Metal-catalysed Alkyl Ketone to Ethyl Ketone Conversions in Chelating Ketones *via* Carbon–Carbon Bond Cleavage

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8-Quinolinyl alkyl ketones, in which the alkyl group has β-hydrogens, react with various Rh^I and Ir^I complexes under ethylene to give, in a catalytic process, 8-quinolinyl ethyl ketone; the same reaction with 8-quinolinyl phenyl ketone produces styrene *via* ethylene insertion into a rhodium–phenyl bond and β-elimination of the resulting phenylethyl complex.

The ability to cleave simple, unstrained carbon–carbon bonds by transition metals makes possible new kinds of reactivity which may be of use in organic synthesis. As one example, we recently observed a novel alkyl ketone to ethyl ketone conversion with 8-quinolinyl alkyl ketones. While 8-quinolinyl ethyl ketone reacts with $[(C_2H_4)_2RhCl]_2$ to give stable acylrhodium(III) ethyl complexes,[1] 8-quinolinyl butyl ketone (**2**), when heated to 80 °C for 5 h in benzene in a screw-cap vial with $[(C_2H_4)_2RhCl]_2$ gave (after addition of pyridine or some other hard Lewis base) only the ethyl complex (**1**) in an isolated yield of >90%, with no rhodium butyl complex observed. Other ketones with non-primary β-hydrogens, such as (**3**)—(**5**) also gave rise to complex (**1**) exclusively.†

We believe that for ketones (**2**)—(**5**), rhodium insertion into the α-ketone carbon–carbon bond occurs, but the resulting alkyl complex β-eliminates to an acylrhodium(III) hydride. This is trapped by ethylene present from the starting metal

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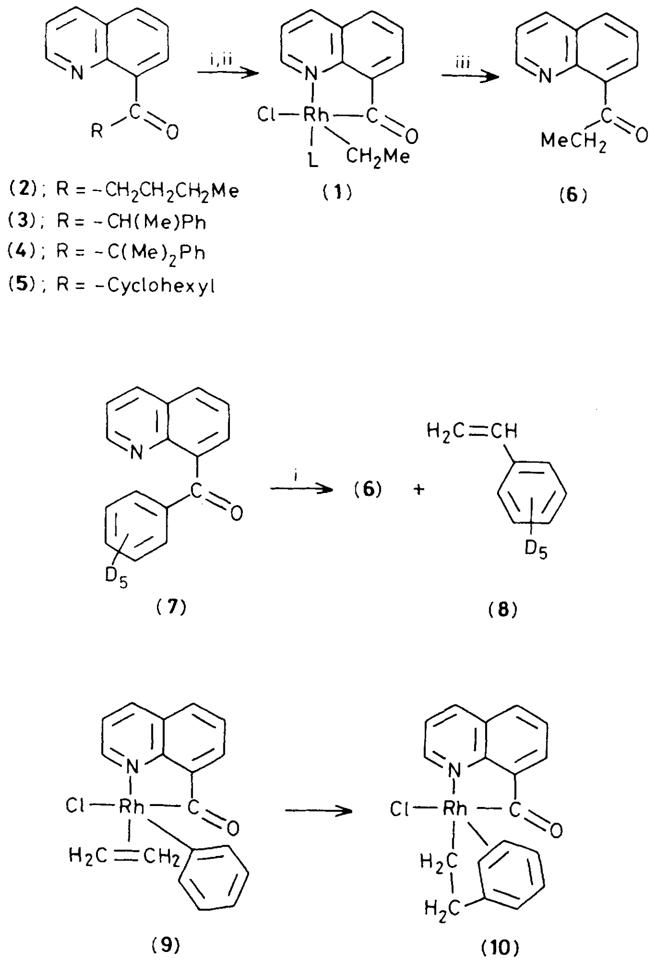
† Ligands were prepared from Grignard reactions on 8-quinoline carbaldehyde followed by Swern oxidation. All new compounds gave confirmatory ^1H and ^{13}C n.m.r. and i.r. spectra and elemental analyses.



Scheme 1. *Reagents and conditions:* i [$(C_2H_4)RhCl]_2$, benzene, 80 °C; ii L = pyridine; iii 100 °C or excess PPh_3.

complex and leads to (**1**) (Scheme 1).[2] Supporting this mechanism, the predicted alkenes derived from β-elimination are seen in the ^1H n.m.r. spectrum when the reaction is run in deuteriobenzene. Some of the ligands, in particular (**3**), react with the Rh^I complex at or slightly above room temperature. However, even under these milder conditions (**1**) was the only product. Apparently, the energy barrier to carbon–carbon bond insertion is greater than the one for β-elimination. It is interesting that the rhodium(I) centre is able to insert into even such a sterically hindered carbon–carbon bond as found in (**4**). No products from competing insertion into carbon–hydrogen bonds (which would produce six-membered or larger chelates) were detected with any of the quinoline ligands.

Using a high temperature (100 °C) and a longer reaction time (48 h) it was possible to achieve a catalytic synthesis of (**6**) from (**2**)—(**5**). Thus, heating (**2**) [or (**3**)—(**5**)] and $[(C_2H_4)_2RhCl]_2$ (9 mol %) under 6 atm (1 atm = 101 325 Pa) of C_2H_4 gave a 61% yield (678% based on the rhodium catalyst) of (**6**). The balance of the reaction was starting material. Given the relative thermodynamic stabilities of substituted alkenes over ethylene[3] (as well as the molar excess of C_2H_4 used) the presence of starting material indicates that catalyst deactivation had occurred rather than equilibrium being reached. The exchange reaction with alkenes other than ethylene was not efficient. It appears β-elimination is too fast to compete with reductive elimination except for ethylene.

At present, we believe that the most useful aspect of this reaction is as a sensitive assay for the ability to cleave carbon–carbon bonds by various metal complexes. The complexes $[(COD)RhCl]_2$, $[(COD)IrCl]_2$ (COD = cyclo-octa-1,5-diene), and $(PPh_3)_3RhCl$ all were catalytically active in the conversion of (**1**) into (**6**) under the standard conditions of 100 °C for 12 h with 10% catalyst. Since phosphines rapidly promote reductive elimination of (**1**) back to (**6**),[4] we found it surprising that even at a Rh : P ratio of 1 : 3 as in $(PPh_3)_3RhCl$ carbon–carbon bond cleavage was possible. Some complexes which exhibited zero catalytic activity under the above conditions were $Pd(PPh_3)_4$, $Pt(PPh_3)_4$, $Pd(OAc)_2$, $RuCl_2(PPh_3)_3$, and $(C_5H_5)Rh(C_2H_4)_2$. A given complex may be catalytically inactive either because the quinoline nitrogen does not co-ordinate to the metal centre so that the metal and carbon–carbon bond are not brought into proximity, or because the resulting complex is not sufficiently activated for insertion to occur.

Unexpectedly, 8-quinolinyl phenyl ketone also reacts with $[(C_2H_4)_2RhCl]_2$ to give (**6**) and styrene. Under the catalytic conditions described above, (**6**) and styrene were formed in 100% yield (1100% based on the catalyst). One possible mechanism for this reaction involves formation of an acyl-rhodium(III) phenyl complex, β-elimination to a benzyne–hydride complex,[5] ethylene addition, reductive elimination to a rhodium phenylethyl complex, and finally, β-elimination to a styrene. This benzyne mechanism is excluded by using the deuteriated ligand (**7**). Since in the product styrene (**8**) the deuterium label is retained on the aromatic ring and none appears on the unsaturated carbon atoms (as determined by 250 MHz ^1H n.m.r. spectroscopy), (**8**) must be formed by rhodium insertion into the phenyl ketone carbon–carbon bond followed by C_2H_4 insertion into the rhodium–phenyl bond, and β-elimination of the resulting phenylethyl group.[6]

This ethylation reaction only occurs into a rhodium–phenyl bond since no ethyl groups are incorporated into the alkyl groups derived from ligands (**2**)—(**5**). With (**7**), neither phenylbutenes nor heavier oligomers are formed from multiple ethylene insertions. We believe the different behaviour of the aryl and alkyl ligands arises from the ability of an aryl group to π-bond to the metal centre during and after C_2H_4 insertion [(**9**) into (**10**)] thereby keeping the electron count at the metal centre unchanged. Analogous ideas have been advanced to explain alkene polymerization (assuming C–H bonds can act as ligands)[7] and reductive elimination in acylmetal alkyls.[8]

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