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Preliminary communication

Synthesis and reactivity of $Ir_2(CO)_6(PPh_3)_2$ and $HIr(CO)_3PPh_3$

L. MALATESTA, M. ANGOLETTA and F. CONTI
Istituto di Chimica Generale ed Inorganica, C.N.R. Center, Milano (Italy)

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The recent communication on the synthesis under high CO and H_2 pressure of $Ir(CO)_6L_2$[1] (I) and $HIr(CO)_3L$[2] (II), where $L = PPh_3$, prompt us to draw attention to the previously announced synthesis of similar complexes under mild conditions[3] and to comment on their reactivity and characterization.

Compound (I) together with an equimolecular quantity of $HIr(CO)L_3$ can be more conveniently obtained by refluxing $Ir(CO)L_2I$ in benzene suspension with sodium ethoxide. A benzene suspension of (I) reacts with hydrogen under ambient conditions to give a yellow solution containing the monohydride (II). This is a very unstable compound, which cannot be isolated; on applying a vacuum to the yellow solution, or on sweeping hydrogen away with nitrogen or carbon monoxide, the starting material (I) is quantitatively recovered.

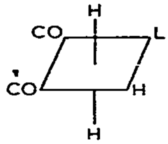
The IR spectrum of (II) shows bands at 1980 cm^{-1} (broad) and 2045 cm^{-1} (sharp), both to be considered as CO stretching. The saturated solution of compound (I) in the same solvent shows a very weak band at 1960 cm^{-1}. We believe that the IrH stretching band, expected at about 2000 cm^{-1}, is obscured by the broad CO band. Two other weak bands at 2110 and 2043 cm^{-1} do not belong to the monohydride (II), since they increase if the bubbling of hydrogen is continued after a clear solution is obtained. In this case the broad band at 1980 cm^{-1} changes into a sharp one at 1994 cm^{-1} and ultimately an IR spectrum with three bands at 2108 (2210 (sh)), 2043 (2055 (sh)) and 1994 cm^{-1} is obtained. We suggest that this spectrum is due to the presence of a new hydride, namely $H_3Ir(CO)_2L$ (III), which is formed by the reactions:

$$Ir_2(CO)_6L_2 \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} 2\ HIr(CO)_3L \underset{-H_2+CO}{\overset{+H_2-CO}{\rightleftharpoons}} H_3Ir(CO)_2L$$

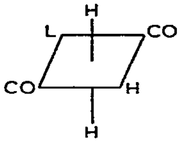
The trihydride (III) can be slowly transformed into (I) by bubbling carbon monoxide through its solution.

By evaporating the solvent in vacuo, the trihydride (III) can be obtained as a solid residue, the analysis of which agrees fairly well with formula (III). However, the infrared spectrum of the solid shows that extensive isomeration and/or decomposition has taken place. When we carried out the reaction on (I) with deuterium, we did not observe any significant change in the spectrum of (II), except for a new band at 1430 cm^{-1} which we consider to be the Ir–D stretching band corresponding to the obscured IrH band. In the spectrum of (III), obtained by deuteration of (I), the band at 2110 cm^{-1} is no longer present, while the bands at 2043 and 1994 are shifted to 2073 and 2025 cm^{-1} respectively.

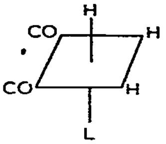
There are three possible structures of (III):



(a)



(b)



(c)

of these, (a) and (b), with *mer*-hydrogen atoms, can be excluded, because they should give rise to two IrH bands, one of which would be at about 1750 cm^{-1} as expected for two hydrogen atoms in *trans* position. Structure (c), with *fac*-hydrogen atoms, should have three IrH stretching bands, at about 2000 cm^{-1}, instead of the one observed, but *mer*-H_3IrL_3 also shows only a single band. We favour structure (c), which is consistent with the observed shift of the carbonyl bands of the deuteride with respect to those of the hydride. Such a shift is generally observed when the carbonyl groups are *trans* to deuterium[4].

The NMR spectrum (Varian 100 mc) was recorded of a THF solution freshly prepared from compound I and gaseous hydrogen. However, in order to obtain a sufficiently concentrated solution, the reaction with hydrogen required almost one hour, so that the solution contained a mixture of the monohydride (II) and the trihydride (III), as expected. The spectrum, under these conditions, shows three doublets centred at 20.6 (J 17 cps), at 21.5 (J 120 cps) and at 21.8 (J 75 cps). Since the solution on further reaction with gaseous hydrogen for about another hour, gives a spectrum with only the two doublets at 20.6 and 21.5, we consider that the doublet at 21.8, which disappears with time, belongs to the monohydride $HIr(CO)_3L$. The doublets at 20.6 and 21.5 must belong to the trihydride, their intensity being in a 2/1 ratio between −50° and +50°C. This spectrum is in agreement with structure (c) having *fac*-hydrogen atoms, two of which are equivalent and in a *cis* position with respect to phosphorus and thus have a low coupling constant, while the third, which is in *trans* to phosphorus, has a high coupling constant[5]. The formation of a trihydride from compound (I) is of interest in connection with speculation about the mechanism of hydrogenation catalysed by $HRh(CO)_2L_2$[6]. Moreover, $Ir_2(CO)_6L_2$ has been shown to be a stoichiometric hydroformylation catalyst under mild conditions[7].

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