μ-Chloro-μ-hydrido-dichlorobis(pentamethylcyclopentadienyl)di-rhodium and -iridium as Homogenous Hydrogenation Catalysts†

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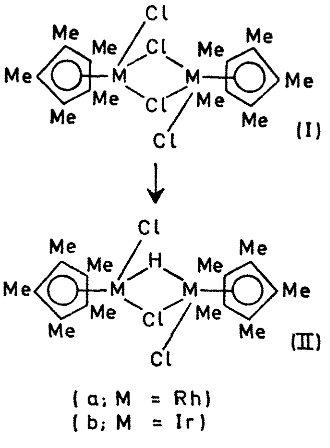
Summary The hydrido-complexes $[\{M(C_5Me_5)\}_2HCl_3]$ (M = Rh, Ir) react readily with 1,3-dienes to give enyl complexes and are also good catalysts for the homogeneous hydrogenation of olefins.

WE have previously reported on the pentamethylcyclopentadienyl-rhodium and -iridium chlorides,[1] $[M(C_5Me_5)Cl_2]_2$, (I), and related complexes.[2] The former underwent stoicheiometric reactions with mono-, di-, and tri-olefins and we suggested that hydrido-complexes were intermediates here.[3] We have now isolated and characterised the hydrido-chlorides which turn out to have totally unexpected structures.

In addition to their stoicheiometric reactions, the chlorides (I), as well as the acetates and a rhodium hydroxo-complex, act as very effective homogeneous hydrogenation catalysts for olefins.[4] They are not reduced to metal under normal conditions and have the advantages of good solubility in a variety of solvents and of *not* requiring the presence of triphenylphosphine or similar ligands which, in fact, cause deactivation. The rates of hydrogenation using the halides are markedly increased on addition of base and a colour change, usually a deepening to red or purple, is observed at the beginning of the reaction. These observations suggest that the true catalysts are hydrido-complexes formed by heterolytic activation of hydrogen accompanied by removal of an anionic ligand,



(I)

(II)

(a; M = Rh)
(b; M = Ir)

$$M\text{-}X + H_2 \rightarrow MH + HX$$

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† Patent applied for.

The acetates, $[M(C_5Me_5)(OAc)_2,H_2O]_n$,[2] and the tri-$\mu$-hydroxo-complex, $[\{Rh(C_5Me_5)\}_2(OH)_3]Cl$,[2] do not require the addition of base and presumably form the hydrides more easily.

The purple (M = Rh) or red (M = Ir) complexes, (II), of formula $[\{M(C_5Me_5)\}_2HCl_3]$, were obtained by reaction of (I) with either hydrogen in the presence of base, or sodium borohydride, or isopropyl alcohol and base, and were characterised by analyses, molecular weights, and spectroscopically.

The n.m.r. spectrum of the iridium complex (IIb) in benzene showed resonances at τ 8·38 (30H, d, J_{Me-H} 0·4 Hz) and 23·55 (1 H, s, br) arising from the C_5Me_5 and hydride ligands, respectively. On irradiation at the high-field resonance the C_5Me_5 doublet collapsed to a singlet.

The n.m.r. spectrum of the rhodium complex (IIa), at τ 8·46 (30 H, s, br) and 21·37 (1H, t, J_{HRh} 23 Hz), was similar, except that the high-field metal hydride resonance was now a triplet, owing to coupling to two equivalent ^{103}Rh nuclei (100% abundance, $I = \frac{1}{2}$). We conclude that the hydride bridges the two metal atoms.

TABLE

Hydrogenation of mono-olefins (11·8 *mmol*) *in isopropyl alcohol* (19 *ml*) *using* (II) (0·08 *mmol*), *at* 1 *atm and* 24°

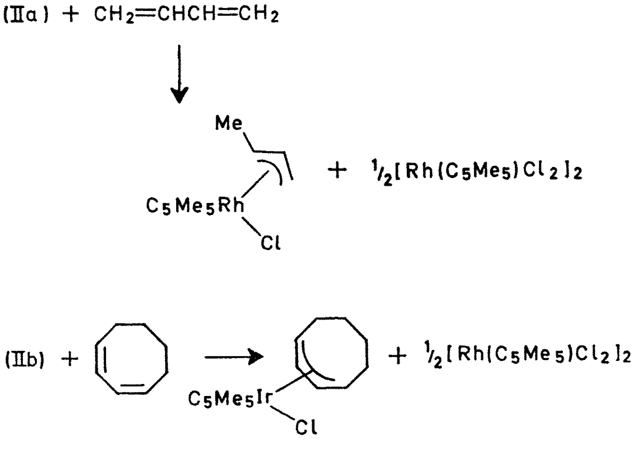
Olefin	Catalyst	Triethylamine (mmol)	H_2-uptake[a] (ml min^{-1})
Cyclohexene	(IIa)	0	1·3
	(IIa)	0·08	2·3
	(IIa)	0·72	4·8
	(IIb)	0	7·8
	(IIb)	0·08	9·9
	(IIb)	0·72	5·0
Cyclopentene	(IIa)	0·72	5·6
	(IIb)	0	5·7
4-Methylpent-1-ene ..	(IIa)	0·72	10·1
	(IIb)	0	3·0
2-Methylpenten-1-ene	(IIa)	0·72	3·1
	(IIb)	0	4·6
cis-4-Methylpent-2-ene	(IIa)	0·72	2·9
	(IIb)	0	4·2
trans-4-Methylpent-2-ene	(IIa)	0·72	1·5
	(IIb)	0	2·7

[a] Initial rate; the catalyst and solvent were pre-saturated with hydrogen for 10 min before the olefin was added.

The i.r. spectra gave no indication of a terminal hydride in the range 1700—2200 cm^{-1}, but bands at 1151 (IIa) and 1155 cm^{-1} (IIb) are assigned to bridging M–H vibrations, by comparison with other bridging hydrides.[5] These bands were shifted to 812 (M = Rh) and 819 cm^{-1} (M = Ir) in the deuterido-complexes $[\{M(C_5Me_5)\}_2DCl_3]$ [ν(M–H)/ν(M–D) = 1·42]. Bands arising from both bridging and terminal M–Cl bonds were also observed [(IIa), 255, 280 cm^{-1}; (IIb) 256, 290 cm^{-1}], and we suggest that the complexes should be formulated as shown with one bridging hydride and one bridging chloride ligand.

The hydrides are very soluble in a variety of organic solvents; they are air-stable in the solid and moderately so in solution. They exhibit high reactivity toward olefins and, for example, react with 1,3-dienes to give enyl complexes,

It therefore appears that these complexes are the intermediates which we had previously postulated to be formed in the reactions of (I) with olefins in ethanol.[3] The iridium complex (IIb) also reacted with triphenylphosphine to give $[Ir(C_5Me_5)H(Cl)PPh_3]$.[3]



The hydrides are also powerful catalysts for homogeneous hydrogenation of olefins (Table).[4] The iridium complex (IIb) was generally more active than the rhodium complex (IIa), but the activity of the latter was greatly increased on addition of base (*e.g.* Et_3N); the iridium complex was deactivated by large amounts of base. Both catalysts were recovered, essentially quantitatively, at the end of the reaction when the olefin had been completely hydrogenated.

Functional groups (-COR, NO_2 or aryl) were not reduced by these catalysts, but their presence on the olefin deactivated it in varying degrees towards hydrogenation. A number of olefins (4-vinylcyclohexene, norbornadiene, cyclo-octa-1,3- and -1,5-dienes, allylbenzene, mesityl oxide) as well as diphenylacetylene, which were not readily hydrogenated as 1 atm., were efficiently reduced under pressure (100 atm, 24°) by (IIa), even in the absence of base.

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