_6\text{H}_5)_4$, which can be precipitated from solution by the addition of methanol. A decomposition of this type in solution has also been reported for a ruthenium carbonyl complex³.

These oxygen derivatives, with the exception of $\{\text{Ir}(\text{O}_2)[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$, are more readily prepared, however, by treating the cyclooctadiene complexes $[(\text{C}_8\text{H}_{12})\text{MCl}]_2$ [$\text{M} = \text{Rh}^4$ or Ir], with the ligands, L , in hot methanol, in air and precipitating the adduct $[\text{M}(\text{O}_2)\text{L}_4]^+$, formed with $\text{B}(\text{C}_6\text{H}_5)_4^-$ ions. For the salt $\{\text{Ir}(\text{O}_2)[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$, the cyclooctene complex $[(\text{C}_8\text{H}_{14})_2\text{IrCl}]_2$ was used in place of $[\text{C}_8\text{H}_{12}\text{IrCl}]_2$ in the above reactions.

The structures proposed for the complexes I–IV (Fig.1) are based upon their ¹H NMR spectra (Table 2). For structures I and II their ¹H NMR spectra were identical with those previously reported for these complexes (see ref. 1). The proton NMR spectrum of III consists of two sharp singlets in the ratio of 1/3 which are ascribed to the methyl groups on the arsine ligands L_1 and L_2 , respectively. For IV ($\text{M} = \text{Ir}$), the methyl resonances of the mutually *cis*-phosphines (L) in the salt $\{\text{Ir}(\text{O}_2)[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$ were observed as a sharp doublet and those on the mutually *trans*-phosphines (L') as a sharp triplet, consistent⁵ with the structure proposed. The corresponding arsine complex $\{\text{Ir}(\text{O}_2)[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\} \text{B}(\text{C}_6\text{H}_5)_4$ contains two sharp singlets in the ratio of 1/1 corresponding to the methyl resonances of the arsine ligands L and L' .

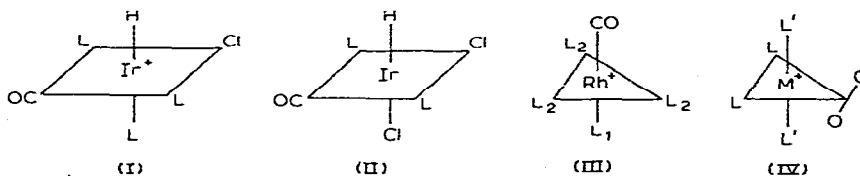


Fig.1. Proposed stereochemistry for the rhodium and iridium complexes. I and II, $\text{L} = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ and $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$; III, $\text{L}_1 = \text{L}_2 = \text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$; IV, $\text{M} = \text{Rh}^4$ and Ir , $\text{L} = \text{L}' = \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ and $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$ (These oxygen complexes can also be envisaged as octahedral M^{III} salts.)

TABLE 2
¹H NMR DATA ON SOME RHODIUM AND IRIIDIUM SALTS

Compound	Solvent	Methyls of L	
{Rh(CO){As(CH ₃) ₂ C ₆ H ₅] ₄ } B(C ₆ H ₅) ₄	CDCl ₃	8.60 s (1)	8.72 s (3)
{Ir(O ₂){P(CH ₃) ₂ C ₆ H ₅] ₄ } B(C ₆ H ₅) ₄	CH ₂ Cl ₂	8.28 d (1)	8.59 t (1)
		<i>J</i> (PH) 9 Hz	² <i>J</i> (PH) + ⁴ <i>J</i> (PH) ^a 8 Hz
{Ir(O ₂){As(CH ₃) ₂ C ₆ H ₅] ₄ } B(C ₆ H ₅) ₄	CDCl ₃	8.41 s (1)	8.60 s (1)

^a Separation of the outer peaks of the 1/2/1 triplet⁶; s, singlet; d, doublet; t, triplet. Ratios of peaks in brackets.

A few oxidative addition reactions to some of these complexes have been completed, *e.g.* {Rh(CO){P(C₂H₅)₂C₆H₅]₃} B(C₆H₅)₄ reacts with iodine to give the neutral complex, {RhI₃(CO){P(C₂H₅)₂C₆H₅]₂}, while the corresponding reaction involving {Ir(O₂){P(CH₃)₂C₆H₅]₄} B(C₆H₅)₄ similarly yields a neutral product, IrI₃{P(CH₃)₂C₆H₅]₃.

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