Rhodium Complex Catalysed Hydrosilylation of Carbonyl Compounds

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Summary Chlorotris(triphenylphosphine)rhodium has been found to be an extremely effective catalyst for the hydrosilylation of carbonyl compounds.

RHODIUM(I) complexes are effective catalysts for various reactions.[1] However, catalysis of the hydrosilylation of carbonyl compounds has not hitherto been reported. Metal halides such as $ZnCl_2$ or H_2PtCl_6 were found[2–4] to catalyse the reaction, but the mechanism was unclear. We report the high catalytic activity of chlorotris(triphenylphosphine)rhodium (**1**) for the hydrosilylation of carbonyl compounds and the identification of an important intermediate. When a mixture of cyclohexanone, Et_3SiH and (**1**) was stirred at room temperature an exothermic reaction occurred and the hydrosilylation was completed within a few minutes to give cyclohexyloxytriethylsilane (98%).

The reaction was slower for aromatic ketones, and some heating was necessary to complete the reaction. Thus, the reaction of acetophenone with Et_3SiH in the presence of (**1**) for 15 min at 60° gave methylphenyltriethylsiloxymethane (97%). When $ZnCl_2$ is used as a catalyst, more vigorous conditions are required.[2]

Where the reaction was relatively slow, precipitation of a yellow solid was observed which later redissolved as the reaction temperature rose. The yellow complex was precipitated by the addition of n-hexane. It was identified as $(PPh_3)_2Rh(H)(SiEt_3)Cl$† (**2**) (m.p. 105° decomp.), which resulted from the oxidative addition of Et_3SiH to (**1**) ν_{Rh-H}, 2100s, 2080 cm^{-1}, δ_{Rh-H} 850 cm^{-1} (KBr disc). Complex (**2**) may be a mixture of stereoisomers, having a different configuration from that obtained by Haszeldine and his co-workers,[5] who reported only one band for complex (**2**) in the Rh–H region at 2020 cm^{-1}.

When metal halides such as $ZnCl_2$ or $NiCl_2$ were employed in the hydrosilylation of benzaldehyde, it was reported[3] that a generated silyl ether disproportionated immediately to dibenzyl ether and hexaethyldisiloxane. No such disproportionation was observed with (**1**), and benzyloxytriethylsilane was obtained (90%).

Hydrosilylation of $\alpha\beta$-unsaturated ketones and aldehydes proceeded smoothly under mild conditions to give silylenol ethers, *via* 1,4 addition, in high yields.

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† A satisfactory elemental analysis was obtained.

[1] *E.g.* J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, (*A*) 1966, 1711; W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J. C. S. Chem. Comm.*, 1972, 10; R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Organometallic Chem.*, 1967, **9**, P13; A. J. Birch and G. S. Subba Rao, *Tetrahedron Letters*, 1968, 2917; M. C. Baird, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc.*, (*A*), 1968, 348; H. Singer and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 849.

[2] R. Calas, E. Frainnet, and J. Bonastre, *Compt. rend.*, 1960, **251**, 2987.

[3] N. E. Glushkova and N. P. Kharitonov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 88.

[4] A. D. Petrov, S. I. Sadykh-Zade, and A. D. Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1958, **121**, 119; S. I. Sadykh-Zade and A. D. Petrov, *Zhur. obschei Khim.*, 1959, **29**, 3194.

[5] R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Chem. Soc.* (*A*), 1969, 683.