Hydrogen Reduction of Co-ordinated Carbon Monosulphide in $[IrH(CS)(PPh_3)_3]$ to the Methanethiolato-ligand and an Iridium Thioformyl Compound $[Ir(CHS)Cl_2(CO)(PPh_3)_2]$

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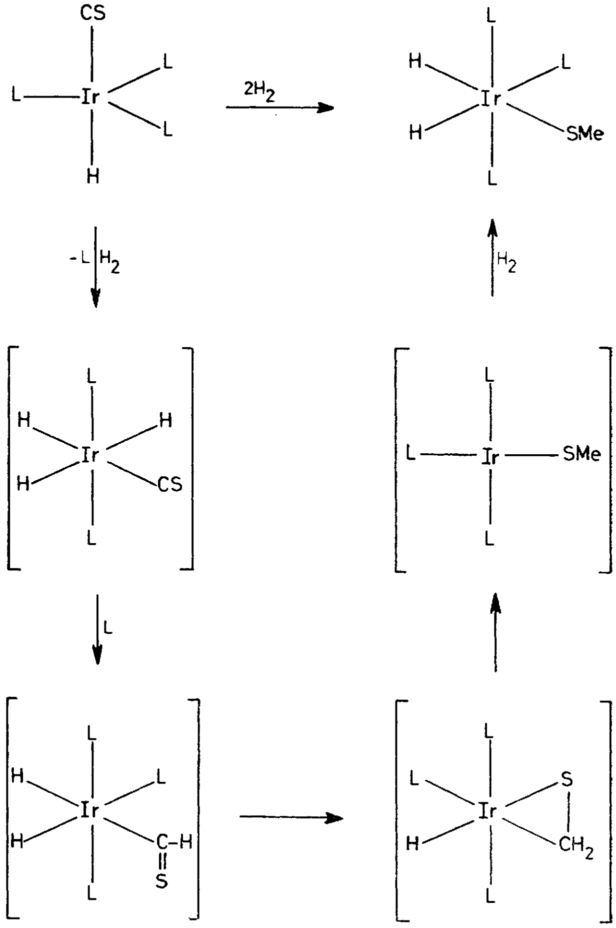
Summary $[IrH(CS)(PPh_3)_3]$ reacts with 2 equiv. of H_2 to give $[IrH_2(SMe)(PPh_3)_3]$, and further reaction with HCl releases MeSH and forms $[IrH_2Cl(PPh_3)_3]$; a thioformyl complex is a likely intermediate in this process and a stable example of such a compound is $[Ir(CHS)Cl_2(CO)(PPh_3)_2]$ from $[IrCl_2(CS)(CO)(PPh_3)_2]^+$ and $NaBH_4$.



SCHEME. L = PPh_3, bracketted compounds not isolated.

THE reduction of carbon monoxide by hydrogen to methanol or hydrocarbons is an important reaction which is catalysed heterogeneously by transition metal catalysts. Several transition metal cluster complexes function as homogeneous catalysts for this same process[1] and mononuclear carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl)zirconium promote stoicheiometric reduction of CO to methanol by H_2.[2] The intermediates involved in these processes remain ill defined but formyl complexes[3] are attractive possibilities for the first step. For the sulphur analogue of carbon monoxide, CS, any intermediates in the reduction process are likely to be more easily isolated and indeed the thioformyl ligand from hydride migration on to CS has already been characterised.[4] In seeking other compounds which might provide further examples of hydride migration to CS we endeavoured to prepare $[IrH_3(CS)(PPh_3)_2]$ by oxidative addition of H_2 to the known compound $[IrH(CS)(PPh_3)_3]$.[5] {H_2 and $[IrH(CO)(PPh_3)_3]$ are in equilibrium with $[IrH_3(CO)(PPh_3)_2]$ and PPh_3}.[6]

Surprisingly, we have identified the yellow crystalline product of hydrogen addition to $[IrH(CS)(PPh_3)_3]$ not as the expected $[IrH_3(CS)(PPh_3)_2]$ but instead as the compound $[IrH_2(SMe)(PPh_3)_3]$. The ^1H n.m.r. spectrum ($CDCl_3$) indicates *cis* hydride ligands and a meridional arrangement of phosphine ligands; the S*Me* resonance occurs at τ 8·64. Reaction with HCl liberates methanethiol and gives $[IrH_2Cl(PPh_3)_3]$.[7] One way in which the formation of the methanethiolato-compound can be explained is by successive hydride transfers to the thiocarbonyl ligand yielding first a thioformyl complex, then a thioformaldehyde complex, and finally a methanethiolato-complex (see Scheme). Under the reaction conditions {benzene as solvent, 20 °C, H_2 at 2 atm, 6 h for complete reaction of 500 mg of $[\mathrm{IrH(CS)(PPh_3)_3}]$} we have not been able to isolate any of the postulated intermediates, suggesting that the hydride transfers are fairly rapid. However, that a thioformyl complex of iridium(III) is a reasonable intermediate is shown by independent synthesis of a stable example. Formyl complexes of iron, chromium, and tungsten result from direct reaction of trialkoxyborohydrides with metal carbonyls[3] and to test a similar approach for thioformyl synthesis we chose the iridium(III) thiocarbonyl cation, $[\mathrm{IrCl_2(CS)(CO)(PPh_3)_2}]^+$ (ref. 8) which has ν_{CS} at the high value of 1409 cm^{-1} and which should therefore be very susceptible to nucleophilic attack at the thiocarbonyl ligand. The cation was produced from $[\mathrm{IrCl}(\eta^2\text{-}\mathrm{CS_2Me})(\mathrm{CO})(\mathrm{PPh_3})_2]^+$ (ref. 9) as the tri-iodide salt by the reaction sequence (1).

$$\begin{array}{l} [\mathrm{IrCl}(\eta^2\text{-}\mathrm{CS_2Me})(\mathrm{CO})(\mathrm{PPh_3})_2]^+ \xrightarrow{\mathrm{Cl}^-} \\ \qquad\qquad [\mathrm{IrCl_2}(\eta^1\text{-}\mathrm{CS_2Me})(\mathrm{CO})(\mathrm{PPh_3})_2] \\ \qquad\qquad\qquad\qquad \downarrow 2\mathrm{I_2} \\ \qquad\qquad [\mathrm{IrCl_2(CS)(CO)(PPh_3)_2}]\mathrm{I_3} \qquad\qquad (1) \end{array}$$

Reaction of the cation with sodium borohydride produced $[\mathrm{Ir(CHS)Cl_2(CO)(PPh_3)_2}]$ as pink crystals, ν_{CO} 2060 cm^{-1}, ^{1}H n.m.r. ($\mathrm{CDCl_3}$) τ $-5{\cdot}06$ [t, ^3J(P–H) 3·3 Hz, C*H*S]. Stable examples of the other postulated intermediates are being sought.

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