An Arene Hydrido-complex of Ruthenium(II) as Catalyst for the Homogeneous Hydrogenation of Benzene and Olefins

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Summary Under mild conditions, the complex [RuHCl(η-C_6Me_6)(PPh_3)] is an active homogeneous catalyst for the addition of molecular hydrogen to benzene giving cyclohexane and for the hydrogenation of olefins using either molecular hydrogen or secondary alcohols.

THERE have been several recent reports of organotransition metal complexes which catalyse homogeneous hydrogenation of arenes.[1-3] We report that the arene hydrido-complex [RuHCl(η^6-C_6Me_6)(PPh_3)] (I) is a stable, long-lived, homogeneous catalyst for the hydrogenation of both benzene and olefins with molecular hydrogen and for the transfer hydrogenation of olefins with secondary alcohols. The catalyst is an air-sensitive, yellow microcrystalline solid† which is easily prepared from the labile *p*-cymene complex [$RuCl_2(\eta^6\text{-}MeC_6H_4CHMe_2)]_2$[4] (Scheme).

$$\begin{tikzcd}
{[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2} \arrow[r, "C_6Me_6"] & {[RuCl_2(C_6Me_6)]_2} \arrow[d, "PPh_3"] \\
RuHCl(C_6Me_6)(PPh_3) & RuCl_2(C_6Me_6)(PPh_3) \arrow[l, "i"']
\end{tikzcd}$$

SCHEME. i, $LiAlH_4$ or $NaBH_4$, tetrahydrofuran, room temp., 4 h (45%), $NaAlH_2(OCH_2CH_2OMe)_2$, C_6H_6, room temp., 2 h (35%), or Pr^iOH—1 M aq. Na_2CO_3, 70 °C, 8 h (98%).

The corresponding mesitylene complex [RuHCl(η^6-$C_6H_3Me_3$)] can be prepared similarly from [$RuCl_2(\eta^6\text{-}C_6H_3Me_3)]_2$,[4] but the benzene and *p*-xylene analogues decompose rapidly in solution even below room temperature.

Hydrogenation of neat benzene to cyclohexane is catalysed by low concentrations of (I) ($<10^{-3}$ M) under mild con-

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† I.r. (Nujol) 1950 cm^{-1} [ν(RuH)]; ^1H n.m.r. (CD_2Cl_2) δ −8·95 [d, 1H, Ru*H*, ^2J (PH) 53 Hz] and 1·97 (s, 18H, *Me*).

ditions (50 °C, 50 atm H_2) with high turnover rates (0·8 min^{-1}). The catalyst is fairly stable: 45% of (I) can be isolated from the reaction mixture after 36 h. Hydrogenation occurs slowly even under ambient conditions (room temp., 1 atm H_2). This is in marked contrast with other catalysts such as $[Co(\eta^3\text{-}C_3H_5)\{P(OPr^i)_3\}_3]$, which either rapidly decompose during hydrogenation or are not particularly active. Slow decomposition of (I) during hydrogenation gives a small amount of catalytically inactive black solid, but as the reaction medium is clear the hydrogenation is homogeneous. No cyclohexadienes or cyclohexene can be detected either during or after the reaction, whereas with $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$[2] as catalyst the cyclohexane produced is contaminated with significant amounts of cyclohexene. This indicates that benzene remains strongly complexed to the active intermediate derived from (I) during all the steps of the hydrogenation. Competition studies show that (I) more readily catalyses hydrogenation of hex-1-ene than benzene. In contrast with the $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ catalyst,[3] (I) functions in the absence of added base, although a system comprising $[RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)]$, Et_3N, and Pr^iOH exhibits the same catalytic activity as (I).

TABLE. Transfer hydrogenation from 1-phenylethanol to olefins catalysed by (I).[a]

Compound	Products (% yield)[b]
Hex-1-ene	Hexane (100)
Cyclopentene	Cyclopentane (100)
Cyclohexene	Cyclohexane (92)
Cycloheptene	Cycloheptane (90)
Cyclo-octene	Cyclo-octane (89)
Cyclohexa-1,3-diene	Cyclohexene (12), cyclohexane (52)
Cyclo-octa-1,5-diene	Cyclo-octene (46)
Cyclo-octa-1,3-diene	Cyclo-octene (88)
Norbornadiene	Norbornene (12)
Cyclo-octatetraene	Cyclo-octa-1,3-diene (88), cyclo-octene (7)
Phenylacetylene	Styrene (28)
Benzene	Cyclohexane (8)

[a] Olefin (0·5 M) and catalyst (10^{-3} M) in 1-phenylethanol were heated at 100 °C for 100 min. Reaction conditions have not been optimised. [b] Analysed by g.l.c.

Complex (I) also shows high catalytic activity for hydrogen transfer from secondary alcohols to olefins (Table) and is recovered unchanged at the end of the reaction. Although both $[RhH(PPh_3)_4]$ and $[RuH_2(PPh_3)_4]$ catalyse transfer hydrogenation of mono-olefins, strongly co-ordinating di-olefins such as cyclo-octa-1,5-diene are unaffected.[5,6] In contrast, (I) catalyses transfer hydrogenation from 1-phenylethanol to cyclo-octa-1,3-diene, cyclo-octa-1,5-diene, and cyclo-octatetraene. Under similar conditions benzene is converted into cyclohexane, but in poor yield.

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