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Preliminary communication

Synthesis of $(C_5H_5)Fe(CO)(SiHPh_2)_2H$, a catalytically active intermediate in the hydrosilylation of acetophenone by diphenylsilane

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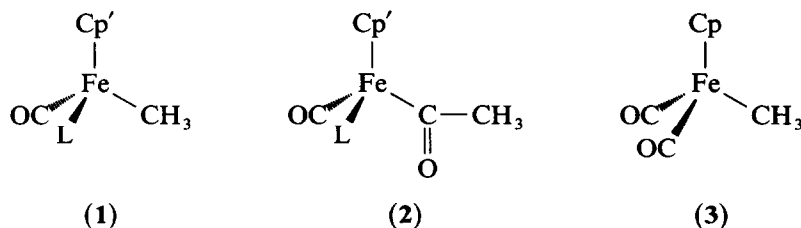
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Abstract

The well-known iron complex $(\eta-C_5H_5)Fe(CO)_2(CH_3)$, **3**, is an efficient catalyst for the hydrosilylation of acetophenone by diphenylsilane. During the reaction the new complex $(C_5H_5)Fe(CO)(SiHPh_2)_2H$, **6**, is formed. This complex is a catalytically active intermediate in the hydrosilylation reaction; it has been characterised by elemental analysis, IR and 1H -NMR spectroscopy. The observed magnetic equivalence of the two Si–H protons is interpreted in terms of classical bonding of the H ligand and the $SiHPh_2$ groups to the metal centre.

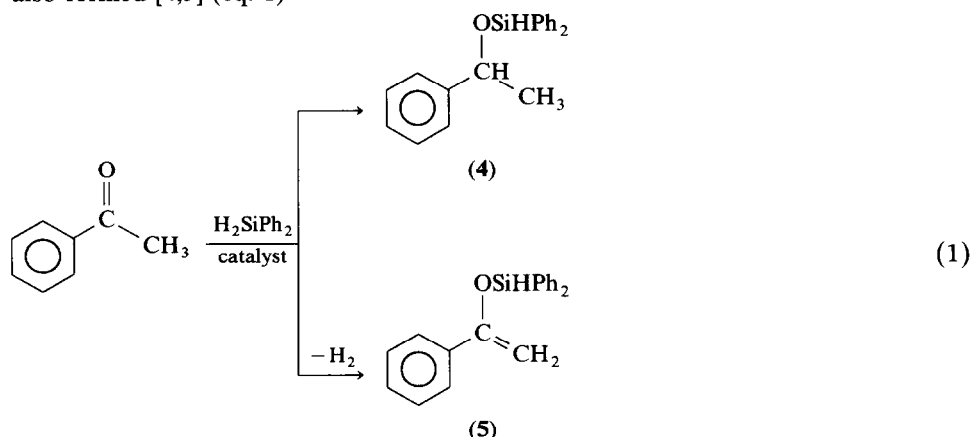
The hydrosilylation of acetophenone by diphenylsilane catalysed by iron complexes of the type $[Cp'Fe(CO)(CH_3)L]$ [1] (**1**), $[Cp'Fe(CO)(COCH_3)L]$ [2] (**2**) and $CpFe(CO)_2(CH_3)$ (**3**) (Cp' = cyclopentadienyl, indenyl) was reported previously [3].



$L = (S)-(+)-(C_6H_5)_2PN(CH_3)CH(CH_3)C_6H_5$

Use of complexes **1–3** leads to exclusive formation of the silylated alcohol **4**, whereas with Rh catalysts varying amounts of the corresponding silylated enol **5** are

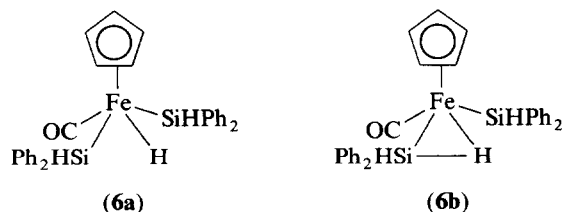
also formed [4,5] (eq. 1)



In the case of the Rh catalysts, the catalytic process is thought to proceed via a species in which three coordination sites are required for the oxidative addition of the silane and the addition of the unsaturated substrate [6–8]. The rate-determining step in the catalysis with iron complexes of the type described above is the thermal loss of the phosphine ligand L in **1** or **2** and the methyl migration in **3**, followed by addition of diphenylsilane and subsequent reaction with acetophenone.

We have now succeeded in isolating a catalytically active Fe-silane complex starting from $(C_5H_5)Fe(CO)_2(CH_3)$ (**3**). Hydrosilylation with 1 mol% of **3** as a catalyst gives the silylated alcohol **4** quantitatively within 24 hours at 70 °C. The reaction mixture darkens significantly during the reaction owing to the formation of the intermediate $(C_5H_5)Fe(CO)(SiHPh_2)_2H$ (**6**). Since species **6** readily reacts with acetophenone, only traces of **6** can be isolated at the end of the reaction. When **3** is heated at 80 °C for 2 hours with an excess of diphenylsilane in the absence of acetophenone, **6** can be isolated in 8% yield. Chromatography of the reaction mixture on silanised silica gel with petroleum ether as eluant at first removed traces of starting materials and then gave **6** and considerable amounts of $[CpFe(CO)_2]_2$. After repeated precipitation of the residue from petroleum ether, **6** remained as a black solid.

The 1H -NMR spectrum of **6** shows singlets for the protons of the cyclopentadienyl ring at 4.10 ppm, for the FeH proton at –12.38 ppm as well as for the silyl protons at 6.06 ppm. The magnetic equivalence of the SiH protons could either arise from oxidative addition of diphenylsilane (**6a**) or from rapid exchange of a hydrogen atom between a nonclassically bonded diphenylsilane and a σ -bonded silyl group (**6b**). There is ample precedence for classically [9,10] and nonclassically [11–14] bonded SiH groups in related complexes. We favour structure **6a** because there is no evidence for two kinds of silyl protons in the 1H -NMR spectrum when the temperature is lowered to –80 °C in toluene- d_8 .



The new complex **6** catalyses the hydrosilylation of acetophenone by diphenylsilane much more effectively than its precursor **3**. For complete conversion of the substrates with 1 mol% of **3** as a catalyst, a reaction time of 24 hours at 70 °C is required, whereas with **6** the reaction is complete after 3 hours at 50 °C.

$(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{SiHPh}_2)_2\text{H}$ (**6**)

A solution of 0.5 g of $\text{CpFe}(\text{CO})_2(\text{CH}_3)$ **3** in 2 ml of diphenylsilane was kept at 80 °C for 2 h. A dark-brown solution resulted. After dilution with 2 ml of petroleum ether, the mixture was chromatographed on a 50 cm column containing silanised silica gel. Petroleum ether initially eluted diphenylsilane and trace amounts of unchanged **3** and then separated the brown complex **6** from the red $[\text{CpFe}(\text{CO})_2]_2$. A considerable amount of decomposition products remained at the top of the column. Evaporation of the eluate containing containing **6** left a brownish black viscous oil and this was dissolved in a minimum amount of petroleum ether to redissolve and the solution cooled to -30 °C to give 110 mg (8%) of **6** as a black solid after vacuum drying.

IR (CH_2Cl_2): 1948 cm^{-1} (CO). $^1\text{H-NMR}$ (C_6D_6 , i-TMS, 250 MHz): δ = -12.38 (s, 1H, FeH), 4.10 (s, 5H, C_5H_5), 6.06 (s, 2H, SiH), 7.08–7.21 (m, 12H, *m*, *p*-ArH), 7.72–7.83 (m, 8H, *o*-ArH). Elemental analysis: Found: C, 69.94; H, 5.34. $\text{C}_{30}\text{H}_{28}\text{FeOSi}_2$ calc.: C, 69.75; H, 5.46%. MW 516.6.

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References

- 1 H. Brunner and H. Vogt, *J. Organomet. Chem.*, 210 (1981) 223.
- 2 H. Brunner and H. Vogt, *J. Organomet. Chem.*, 191 (1980) 181.
- 3 H. Brunner and K. Fisch, *Angew. Chem.*, 102 (1989) 1189; *Angew. Chem., Int. Ed. Engl.*, 29 (1990) 1131.
- 4 K. Yamamoto, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 46 (1972) C65.
- 5 H. Brunner and U. Obermann, *Chem. Ber.*, 122 (1989) 499.
- 6 J.L. Speier, *Adv. Organomet. Chem.*, 17 (1979) 407.
- 7 I. Ojima and K. Hirai, in J.D. Morrison (Ed.), *Asymmetric Synthesis*, Vol. 5, Academic Press, Orlando, 1985, p. 103.
- 8 F. Seitz and M.S. Wrighton, *Angew. Chem.*, 100 (1988) 28; *Angew. Chem., Int. Ed. Engl.*, 27 (1989) 289.
- 9 X.-L. Luo, G.K. Schulte, P. Demon and R.H. Crabtree, *Inorg. Chem.*, 29 (1990) 4268.
- 10 S.B. Duckett and R.N. Perutz, *J. Chem. Soc., Chem. Commun.*, (1991) 28.
- 11 A.J. Chalk and J.F. Harrod, *J. Am. Chem. Soc.*, 87 (1965) 1131.
- 12 A.J. Chalk and J.F. Harrod, *J. Am. Chem. Soc.*, 89 (1965) 1640.
- 13 E. Lukevics, Z.V. Belyakova, M.G. Pomeratseva and M.G. Voronkov, *J. Organomet. Chem. Lib.*, 5 (1977) 1.
- 14 U. Schubert, G. Scholz, J. Müller, K. Ackermann, B. Wörle and R.F.D. Stansfield, *J. Organomet. Chem.*, 306 (1986) 303.