# Hydrido–Deuterio-complexes of Iridium

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ALTHOUGH a considerable number and types of *poly*hydrido-complexes of transition metals are known[1] and some of these have also been prepared as their deuterio-analogues, there appears to be no previous report of distinct hydrido–deuterio-complexes, *i.e.*, compounds in which the two hydrogen isotopes are simultaneously bonded to the same metal atom and occupy specific stereochemical positions. Apart from an inherent interest, such compounds have become important as likely intermediates in homogeneous $H_2$–$D_2$ exchange reactions catalyzed by transition-metal complexes in solution.[2,3]

We have investigated two synthetic routes to HD complexes, and have examined the structures of the resulting products by infrared spectroscopy. In the first approach we utilized the known reaction of $[IrCl(CO)(Ph_3P)_2]$ with hydrogen[4,5] by using hydrogen deuteride as addendum (eq. 1). The product, however, was found to contain, in addition to two isomers of the HD complex, an equimolar mixture of $[H_2IrCl(CO)(Ph_3P)_2]$ and

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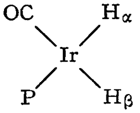
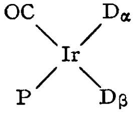
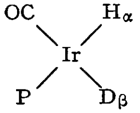
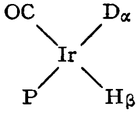
TABLE. *Structures and infrared spectral data* (*cm.*$^{-1}$)[a] *of* $[Ir(H_2,D_2,HD)(CO)(Ph_3P)_3]^+$

| No. | Structure[b] | $\nu_{Ir-H,D}$ | $\nu_{CO}$ |
|---|---|---|---|
| (I) |  | 2160 m<br>2107 s | 2005s |
| (II) |  | 1620 w (?)<br>1548 w (?) | 2040 s |
| (IIIa) |  | 2160 s<br>1548 w (?) | 2040 s |
| (IIIb) |  | 1620 w (?)<br>2107 s | 2005 s |

[a] Measured as Nujol or halocarbon mulls. [b] P = $Ph_3P$; the two *trans*-$Ph_3P$ (not shown in the diagram) are normal to the plane of the paper. α and *β* refer to the two different hydrogens (deuteriums).

$[D_2IrCl(CO)(Ph_3P)_2]$. A subsequent inquiry showed that this result was a consequence of $H_2$–HD–$D_2$ exchange reactions,[3] and the reversibility of reaction (1).

$$(1)\ [IrCl(CO)(Ph_3P)_2] + HD \rightleftharpoons [(HD)IrCl(CO)(Ph_3P)_2]$$

In another approach, the following reactions have been carried out:

$$(2)\ [IrH(CO)(Ph_3P)_3] + HX \rightarrow [IrH_2(CO)(Ph_3P)_3]X \quad (I)$$

$$(3)\ [IrD(CO)(Ph_3P)_3] + DCl \rightarrow [IrD_2(CO)(Ph_3P)_3]Cl \quad (II)$$

$$(4)\ [IrH(CO)(Ph_3P)_3] + DCl \rightarrow [Ir(HD)(CO)(Ph_3P)_3]Cl \quad (IIIa)$$

$$(5)\ [IrD(CO)(Ph_3P)_3] + HX \rightarrow [Ir(HD)(CO)(Ph_3P)_3]X \quad (IIIb)$$

$$X = F, Cl, Br, I.$$

The *crystals* of the five-co-ordinated hydride complex[6] (and its deuteride[7]) react almost instantly with gaseous hydrogen halides to give white or pale yellow ionic adducts (I—III) which, with excess of HX, incorporate another molecule of the acid, *e.g.*, $[IrH_2(CO)(Ph_3P)_3]$ $[HCl_2]$.[8,9] That the second HX molecule is associated with the anion as shown, has been verified by replacing the hydrogen dihalide with $Ph_4B^-$; the resulting complex contains no halogen. Several derivatives of (I) have been characterized by elemental analysis. The compounds are diamagnetic and behave as uni-univalent electrolytes in acetone and methanol. The crystalline complexes are stable in air, but can be re-converted into $[IrH(CO)(Ph_3P)_3]$ by treatment with KOH in ethanol, heating in solution (benzene, ethanol), or pumping on the solid in the presence of a base.

The structure and the infrared data of the cation, $[IrH_2(CO)(Ph_3P)_3]^+$, and its isotopic analogues are given in Table 1. The pertinent stretching frequencies ($\nu_{Ir-H,D}$, $\nu_{CO}$) for the various derivatives with different anions lie within a few wavenumbers (average values are given in the Table) which shows that the configuration of the cation is the same in all these complexes.[10] This configuration has been determined from an analysis of the vibrational spectra of the dihydride and the dideuteride (Table) and the observed resonance interaction between $\nu_{Ir-H(\beta)}$ and $\nu_{CO}$ in (I).[11] There are three possible geometrical isomers of $[IrH_2(CO)(Ph_3P)_3]^+$, but only (I) is expected to exhibit the vibrational interaction [in the remaining two, (i) the two H's are *trans* to one another, and (ii) both H's are *trans* to P's].

The infrared spectra of the products of reactions (4) and (5) show that each consists of a mixture of the two isomers of $[Ir(HD)(CO)(Ph_3P)_3]X$ (IIIa and IIIb). This result could be a reflection of either the mechanism of protonation of the crystalline five-co-ordinated deuteride (hydride), or a secondary isomerization of the hydrido-deuterio-complex in the solid state (or both). Preliminary and unconfirmed data indicate that the isomeric composition of the products of reaction (5) varies with the halogen acid used, from *ca.* 40% of (IIIa) for X = F to *ca.* 60% of (IIIb) for X = I.

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[1] For recent comprehensive Reviews, see (a) A. P. Ginsberg in "Transition Metal Chemistry," Vol. 1, R. L. Carlin, ed., Marcel Dekker, Inc., New York, 1965, ch. 3; (b) M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, 7, 115.

[2] L. Vaska, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 89, and references quoted therein.

[3] G. G. Eberhardt and L. Vaska, submitted for publication.

[4] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[5] L. Vaska and R. E. Rhodes, *J. Amer. Chem. Soc.*, 1965, **87**, 4970.

[6] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

[7] L. Vaska, "Proc. 8. I.C.C.C.," V. Gutmann, ed., Springer-Verlag, Wien/New York, 1964, p. 99.

[8] For related rhenium complexes, see M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1958, 3916.

[9] In the presence of oxygenated solvents ($H_2O$, alcohols, ethers), or, when the reactions are carried out in solution, the complexes crystallize also with one solvent molecule.

[10] *X*-Ray-diffraction patterns of the different derivatives supply some support for this conclusion. Most of the patterns show only broad lines, however.

[11] L. Vaska, *J. Amer. Chem. Soc.*, in the press.