Dinuclear Arene Hydrido-complexes of Ruthenium(II): Reactions with Olefins and Catalysis of Homogeneous Hydrogenation of Arenes

By Martin A. Bennett,* Tai-Nang Huang, and Terence W. Turney

(Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia 2600)

Summary The dinuclear hydrido-complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H)_2(\mu\text{-}Cl)Ru(\eta^6\text{-}C_6Me_6)]Cl$ reacts with mono-olefins to give the corresponding alkanes and either η^3-allylruthenium(II) or dieneruthenium(0) complexes; it also catalyses efficient homogeneous hydrogenation of a range of arenes to the corresponding cyclohexanes under mild conditions.

We have shown[1] that treatment of the η^6-hexamethyl-benzene complex $[RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)]$ with aqueous sodium carbonate in propan-2-ol gives a monomeric hydrido-complex $[RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)]$ (1) which is a homogeneous hydrogenation catalyst for olefins and benzene. We now find that under similar conditions (80 °C, 10 min, 1 M Na_2CO_3) the parent dimer $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ affords in 80% yield a purple, air-stable hydride $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H)_2(\mu\text{-}Cl)Ru(\eta^6\text{-}C_6Me_6)]Cl$ (2) which is soluble in water and many organic solvents and behaves as a 1:1 electrolyte in nitromethane.† Addition of NH_4PF_6 to a propan-2-ol

† Λ_M $(10^{-3}$ M$)$ = 53 Ω^{-1} cm^2 mol^{-1}; δ (CD_2Cl_2) -14.07 (s, 2H, RuH) and 2.21 (s, 36H, C$_6Me_6$); ν (Nujol) 1165 (RuHRu) and 239 cm^{-1} (RuClRu). In the corresponding deuteride, the band at 1165 cm^{-1} is replaced by a band at 825 cm^{-1} due to (RuDRu).

solution of (2) immediately precipitates the corresponding PF_6^- salt. Spectroscopic data† are compatible only with a structure in which the cation contains three bridging anionic ligands, in contrast with the formally analogous η^5-pentamethylcyclopentadienylhydrido-rhodium(III) and -iridium(III) complexes [{M(η^5-C_5Me_5)}$_2$HCl$_3$] [M = Rh (3); M = Ir (4)] and [{Ir(η^5-C_5Me_5)}$_2$H$_2$Cl$_2$] (5),[2] which adopt a structure containing only two bridging groups in the solid state.[3]

$$[RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)]$$

(1)

(2); R = Me
(6); R = H

(3); M = Rh, X = Cl
(4); M = Ir, X = Cl
(5); M = Ir, X = H
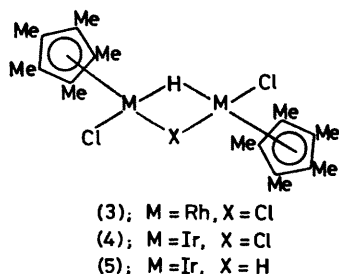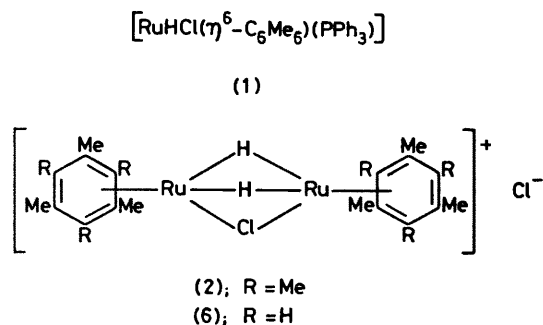
An η^6-mesitylene analogue (6) can be prepared similarly from [RuCl$_2$(η^6-$C_6H_3Me_3$)]$_2$,[4] but in this case prolonged heating gives a second species not yet isolated in a pure state but characterised spectroscopically as a tri-μ-hydride [(η^6-$C_6H_3Me_3$)Ru(μ-H)$_3$Ru(η^6-$C_6H_3Me_3$)]Cl.‡. Brief heating of propan-2-ol solutions of the p-xylene or p-cymene complexes [RuCl$_2$(arene)]$_2$[4] with 1 M Na$_2$CO$_3$ immediately gives inseparable mixtures of di-μ-hydrido-μ-chloro and tri-μ-hydrido complexes.
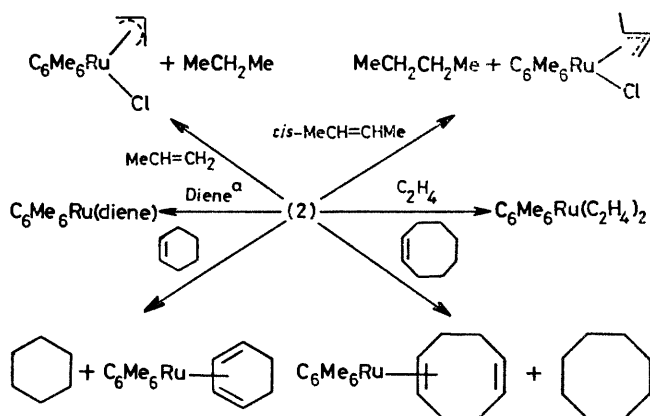
SCHEME 1.   a Diene = cyclo-octa-1,5-diene, norbornadiene, or 2,3-dimethylbutadiene.

Complex (2) reacts with triphenylphosphine to give (1) and with dienes to give initially en-yl- or η^3-allyl-ruthenium-(II) complexes which, in some cases, eliminate HCl to form dieneruthenium(0) complexes (Scheme 1). The latter can also be made directly from ethanolic [RuCl$_2$(C$_6$Me$_6$)]$_2$, Na$_2$CO$_3$, and the diene.[5] Reaction of (2) with ethylene gives (η^6-C_6Me_6)Ru(C$_2$H$_4$)$_2$, but with other alkenes hydrogen atoms undergo redistribution to give alkanes and either η^3-allylruthenium(II) or dieneruthenium(0) complexes with yields of $ca.$ 60—70% (Scheme 1). A suggested mechanism is shown in Scheme 2. Catalytic disproportionation of

SCHEME 2
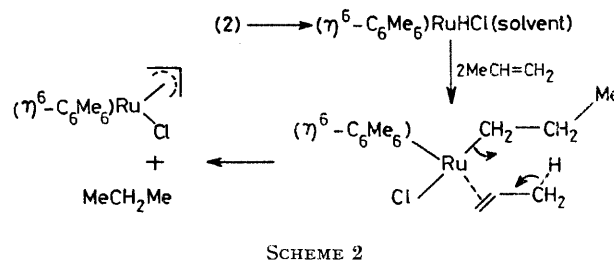
alkenes to alkanes and 1,3-dienes has been observed in reactions with IrH$_5$L$_2$ (L = PPh$_3$ or PPr$^i_3$)[6] and a stoicheiometric disproportionation occurs in the reaction of alkenes with a solution containing [(η^6-C_6H_6)Mo(η^3-allyl)Cl]$_2$ and [EtAlCl$_2$]$_2$.[7]

Complex (2) is the most stable and active catalyst so far discovered for homogeneous hydrogenation of arenes to cyclohexanes (Table). In contrast with the closely related

TABLE. Hydrogenation of substituted benzenes.[a]

Compound	Products (% yield)[b]
Styrene	Ethylcyclohexane (100)
Phenylacetylene	Ethylbenzene (32), styrene (8)
Anisole	Methoxycyclohexane (100)
Phenol	Cyclohexanol (62)
Methyl benzoate	Methyl cyclohexanoate (100)
Acetophenone	Methyl cyclohexyl ketone (100)
Benzophenone	Dicyclohexyl ketone (100)
NN'-Dimethylaniline	NN'-Dimethylcyclohexylamine (86)
Nitrobenzene	Aniline (38)
Fluorobenzene	Fluorocyclohexane (15), cyclohexane (20)
Chlorobenzene	Cyclohexane (8)
Bromobenzene	Cyclohexane (6)
Diphenyl ether	Cyclohexane, cyclohexanol, phenol

a Conditions: catalyst (2) (0·02 mmol), propan-2-ol (18 ml), substrate (22·5 mmol), 50 °C, 50 atm, 36 h.   b Products and percentages (relative to appropriate benzene) were estimated by g.l.c.–mass spectrometry.

[RhCl$_2$(η^5-C_5Me_5)]$_2$–Et$_3$N system,[8] base is not required as a co-catalyst. Under conditions similar to those employed by Maitlis *et al.*,[8] *viz.* neat benzene, 0·02 mmol of (2), 50 °C, 50 atm of H$_2$ for 36 h, *ca.* 9000 molecules of benzene are reduced to cyclohexane per molecule of catalyst, corresponding to a turnover rate of 4·1 min^{-1}; the corresponding value for (1) as catalyst is 0·8 min^{-1}.[1] Hydrogenation of C$_6$D$_6$ gives C$_6$D$_6$H$_6$ (>95%). Catalyst activity is reduced but not completely suppressed by elemental sulphur (0·05 mmol, 10 p.p.m. S: turnover rate 1·05 min^{-1}) and by thiophen (0·002 mmol, 10 p.p.m.: turnover rate 0·3 min^{-1}).

‡ δ (CD$_2$Cl$_2$) −19·05 (s, 3H, RuH), 2·3 (s, 18H, Me), and 5·12 (s, 6H, C$_6$H$_3$Me$_3$); ν (Nujol) 1180 cm^{-1} (RuHRu) (bands due to RuCl below 300 cm^{-1} are absent).

In further contrast with the $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ system, styrene is hydrogenated completely to ethylcyclohexane rather than to ethylbenzene, and the aromatic rings of methyl benzoate, anisole, and phenol are fully hydrogenated without appreciable hydrogenolysis of the functional group.

However, hydrogenolysis does occur with diphenyl ether and halogenobenzenes, and nitrobenzene is reduced to aniline.

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