

Preliminary communication

Some unusual cationic complexes of iridium

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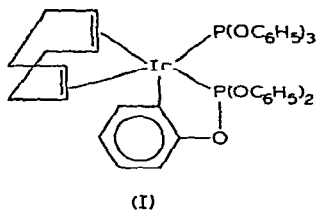
Interest has recently been focused on transition-metal cations and in particular on the use of such species as catalysts for the homogeneous hydrogenation of unsaturated organic molecules^{1,2}. A valuable method for the preparation of metal cationic derivatives involves the displacement of a halogen group from a neutral complex by a neutral ligand in an ionizing solvent, and precipitation of the resultant cation from solution by addition of a large inert anion. We have now used this method to prepare a series of cationic complexes of iridium(I), and some of the results of this study are reported here.

Excess triphenylphosphine is known to react with $[\text{C}_8\text{H}_{12}\text{IrCl}]_2$ in methanol at room temperature to give $\{\text{C}_8\text{H}_{12}\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+$ (refs. 1 and 3). We now find that when the less sterically hindered ligands, $\text{L} = \text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$, $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ and $\text{P}(\text{OR})_3$ ($\text{R} = \text{CH}_3$, C_2H_5 and C_6H_5), are used in this reaction the five-coordinate cations, $[\text{C}_8\text{H}_{12}\text{IrL}_3]^+$, are formed. Treatment of one mole of $[\text{C}_8\text{H}_{12}\text{IrCl}]_2$ with eight moles of the ligands, $\text{L} = \text{P}(\text{OCH}_3)_{3-n}(\text{C}_6\text{H}_5)_n$ and $\text{P}(\text{CH}_3)_{3-n}(\text{C}_6\text{H}_5)_n$ ($n = 1$ and 2), in refluxing ethanol under anaerobic conditions gives the four-coordinate species, $[\text{IrL}_4]^+$. In the reaction involving the ligand, $\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$, a second product, $\text{IrHCl}_2[\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]_3$ is also isolated, the yield of this neutral hydride increasing with increased reaction time. The reaction of excess tri-*n*-butylphosphine with $[\text{C}_8\text{H}_{12}\text{IrCl}]_2$ in refluxing ethanol gives the *cis* dihydride, $\{\text{Ir}[\text{P}(\text{n-C}_4\text{H}_9)_3]_4\text{H}_2\}^+$. Attempts to prepare $\{\text{Ir}[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4\}^+$ by treating $[\text{C}_8\text{H}_{12}\text{IrCl}]_2$ with a large excess of $\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5$ in boiling ethanol proved unsuccessful; $\{\text{C}_8\text{H}_{12}\text{Ir}[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3\}^+$ is the only cationic species formed in this reaction. All these cations were isolated and characterised as the tetraphenylborates or hexafluorophosphates and these derivatives were shown to be 1/1 electrolytes in solution.

$\{\text{C}_8\text{H}_{12}\text{Ir}[\text{P}(\text{OC}_6\text{H}_5)_3]_3\} \text{B}(\text{C}_6\text{H}_5)_4$ decomposes rapidly in hot ethanol to give a neutral complex of stoichiometry, " $\text{C}_8\text{H}_{12}\text{Ir}[\text{P}(\text{OC}_6\text{H}_5)_3]_2$ ", for which the structure I is favoured from NMR and IR spectral data.

The action of carbon monoxide on $\{\text{C}_8\text{H}_{12}\text{Ir}[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_3\} \text{PF}_6$ does not effect diene replacement but gives the novel salt, $\{\text{C}_8\text{H}_{12}\text{Ir}[\text{As}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{CO}\} \text{PF}_6$.

The complexes of the type, $[\text{IrL}_4][\text{Anion}]$, are extremely reactive towards carbon monoxide, hydrogen, oxygen and a variety of other addenda molecules. For instance carbon monoxide effects ligand displacement in $[\text{IrL}_4]\text{PF}_6$, $[\text{L} = \text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$ and



$\text{P}(\text{OCH}_3)(\text{C}_6\text{H}_5)_2$], to give the five-coordinate cationic derivatives, $[\text{Ir}(\text{CO})_2\text{L}_3]\text{PF}_6$. The IR spectra of dichloromethane solutions of these latter complexes contain two CO-stretching bands, indicating *cis* carbonyl groups. Treatment of $\{\text{Ir}[\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5]_4\}\text{PF}_6$ with excess bromine gives the ionic complex, $\{\text{Ir}[\text{P}(\text{OCH}_3)_2(\text{C}_6\text{H}_5)]_4\text{Br}_2\}\text{PF}_6$, whereas the corresponding reaction involving $\{\text{Ir}[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_4\}\text{PF}_6$ gives the neutral derivative, $\text{IrBr}_3[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_3$. The salt, $\{\text{Ir}[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)_4]_2\}\text{B}(\text{C}_6\text{H}_5)_4$, can be prepared however by reaction of *mer*- $\text{IrCl}_3[\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_3$ with excess $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$ in refluxing methanol and subsequent addition of sodium tetraphenylboron.

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