

Hydrogen transfer reactions in routes to μ -methylene-dirhodium or -di-iridium complexes

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Treatment of $[(C_5Me_5Rh)_2Cl_4]$ with Al_2Me_6 gives $[C_5Me_5RhMe_2-Me-AlClMeL]$ ($L = AlMe_2Cl$ etc.) which reacts smoothly with acetone to give first *cis*- and then *trans*- $[C_5Me_5Rh(Me)(\mu-CH_2)_2Rh(Me)C_5Me_5]$ in nearly quantitative yield; isopropanol is also formed.

The synthesis and reactions of μ -methylene-transition metal complexes are of considerable current interest,¹ especially in connection with their possible relevance to Fischer-Tropsch reactions.²

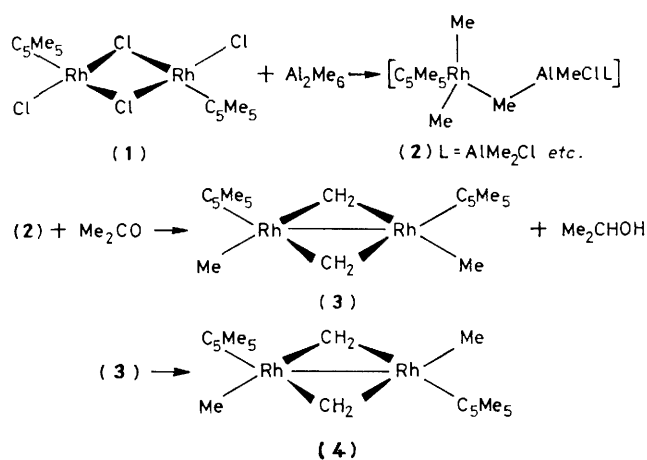
We have previously reported the synthesis of the *trans*-di- μ -methylene-dirhodium complex (4) by treatment of $[(C_5Me_5Rh)_2Cl_4]$ (1) with Al_2Me_6 .³ The low yield (15%) arises from the fact that in going from (1) to (4) there is an increase in the formal oxidation state of the metal from (+III) to (+IV). Since Al_2Me_6 is, if anything, a reducing agent, this implies the importance of an oxidation step somewhere. In practice this was accomplished by exposure to air at a defined point in the reaction sequence.†

We have now found that we can circumvent this autoxidation step entirely by adding an excess of acetone to the reaction mixture of (1) and Al_2Me_6 in hydrocarbon solution.† After addition of water and removal of solvent this gives the *trans*-

complex (4) essentially quantitatively ($\geq 85\%$ isolated yield of pure crystalline material). G.c. analysis shows the presence of a substantial amount of isopropanol [*ca.* 0.6 equivalents per mol of (1)] as well as a small quantity of *t*-butanol.

No significant amounts of methane are liberated on adding a solution of Al_2Me_6 to a suspension of (1) in toluene under argon at temperatures below 0 °C. The $^{13}C\{^1H\}$ n.m.r. spectra of such solutions (C_7D_8) at -90 °C consistently show the presence of only one rhodium-containing species characterised by sharp resonances at δ -18.9 [d, $J(Rh-C)$ 28 Hz], +1.7 [d, $J(Rh-C)$ 23 Hz], +7.6 (s), and +97.0 p.p.m. [d, $J(Rh-C)$ 3 Hz]. Off-resonance decoupling shows the δ -18.9, +1.7, and +7.6 p.p.m. resonances to arise from methyl groups. Assuming similar n.o.e.'s the relative intensities of the signals (2:1:5) indicate the presence of a ' $C_5Me_5RhMe_3$ ' unit where one of the Rh-bound methyl groups is different from the other two, presumably because it is also bound to an Al atom. These signals do not alter over the temperature range -90 to *ca.* -30 °C or between Al_2Me_6 -complex (1) ratios from 2.5:1 to 10:1, and we propose structure (2) for this species. Some four methyl-aluminium resonances (δ -8 to -5 p.p.m., arising from various $Al_2Me_{6-x}Cl_x$ compounds) are resolved at -90 °C; they coalesce by -60 °C and further coalescence of these resonances with the Rh-methyls

† CAUTION: These reactions are potentially hazardous and should be attempted only by experienced workers. We typically use solutions containing no more than 5 mmol Al_2Me_6 in 5 cm³ of hydrocarbon solvent and do not counsel working with larger amounts.



Scheme 1

begins above -30°C . The solutions are stable to *ca.* $+40^\circ\text{C}$.

No low field signals due to μ -methylene or carbene complexes are present in either the ^1H or the ^{13}C n.m.r. spectrum of solutions of (2). This is consistent with methane not being formed in this reaction.⁴

On addition of acetone to the solution of (2) a smooth and fast reaction takes place even at -60°C ; no intermediates are detectable by n.m.r. spectroscopy nor are any radical species seen by e.s.r. spectroscopy. The immediate product is the *cis*-complex (3) which rapidly isomerises to the *trans*-complex (4); separate experiments show this to be a general Lewis-acid catalysed process.

No H/D scrambling was observed between the C_5Me_5 and the methylene or methyl ligands when $[\{\text{C}_5(\text{CD}_3)_5\text{Rh}\}_2\text{Cl}_4]$ was treated with Al_2Me_6 and then $(\text{CD}_3)_2\text{CO}$. Under these conditions therefore there is no evidence for the existence of free mononuclear $[\text{C}_5\text{Me}_5\text{Rh}(\text{=CH}_2)(\text{-CH}_3)]$.[‡] We propose the overall reaction sequence shown in Scheme 1.

Only certain hydrogen acceptors are effective in this reaction. For example, when ethylene is reacted with the solution containing (2), only $[\text{C}_5\text{Me}_5\text{Rh}(\text{C}_2\text{H}_4)_2]$ and $[\text{C}_5\text{Me}_5\text{Rh}(\text{C}_2\text{H}_4)\text{Me}_2]$ are obtained; no (3) or (4) could be found. Reaction of $[(\text{C}_5\text{Me}_5\text{Ir})_2\text{Cl}_4]$ with Al_2Me_6 in pentane followed by acetone gives the iridium analogues of (3) and (4). However the yields are lower (20–30%) since a number of competing reactions take place.

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[‡] In contrast, extensive scrambling does occur when the reaction mixture from $[\{\text{C}_5(\text{CD}_3)_5\text{Rh}\}_2\text{Cl}_4]$ and Al_2Me_6 is allowed to autoxidise.