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Preliminary communication

DIHYDRIDO-DIOLEFIN COMPLEXES AS INTERMEDIATES IN THE CATALYTIC HYDROGENATION OF CYCLOOCTA-1,5-DIENE BY THE COMPLEXES $[Ir(cod)L_2]PF_6$

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

Novel dihydrido-diolefin complexes have been isolated during the hydrogenation of (cod) by $[Ir(cod)L_2]PF_6$ (cod = cycloocta-1,5-diene; L = tertiary phosphine) and related complexes; a coplanar M(C=C)H system seems to be required for the insertion of the coordinated olefin into the M—H bond, since *cis*-$[IrH_2(cod)L_2]PF_6$, which possess this system, hydrogenate coordinated (cod) at least 40 times faster than *cis,trans*-$[IrH_2(cod)L_2]PF_6$, which do not possess it.

Dihydrido-olefin complexes, believed to be intermediates [1] in the homogeneous hydrogenation of olefins, were never directly observed until our own report [2a] ** that the red hydrogenation catalysts $[Ir(cod)L_2]PF_6$ [3] (Ia: L = $PMePh_2$; Ib: L = PPh_3; Ic: L = diphenylphosphino-1,2-ethane (dpe)) in CD_2Cl_2 at —80°C react with H_2 to give the colourless, air-stable complexes *cis*-$[IrH_2(cod)L_2]PF_6$ (II). We wondered whether these complexes might be intermediates in the hydrogenation of (cod) by I.

We now find that the hydrogenation of (cod) (1 *M*) by Ia or Ib (0.15 *M*) in CH_2Cl_2 at 0°C proceeds in two stages. In the first, two mol*** of H_2 per mol of iridium are absorbed by the solution over 8 min, during which time 1 mol of cyclooctene (coe) is formed. In the second stage (coe) is formed much more slowly. ^1H NMR measurements at —80°C on samples of these colourless solutions show that the complexes II are only present in the first stage of the reaction and that during this time they are smoothly replaced by the new isomer

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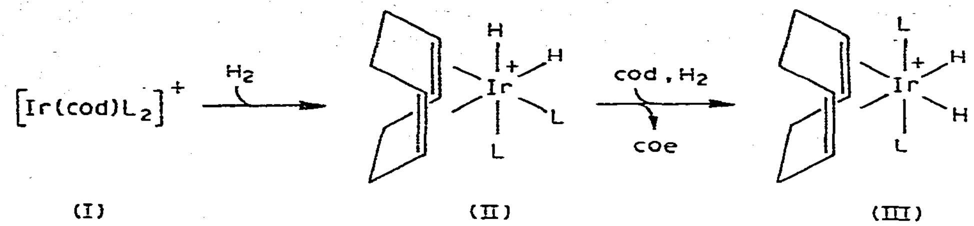
* Address correspondence to this author at: Sterling Chemistry Laboratory, Yale University, 225 Prospect St., New Haven, Ct., 06520 (U.S.A).

** A complex Pennella suggested was $[RuH_2(C_5H_{10})(PPh_3)_3]$ has now been shown to be $[RuH_4(PPh_3)_3]$ [2b].

*** The relatively high vapour pressure of CH_2Cl_2 interfered with the manometric measurements. Chlorobenzene, a much more satisfactory solvent, gave an H_2 uptake value, for Ia → IIIa, of 1.95 ± 0.1 mol (mol Ir)$^{-1}$ h^{-1}.



(1)

(a: L = $PMePh_2$; b: L = PPh_3)

cis,trans-$[IrH_2(cod)L_2]PF_6$ (III, see eq.1). These new complexes can be isolated from the reaction mixture by the addition of Et_2O at −30° C. The resulting white, microcrystalline solids are thermally stable at room temperature and even survive brief heating to 80° C in air. In contrast, the *cis*-isomers II slowly decompose at 0° C. The identity of the new complexes III follow from their ^1H NMR spectra in CD_2Cl_2 at 0° C. A triplet at high field is assigned to the hydrido ligands, each coupled to two equivalent *cis*-phosphorus nuclei (typically, for IIIa: δ −13.6 ppm; ^2J(P—H, *cis*) 20 Hz). Only one broad resonance (for IIIa: δ 4.1 ppm) can be assigned to the equivalent (cod) vinyl protons, in contrast with the spectra of the complexes II where four such resonances are found [2]. In the case of IIIa, the virtually coupled $PMePh_2$ protons resonate as a triplet [δ 2.5 ppm; $^2J(P—H) + {}^4J(P'—H)$ 7 Hz] implying [4] a *trans* arrangement of these ligands. Resonances due to the aromatic groups (δ 7.3—7.8 ppm) and the (cod)CH_2 protons (δ 1.8—2.6 ppm) are also found.

$[IrH_2(Me_2CO)_2L_2]PF_6$ [3] (IVa: L = $PMePh_2$; IVb: L = PPh_3), obtained by hydrogenation of complexes I in acetone, also gave III by treatment with (cod) in acetone or dichloromethane. We have therefore obtained the dihydrido-diolefin complexes III both by H_2 addition to an olefin complex I, the "unsaturated" route, and by olefin addition to a hydrido complex IV, the "hydride" route. Both these pathways have been considered [1,5] for the formation of these complexes in homogeneous hydrogenation. We have now observed each directly for the first time.

Manometric and GLC measurements on the hydrogenation solutions derived from the catalysts Ia and Ib, show that the fastest rates of (coe) formation occur during the first minute of the reaction, when, from the ^1H NMR spectra of the solutions at −80° C, essentially only the *cis*-dihydrido-diolefin complex II is present; for IIa, the hydrogenation rate at that time is 35 mol of H_2 per mol of catalyst per hour*. After 8 min, when essentially the only complexes present are the *cis,trans*-isomers III, the hydrogenation is much slower (for IIIa, 0.9 mol (mol Ir)$^{-1}$ h^{-1}). It appears that the rate-limiting step in the hydrogenation of (cod) may be the insertion of the coordinated olefin into the M—H bond, since only dihydrido-diolefin complexes were ever observed in these solutions. We

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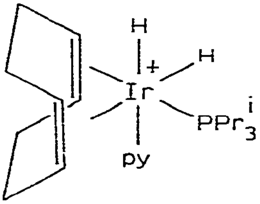
* In a constant-volume apparatus [$p(H_2)$(initial) = 55 cmHg] measured by GLC and manometry. The slow rate of hydrogenation during the second stage of the reduction may be due to IIIa itself or to a small equilibrium concentration of IIa although the latter was never directly observed at this stage.

propose that this insertion process requires a coplanar M(C=C)H system, since the complexes II, which possess such a system, appear to undergo the insertion reaction at least 40 times faster than the complexes III, where the M—H bonds are perpendicular to the M(C=C) planes. This proposal parallels that of Whitesides [6] that the β-elimenation reaction, the inverse of olefin insertion, also requires a coplanar M—C—C—H system.

$[\mathrm{Ir(cod)_2}]\mathrm{ClO_4}$ in acetone has been shown [7] to be an excellent catalyst for the selective reduction of (cod) to (coe). The same is true for the hexafluorophosphate salt Id under our conditions (rate: 60 mol (mol Ir)$^{-1}$ h^{-1}). We find that at 0°C the dark red hydrogenation solution contains largely the precursor Id itself, but on cooling to —80°C under H_2, the solution decolourises to give the new complex *cis*-$[\mathrm{IrH_2(cod)_2}]\mathrm{PF_6}$ (IId: L_2 = cod), which was never crystallised. The ^{1}H NMR spectrum of the solution at —80°C consists of a singlet resonance (δ —14.8 ppm) for the hydrides and four resonances (δ 3.3—5.1 ppm) for the four pairs of inequivalent (cod)vinyl protons; a complex resonance (δ 1.8—2.6 ppm) due to the (cod)CH_2 protons is also found. The complex IId, which possesses a coplanar M(C=C)H system, is probably an intermediate in the catalytic process.

Unexpectedly, $[\mathrm{Ir(cod)(P\text{-}i\text{-}Pr_3)py}]\mathrm{PF_6}$ (V; py = C_5H_5N) was also an excellent selective catalyst (rate 25 mol (mol Ir)$^{-1}$ h^{-1}) for the same reduction. The yellow catalyst solution decolourised on cooling to —80°C and ^{1}H NMR spectroscopy of this solution revealed that only the new complex VI (see Fig. 1) was present at that temperature. The hydride ligands each resonate as doublets and each is coupled to a *cis*-phosphorus nucleus (δ —18.0 ppm; ^2J(P—H, *cis*) 19 Hz and δ —12.7 ppm; ^2J(P—H, *cis*) 20 Hz]. Only two (cod)vinyl resonances are found (δ 4.5 and 4.9 ppm). This complex, which possesses a coplanar M(C=C)H system, is probably also a catalytic intermediate.



(VI)

Fig. 1.

References

1 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J.Chem.Soc. (A), (1966) 1711; C.A. Tolman, P. Meakin, D.L. Lindner and J.P. Jesson, J. Amer. Chem. Soc.,96 (1974) 2762.
2a R.H. Crabtree, H. Felkin and G.E. Morris, J. Chem. Soc. Chem. Commun., (1976) 716.
2b D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc. Chem. Commun., (1977) 59.
3 J.R. Shapley, R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc.,91 (1969) 2816.
4 P.G. Douglas and B.L. Shaw, J. Chem. Soc. A, (1969) 1491.
5 G. Dolcetti and N.W. Hoffman, Inorg. Chim. Acta ,9 (1974) 269.
6 J.X. McDermott, J.F. White and G.M. Whitesides, J. Amer. Chem. Soc.,98 (1976) 6521.
7 R.R. Schrock and J.A. Osborn, J.Amer. Chem. Soc.,93 (1971) 3089.