*Journal of Organometallic Chemistry*, 233 (1982) C17—C20
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**Preliminary communication**

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# DINUCLEAR $\mu$-HYDRIDO ARENE COMPLEXES OF RUTHENIUM(II)

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(Received April 2nd, 1982)

## Summary

Reaction of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ with aqueous $Na_2CO_3$ in propan-2-ol or with hydrogen in the presence of triethylamine gives a dinuclear mono-$\mu$-hydrido complex $[Ru_2(\mu\text{-}H)(\mu\text{-}Cl)_2(\eta\text{-}C_6Me_6)_2]Cl$ which is reduced by $NaBH_4$ in ethanol to a tri-$\mu$-hydrido species, isolated as its $PF_6$ salt $[Ru_2(\mu\text{-}H)_3(\eta\text{-}C_6Me_6)_2]PF_6$. Related complexes, e.g. $[Ru_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(\mu\text{-}X)(\eta\text{-}C_6Me_6)_2]PF_6$ ($X = O_2CMe$, Cl) have been isolated from the reaction of acetato complexes $Ru(O_2CMe)X(\eta\text{-arene})$ ($X$ = Cl, $O_2CMe$) with propan-2-ol.

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Maitlis et al. [1—4] have prepared a series of dinuclear $\mu$-hydrido complexes of $\eta$-pentamethylcyclopentadienyl-rhodium(III) and -iridium(III) exemplified by I and II and have demonstrated their ability to function as homogeneous catalysts for olefin hydrogenation. Since the $M(\eta\text{-}C_5Me_5)$ (M = Rh, Ir) and $Ru(\eta\text{-arene})$ fragments are isoelectronic [5], arene ruthenium(II) hydrides analogous to I and II might be expected to exist, and we present here some preliminary results in this area.

The reported formation of a di-$\mu$-hydrido complex $[Ru_2(\mu\text{-}H)_2Cl(\eta\text{-}C_6Me_6)_2]Cl$ [6] from the reaction of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ in propan-2-ol with aqueous sodium carbonate has proved inexplicably irreproducible*. We find that, under conditions similar to those employed previously, viz. treatment of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ in propan-2-ol at 85°C with aqueous 1 *M* sodium carbonate (1 mol per mol of dimer) and subsequent stirring at room temperature for 10 min, a red solution is obtained. After chromatography on neutral alumina using $CHCl_3$/propan-2-ol (10/1) as eluant and crystallization from methanol/ether, a deep red mono-$\mu$-hydrido complex (III; Y = Cl) is obtained in ca. 60% yield, which shows a singlet

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*A similar difficulty has been encountered by Professor P.M. Maitlis (Sheffield University) and Dr. S.D. Ittel (Dupont Central Research Laboratories) (personal communications).

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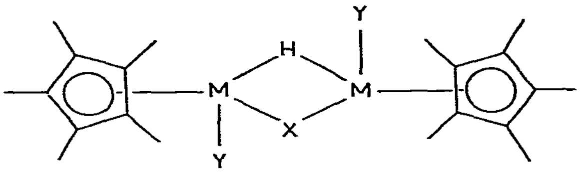
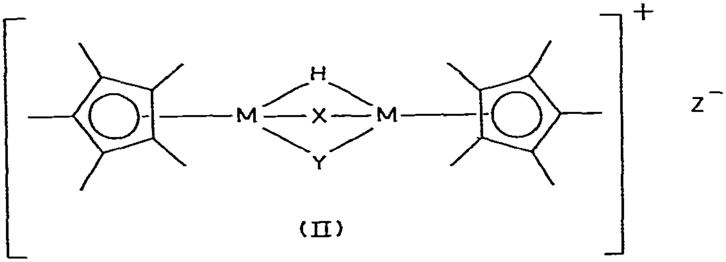


(I)

M = Rh, Ir; X = Y = Cl.

M = Ir; X = H; Y = Cl.



(II)

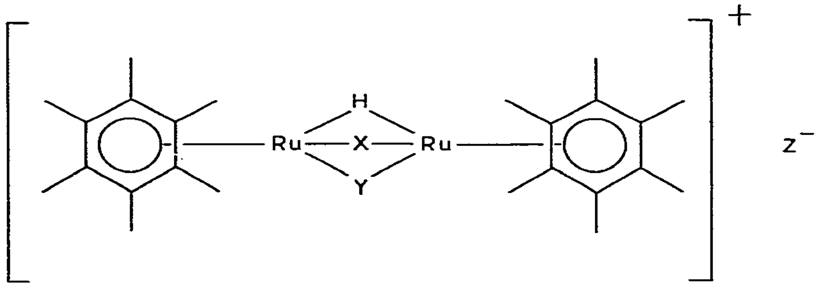
M = Rh, Ir; X = Y = $O_2CMe$, $O_2CCF_3$; Z = $H(O_2CMe)_2$, $H(O_2CCF_3)_2$, $PF_6$.

M = Rh, Ir; X = H; Y = $O_2CMe$, $O_2CCF_3$; Z = $H(O_2CMe)_2$, $H(O_2CCF_3)_2$, $PF_6$.

M = Ir; X = Y = H; Z = $H(O_2CCF_3)_2$, $PF_6$.

hydride resonance at $\delta$ −11.8 ppm in $CD_2Cl_2$. III is formed in similar yield by hydrogenation (4 atm, 48 h) at room temperature of a suspension of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ in dichloromethane containing at least 2 mol of triethylamine per mol of dimer and is separated from $[Et_3NH]Cl$ by chromatography as above. The compound is monomeric in dichloromethane but behaves as a 1/1 electrolyte in nitromethane ($\Lambda$ = 73 S $cm^2$ $mol^{-1}$). Treatment with aqueous $NH_4PF_6$ gives the dark red-purple $PF_6$ salt, which shows a singlet hydride resonance at $\delta$ −9.0 ppm in $CD_2Cl_2$. Reaction of $[RuCl_2(\eta\text{-}C_6Me_6)]_2$ in propan-2-ol with aqueous sodium carbonate (2 mol per mol of dimer) for periods ranging from 20 min to 4 h at 85°C gives complex mixtures of products in variable proportions, among which the di-$\mu$-hydride $[Ru_2(\mu\text{-}H)_2Cl(\eta\text{-}C_6Me_6)_2]Cl$ and a tri-$\mu$-hydride $[Ru_2(\mu\text{-}H)_3(\eta\text{-}C_6Me_6)_2]Cl$ can be identified by their characteristic high-field singlets at $\delta$ −14.1 and −16.3 ppm in $CD_2Cl_2$. The complex $[Ru_2(\mu\text{-}H)_3(\eta\text{-}C_6Me_6)_2]Cl$ (IV) can be isolated as brown crystals by reduction of III with ethanolic $NaBH_4$. The corresponding $PF_6$ salt is obtained as dark green-grey crystals by metathesis with $NH_4PF_6$ and shows a singlet hydride resonance at $\delta$ −15.9 ppm in $CD_2Cl_2$.

Complexes III and IV catalyse hydrogenation of benzene to cyclohexane at 50°C/50 atm $H_2$. Using 0.02 mmol of catalyst and 25 ml of benzene the turnover numbers for cyclohexane production are about 900 (rate 0.3 $min^{-1}$) for



(III, X = Y = Z = Cl.
IV, X = Y = H; Z = Cl.
V, X = Y = $O_2CMe$; Z = $H(O_2CMe)_2$, $PF_6$.
VI, X = $O_2CMe$; Y = Cl; Z = Cl, $PF_6$)

III and 350 (rate 0.2 $\text{min}^{-1}$) for IV, so that these catalysts are clearly less active than either $RuHCl(PPh_3)(\eta\text{-}C_6Me_6)$ [7] or $[Ru_2(\mu\text{-}H)_2Cl(\eta\text{-}C_6Me_6)]Cl$ [6].

$\mu$-Hydrido arene complexes are also generated by reaction of areneruthenium(II) carboxylates $Ru(O_2CR)_2(\eta\text{-arene})$ and $Ru(O_2CR)Cl(\eta\text{-arene})$ (R = Me, $CF_3$) [8,9] with propan-2-ol at 60—80°C for 3—4 h. Thus $Ru(O_2CMe)_2(\eta\text{-}C_6Me_6)\cdot H_2O$ affords $[Ru_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2(\eta\text{-}C_6Me_6)_2]H(O_2CMe)_2\cdot H_2O$ (V) as dark red-brown microcrystals in 79% yield ($^1H$ NMR, $\delta$(ppm, $CD_2Cl_2$, 32°C) −11.6(s,RuH), 2.16(s,$O_2CMe$), 2.0(s,$O_2CMe$), 2.12(s,$C_6Me_6$)), from which the $PF_6$ salt may be obtained by addition of $NH_4PF_6$. Similarly, $Ru(O_2CMe)Cl(\eta\text{-}C_6Me_6)$ gives the salts $[Ru_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(\mu\text{-}Cl)(\eta\text{-}C_6Me_6)_2]Z$ (Z = $Cl\cdot H_2O$, $PF_6$) (VI) containing three different bridging ligands, which show a singlet hydride resonance at $\delta$ −10.2 ppm in $CD_2Cl_2$. This synthetic route works for less highly substituted arenes, and although mixtures of hydrido complexes are sometimes formed in the reaction with propan-2-ol, addition of $NH_4PF_6$ usually precipitates the pure mono-$\mu$-hydrido complex. Salts prepared in this way include $[Ru_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(\mu\text{-}Cl)(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2]Z$ (Z = $Cl\cdot 2H_2O$, $PF_6$), $[Ru_2(\mu\text{-}H)(\mu\text{-}O_2CMe)(\mu\text{-}Cl)(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)_2]Z$ (Z = $Cl\cdot H_2O$, $PF_6$) and $[Ru_2(\mu\text{-}H)(\mu\text{-}O_2CMe)_2(\eta\text{-}C_6H_6)_2]PF_6$, which show singlet hydride resonances at ca. $\delta$ −8.6, −7.3 (in $CD_2Cl_2$) and −6.6 ppm (in acetone-$d_6$), respectively; the shift to higher frequency with decreasing alkyl substitution of the arene is noteworthy. The IR spectra of all the hydrido(acetato) complexes show the expected strong absorptions at 1540—1580 $cm^{-1}$ and 1380—1450 $cm^{-1}$ due respectively to $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$. However, we have been unable to locate bands due to $\nu$(Ru—H—Ru) in the IR spectra of any of the hydrido complexes described in this note.

In contrast with the corresponding $M(C_5Me_5)$ compounds, the areneruthenium(II) carboxylates do not react with hydrogen under ambient conditions, but do so under 5—10 atm to give hydrido species which are being investigated.

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