Reinvestigation of the Reactions of Carbonylhydridotris(phosphine) Complexes of Rhodium and Iridium with Sulphur Dioxide

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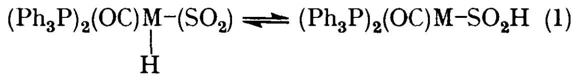
The reactions of SO_2 with $[RhH(CO)(PPh_3)_3]$ and $[IrH(CO)(PPh_3)_3]$ have been reinvestigated and the products have been shown to be the hydrido(sulphur dioxide) complexes $[MH(CO)(SO_2)(PPh_3)_2]$, where M = Rh or Ir, on the basis of ^1H and ^{31}P-$\{^1H\}$ n.m.r. studies. In the case of the iridium complex, n.m.r. studies at low-temperatures have indicated the intermediate formation of the six-co-ordinate hydrido(sulphur dioxide) complex, $[IrH(CO)(SO_2)(PPh_3)_3]$.

In 1972 Levison and Robinson[1] established that SO_2 reacts with the hydridocarbonyl complexes $[MH(CO)(PPh_3)_3]$ (M = Rh or Ir), to give complexes which analysed correctly as $[MH(CO)(SO_2)(PPh_3)_2]$. However, some anomalous spectroscopic features of these complexes and in particular the inability to detect high-field resonances in the ^1H n.m.r. spectra characteristic of the hydrido-ligand led these authors to propose the tautomeric equilibrium (1) involving a rapid hydride migration



$$(Ph_3P)_2(OC)\underset{\displaystyle H}{\underset{|}{M}}\text{-}(SO_2) \rightleftharpoons (Ph_3P)_2(OC)M\text{-}SO_2H \quad (1)$$

between the central metal atom and the co-ordinated sulphur dioxide ligand. A similar insertion reaction has been proposed by Komiya and Yamamoto[2] to account for the reaction products resulting from the addition of SO_2 to the hydridoruthenium complexes $[RuH_2(PR_3)_4]$ ($PR_3 = PPh_2H$ or PPh_2Me). The current resurgence of interest in the co-ordination chemistry of SO_2,[3,4] and a desire to define more precisely the tautomeric equilibrium proposed by Levison and Robinson, prompted us to reinvestigate the reactions of SO_2 with rhodium and iridium hydridocarbonyl complexes.

EXPERIMENTAL AND RESULTS

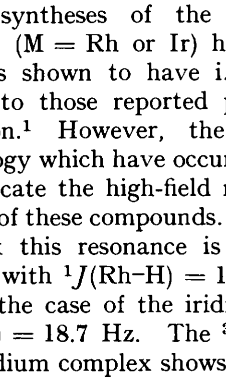
Proton n.m.r. spectra were recorded on a Bruker WH300 spectrometer, and ^{31}P-$\{^1H\}$ n.m.r. spectra on a Bruker WH90 spectrometer operating at 36.430 MHz. The ^{31}P chemical shifts are reported with respect to $PO(OMe)_3$ (external) and are taken as positive to low field (high frequency). Infrared spectra were recorded on a Pye-Unicam SP2000 spectrophotometer. The complexes $[RhH(CO)(PPh_3)_3]$ and $[IrH(CO)(PPh_3)_3]$ were prepared by standard literature methods.[5,6]

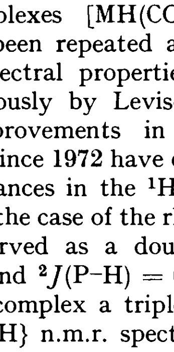
Carbonylhydrido(sulphur dioxide)bis(triphenylphosphine)-rhodium(I).—The complex was prepared following the method reported by Levison and Robinson,[1] and shown to have physical and i.r. characteristics very similar to those reported; $\nu_{max.}$ (CO) (Nujol) at 2 050 cm^{-1}, $\nu_{max.}$ (SO_2) at 1 184 and 1 037 cm^{-1}. N.m.r.: ^1H ([$^2H_2$]methylene chloride), δ -4.89 [d of t, 1 H, H–Rh, ^2J(P–H) 6.6, ^1J(Rh–H) 10.7 Hz], 7.30 p.p.m. (m, 30 H, C_6H_5); ^{31}P-$\{^1H\}$ (methylene chloride, external D_2O lock), δ 35.5 p.p.m. [d, PRh, ^1J(Rh–P) 145 Hz].

Carbonylhydrido(sulphur dioxide)bis(triphenylphosphine)-iridium(I).—The complex was prepared by the method reported by Levison and Robinson and shown to have similar physical and i.r. characteristics; $\nu_{max.}$ (CO) at 2 063 cm^{-1}, $\nu_{max.}$ (Ir–H) at 1 966 cm^{-1}, $\nu_{max.}$ (SO_2) at 1 174 and 1 033 cm^{-1}. N.m.r.: ^1H ([$^2H_2$]methylene chloride), δ -2.8 [t, 1 H, H–Ir, ^2J(P–H) 18.7 Hz], 7.30 p.p.m. (m, 30 H, C_6H_5); ^{31}P-$\{^1H\}$ (methylene chloride, external D_2O lock) δ 15.8 (s) p.p.m.

DISCUSSION

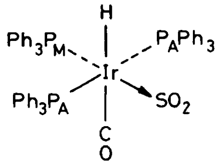
The syntheses of the complexes $[MH(CO)(SO_2)(PPh_3)_2]$ (M = Rh or Ir) have been repeated and the products shown to have i.r. spectral properties very similar to those reported previously by Levison and Robinson.[1] However, the improvements in n.m.r. technology which have occurred since 1972 have enabled us to locate the high-field resonances in the ^1H n.m.r. spectra of these compounds. In the case of the rhodium complex this resonance is observed as a doublet of triplets with ^1J(Rh–H) = 10.7 and ^2J(P–H) = 6.6 Hz, and in the case of the iridium complex a triplet with ^2J(P–H) = 18.7 Hz. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the rhodium complex shows a doublet [^1J(Rh–P) = 145 Hz] and the iridium complex shows a singlet. The ^{31}P-$\{^1H\}$ spectra were recorded in the temperature range 35 to −70 °C and showed only small changes which were attributed to the temperature dependence of the chemical shifts. Although the spectroscopic evidence is consistent with either of the five-co-ordinate hydrido(sulphur dioxide) structures shown below, the former is preferred in view of the structures of the starting complexes. No evidence was obtained from the n.m.r. studies either for the tautomeric process involving the hydrido- and





sulphur dioxide ligands or for any fluxional process involving the co-ordination sphere of these five-co-ordinate d^8 complexes.

When SO_2 is introduced into a solution of $[IrH(CO)(PPh_3)_3]$ in methylene chloride at −70 °C and the n.m.r. spectrum recorded, only the resonance characteristic of the starting material was observed. However, when the solution was allowed to warm to −50 °C the intensity of the resonance due to the starting material descreased and lines characteristic of an A_2M spin system [δ_A 4.0, δ_M −2.0 p.p.m., $^2J(P_A{-}P_M) = 13.2$ Hz] were observed. This suggested that the SO_2 is reacting with $[IrH(CO)(PPh_3)_3]$ to give the six-co-ordinate intermediate shown above. When the solution was allowed to warm to room temperature the resonances attributable to this six-co-ordinate intermediate disappeared and were replaced by those of the final product, $[IrH(CO)(SO_2)(PPh_3)_2]$, and free triphenylphosphine. When the reaction of SO_2 with $[RhH(CO)(PPh_3)_3]$ was investigated under similar conditions to those described above a similar intermediate could not be detected and even at −70 °C only those resonances characteristic of the starting material and final product could be observed.



If SO_2 is viewed as a two-electron ligand the proposed six-co-ordinate intermediate in the case of the iridium complex represents a 20-electron complex, however it seems to be more reasonable to formulate it with a dative bond from the metal to the SO_2 ligand,[1] in which case it is most likely that the SO_2 ligand is bonded in a pyramidal mode in this intermediate.

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