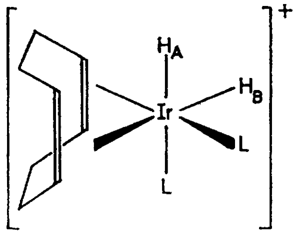
Activation of Molecular Hydrogen by Cationic Iridium Diene Complexes

By ROBERT H. CRABTREE,* HUGH FELKIN, and GEORGE E. MORRIS
(*Institut de Chimie des Substances Naturelles, C.N.R.S.,* 91190 *Gif-sur-Yvette, France*)

Summary The cationic complexes $[Ir(cod)L_2]PF_6$ (**1**; L = tertiary phosphine; cod = cyclo-octadiene) react with dihydrogen at −80 °C in CD_2Cl_2 to give *cis*-$[IrH_2(cod)L_2]PF_6$ complexes which revert to (**1**) on warming; at 0 °C in CH_2Cl_2 complex (**1**; L = $PMePh_2$) is a highly active hydrogenation catalyst.

ALTHOUGH addition of dihydrogen to metal–olefin complexes has been invoked in some olefin hydrogenation catalyst systems,[1] such a process has never been directly observed, and indeed only one example of a metal–olefin dihydro-complex has been reported.[2] We now report the direct observation of a *cis* addition of dihydrogen to the red cationic complexes[3] $[Ir(cod)L_2]PF_6$ (**1**; L = $PMePh_2$, PBu^n_3, or PPh_3; L_2 = dpe†) in CD_2Cl_2 at −80 °C. The ^1H n.m.r. spectra at −80 °C unambiguously characterise the colourless products as *cis*-$[IrH_2(cod)L_2]PF_6$ (**2**). The high-field regions of the ^1H n.m.r. spectra of all the dihydrido-cations are similar, consisting of a doublet of doublets for H_A due to coupling with one *cis*- and one *trans*-phosphorus nucleus [typically, for (**2**; L = $PMePh_2$) τ 19·8; ^2J(P–H, *trans*) 90, ^2J(P′–H, *cis*) 20 Hz] and a doublet of doublets, generally overlapping to give an apparent triplet, for H_B due to coupling with two inequivalent *cis*-phosphorus nuclei [typically, for (**2**; L = $PMePh_2$) τ 23·7; ^2J(P–H)) = *ca.* ^2J(P′–H) = *ca.* 16 Hz]. In addition four broad resonances at τ 5·0—6·5 arise from the four inequivalent (cod) vinyl protons.



(2)

---

† cod = cyclo-octa-1,5-diene; dpe = 1,2-bisdiphenylphosphinoethane.

On warming the solutions in the absence of excess of dihydrogen, dihydrogen is lost and the red parent complexes are recovered. In contrast, if dihydrogen is bubbled through the solutions while they are being warmed to room temperature the (cod) ligand is rapidly hydrogenated to give cyclo-octane. The dihydride (**2**) is probably an intermediate in the hydrogenation of the co-ordinated diolefin. We have not been able to observe any intermediates in this hydride transfer to the (cod) ligand.

The cationic complexes (**1**) are catalyst precursors for the homogeneous hydrogenation of olefins in CH_2Cl_2 at 0 °C and atmospheric pressure. The complex (**1**; L = $PMePh_2$) is particularly active‡ and at 0·5 mM concentration catalyses the hydrogenation of 1-methylcyclohexene (0·5 M) to methylcyclohexane in 50 min with a maximum turnover of 2200 mol of H_2 per mol of catalyst per hour.§

We thank the Compagnie des Métaux Précieux (Ivry) for a generous loan of iridium and Mr. B. Septe for assistance in obtaining the ^1H n.m.r. spectra.

(*Received*, 22*nd June* 1976; *Com.* 702.)

---

‡ The olefin must be added before the dihydrogen is introduced otherwise formation of the catalytically inactive yellow $[Ir_2(\mu\text{-}H)_3\text{-}H_2(PMePh_2)_4]PF_6$ occurs (*cf.* R. H. Crabtree, H. Felkin, G. E. Morris, T. J. King, and J. A. Richards, *J. Organometallic Chem.*, 1976, **113**, C7).

§ This is *ca.* 75 times faster than found for the reduction of 1-methylcyclohexene (0·95 M) with $[RhCl(PPh_3)_3]$ (2·4 mM) in benzene–ethanol (1:3, v/v) at 25 °C; in CH_2Cl_2; this hydrogenation is about 6 times slower (A. S. Hussey and Y. Takeushi, *J. Org. Chem.*, 1970, **35**, 643).

[1] C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 2762; R. R. Schrock and J. A. Osborn, *ibid.*, 1976, **98**, 2134.

[2] The only other metal–olefin–dihydrido-complex known has recently been characterised by F. Pennella (*Co-ordination Chem. Rev.*, 1975, **16**, 51), who obtained $[RuH_2(\text{pent-2-ene})(PPh_3)_3]$ from $[RuH_2(N_2)(PPh_3)_3]$ by addition of olefin. We thank a referee for drawing our attention to this work.

[3] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 3089; L. M. Haines and E. Singleton, *J.C.S. Dalton*, 1972, 1891.