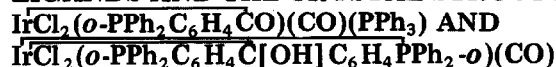


Preliminary communication

IRIDIUM(III) METALLACYCLES FROM ELECTROPHILIC ADDITION OF DICHLOROCARBENE LIGANDS TO TRIPHENYLPHOSPHINE LIGANDS AND THE CRYSTAL STRUCTURES OF



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Summary

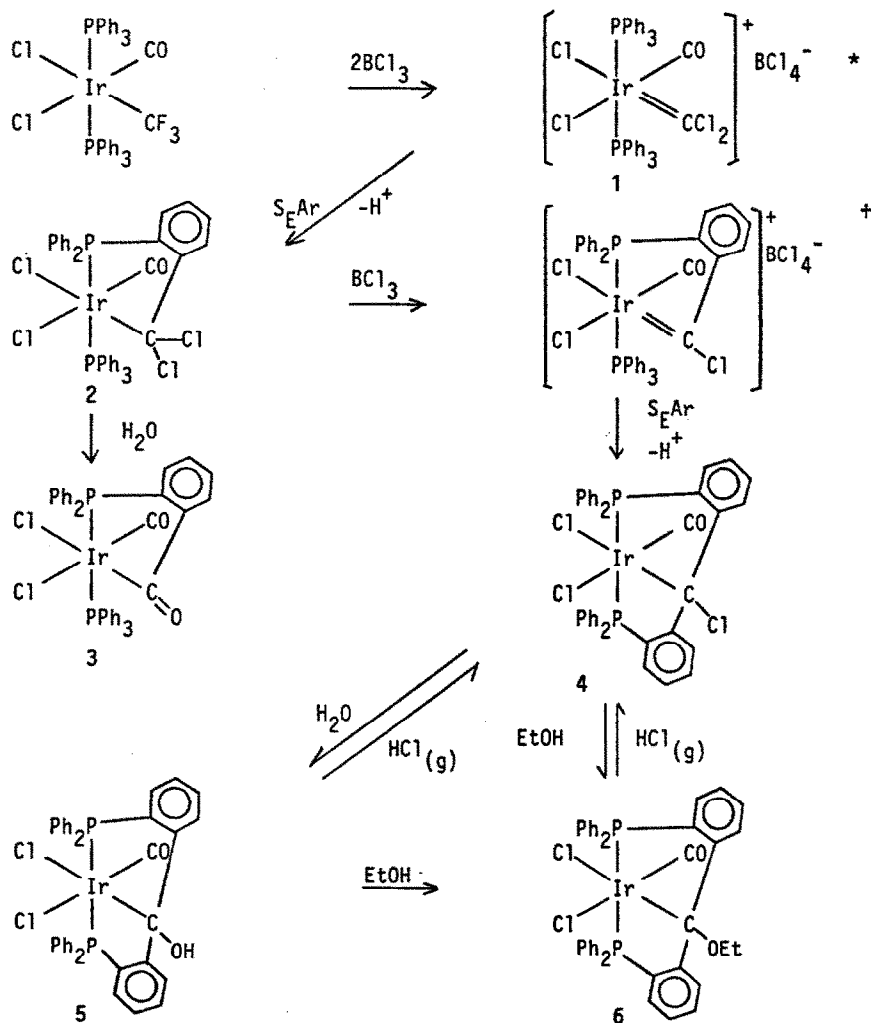
Treatment of $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ with BCl_3 yields $[\text{IrCl}_2(=\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2]^+$ (1), which immediately undergoes metallacycle formation by electrophilic attack of the CCl_2 ligand on a benzene ring of one PPh_3 ligand to give $\text{IrCl}_2(\text{o-PPh}_2\text{C}_6\text{H}_4\text{CCl}_2)(\text{CO})(\text{PPh}_3)$ (2). 2 is readily hydrolysed to $\text{IrCl}_2(\text{o-PPh}_2\text{C}_6\text{H}_4\text{CO})(\text{CO})(\text{PPh}_3)$ (3), while further reaction between 2 and BCl_3 results in a metallabicyclic complex, $\text{IrCl}_2(\text{o-PPh}_2\text{C}_6\text{H}_4\text{CClC}_6\text{H}_4\text{PPh}_2\text{-o})(\text{CO})$ (4). Hydrolysis of 4 affords $\text{IrCl}_2(\text{o-PPh}_2\text{C}_6\text{H}_4\text{C}[\text{OH}]\text{C}_6\text{H}_4\text{PPh}_2\text{-o})(\text{CO})$ (5). Similarly, 4 reacts with ethanol to give $\text{IrCl}_2(\text{o-PPh}_2\text{C}_6\text{H}_4\text{C}[\text{OEt}]\text{C}_6\text{H}_4\text{PPh}_2\text{-o})(\text{CO})$ (6). The structures of 3 and 5 have been confirmed by X-ray crystallography.

Dihalocarbene complexes are characteristically electrophilic, the halogen atom substituents being electron-withdrawing without being particularly good π -donors. This electrophilicity of dihalocarbene complexes is a sensitive function of the electron density at the metal centre, such that the carbene ligand will be more electrophilic when the metal is in a higher oxidation state [1], when there are more π -accepting spectator ligands, or when the complex is cationic.

Thus, although the neutral osmium(II) dichlorocarbene complex, $\text{OsCl}_2(=\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$ is a stable species [2], we show here that the iso-electronic iridium(III) compound, $[\text{IrCl}_2(=\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2]^+$ (1), cannot be isolated since the electrophilicity of the CCl_2 ligand has been so enhanced by the positive charge on the complex that a further reaction occurs. A facile, intramolecular, Friedel—Crafts reaction between the CCl_2 ligand and a benzene

ring of one PPh_3 group results in the direct formation of a bidentate ligand. Similar metallacyclisations have been reported for cationic chloromethylene [3] and methylene [4] complexes. However, heteroatom substituted carbene complexes directly analogous to 1, such as $[\text{IrCl}_2(=\text{CNHCHMeS})(\text{PMe}_2\text{Ph})_2]^+$, do not display marked electrophilic reactivity [5].

BCl_3 was employed in its potential capacity to effect conversion of the CF_3 ligand of $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ [6] to a CCl_3 group [7], and to subsequently abstract Cl^- [8] from the resultant trichloromethyl ligand to give the cationic dichlorocarbene complex, 1. However, as depicted in Scheme 1, the isolated product was the metallacycle, 2. The two α -chlorine atoms of 2 are reactive, as demonstrated by the extreme moisture-sensitivity of 2, which readily hydrolyses to the metallacyclic acyl compound, 3.



SCHEME 1. Synthesis and reactions of Ir^{III} metallacyclic and metallabicyclic compounds. Infrared spectra of compounds 2–6 display $\nu(\text{CO})$ bands as follows: 2 2066, 3 2076, 4 2053, 5 2065, 6 2049 cm^{-1} .

*Not isolated. †Characterised by spectroscopic evidence only.

The structure of **3** has been confirmed by a single crystal X-ray diffraction study, and Figure 1 displays the molecular geometry. **3** forms pale lemon plates; a 12.089(2), b 14.975(2), c 19.935(2) Å, β 111.98(1)°, monoclinic, space group $P2_1/c$, $Z = 4$. The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms except the carbons of the triphenylphosphine ligands. The final residual, R , is 0.044 for 3938 observed reflections.

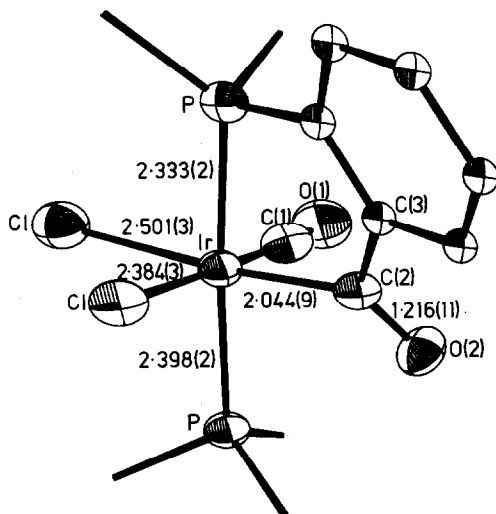


Fig. 1. Molecular structure of $\text{IrCl}_2(\text{o-PPh}_2\text{C}_6\text{H}_4\text{CO})(\text{Co})(\text{PPh}_3)$ with phenyl rings omitted for clarity. Important bond angles are: $\text{P}-\text{Ir}-\text{P}$ 173.2(1), $\text{Ir}-\text{C}(2)-\text{O}(2)$ 124.7(7), $\text{Ir}-\text{C}(2)-\text{C}(3)$ 115.8(6), $\text{C}(3)-\text{C}(2)-\text{O}(2)$ 119.5(9)°.

Comparison of the Ir—Cl bond lengths for the chlorine atoms *cis* and *trans* to the acyl moiety reveal an extremely high *trans*-influence to be exerted by the acyl ligand, indicating a probable lability of the *trans*-chloride. A further point of interest is the shortening of the Ir—P bond length for the phosphorus atom contained in the bidentate ligand relative to the Ir—P bond length for the phosphorus atom of the PPh_3 group. Also of note is the shortening of the Ir—C bond length for the acyl ligand compared with the corresponding Ir—C bond length shown in Fig. 2, for the tridentate ligand of **5**. The shortening is significantly greater than that expected upon changing from an sp^3 to an sp^2 hybridised carbon [9].

The α -chlorine atoms of **2** are also reactive towards excess BCl_3 , and longer reaction times lead to a further Friedel—Crafts reaction with a benzene ring of the second PPh_3 ligand, resulting in the tridentate ligand contained in **4**. Once again, **4** is moisture-sensitive, and the reaction with water yields the metallabicyclic hydroxyalkyl compound, **5**. Similarly, the addition of ethanol to **4** gives the ethoxyalkyl complex, **6**. Both **5** and **6** can be reconverted to **4** by the action of gaseous HCl . Interestingly, **6** could also be obtained by reaction between **5** and ethanol.

5 has been structurally characterised, and Figure 2 shows the molecular geometry. **5** forms colourless parallelepipeds which turn wine-coloured on

prolonged exposure to X-rays; a 15.285(3), b 12.236(3), c 17.900(3) Å, β 102.04(1)°, monoclinic, space group $P2_1/n$, $Z = 4$. The structure was solved and refined as for 3 to a final R of 0.058 for 2938 observed reflections.

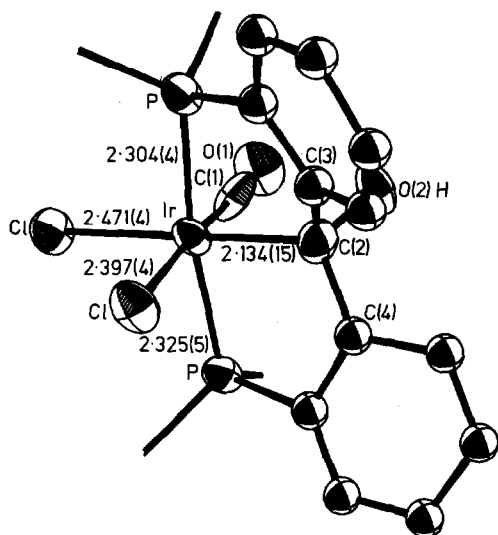


Fig. 2. Molecular structure of $\text{IrCl}_2(\text{o-PPh}_2\text{C}_6\text{H}_4\text{C[OH]C}_6\text{H}_4\text{PPh}_2\text{-o})(\text{CO})$ with phenyl rings omitted for clarity. Important bond angles are: P-Ir-P 167.9(1), Ir-C(2)-O(2) 109.9(9), Ir-C(2)-C(3) 112(1), Ir-C(2)-C(4) 107(1), C(3)-C(2)-O(2) 109(1), C(4)-C(2)-O(2) 108(1), C(3)-C(2)-C(4) 115(1)°.

The *trans*-influence of the hydroxyalkyl group, although relatively high as shown by the Ir-Cl bond lengths for the *cis*- and *trans*-chlorine atoms, is less marked than the *trans*-influence of the acyl ligand of 3. The P-Ir-P bond angle of 173.2(1)° demonstrates the distortion of the octahedral geometry by the chelating group. However, the distortion is somewhat less severe than that reported for the similar complex, $\text{OsCl[} \text{o-PPh}_2\text{C}_6\text{H}_4\text{CHC}_6\text{H}_4\text{PPh}_2\text{-o]}(\text{CO})_2$ [3]. The apparent generality of the metallacyclisation reaction for extremely electrophilic carbene complexes, while providing a convenient route to chelating ligands such as those described herein, will necessarily limit the synthesis of dihalocarbene compounds containing aromatic phosphines to cases in which the metal centre is relatively electron-rich.

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