Trialkylsilyl(hydrido)(ethylene)pentamethylcyclopentadienylrhodium(III) Complexes

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The equilibria $[(C_5Me_5)Rh(H)_2(SiEt_3)_2] + C_2H_4 \rightleftharpoons HSiEt_3 + [(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)]$, and $[(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)] + C_2H_4 \rightleftharpoons HSiEt_3 + [(C_5Me_5)Rh(C_2H_4)_2]$, can be induced either thermally or photochemically starting from either side.

In recent papers we reported the reaction of the rhodium(V) complex $[(C_5Me_5)Rh(H)_2(SiEt_3)_2]$ (**1**) with triphenylphosphine to give $[(C_5Me_5)Rh(H)(SiEt_3)(PPh_3)]$ (**4**)[1] and we also suggested that a related species, $[(C_5Me_5)Rh(H)(SiEt_3)(olefin)]$, may be intermediate in the olefin hydrosilylation and hydrosilylation-with-dehydrogenation reactions.[2]

We have now extended these investigations and report the characterisation of the complex $[(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)]$ (**2**), and the existence of the equilibria (1) and (2), which can be induced either thermally or photochemically, starting from either (**1**) or (**3**).

$$\underset{(\mathbf{1})}{[(C_5Me_5)Rh(H)_2(SiEt_3)_2]} + C_2H_4 \rightleftharpoons HSiEt_3 + \underset{(\mathbf{2})}{[(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)]} \quad (1)$$

$$\underset{(\mathbf{2})}{[(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)]} + C_2H_4 \rightleftharpoons HSiEt_3 + \underset{(\mathbf{3})}{[(C_5Me_5)Rh(C_2H_4)_2]} \quad (2)$$

$$\underset{(\mathbf{4})}{[(C_5Me_5)Rh(H)(SiEt_3)(PPh_3)]}$$

Irradiation of a cyclohexane solution of (**1**) under an atmosphere of ethylene (1 atm, 20 °C, 16 h) gave a mixture which was shown by n.m.r. spectroscopy to contain (**1**), (**2**), and (**3**) in the ratio 4 : 3 : 21. Complex (**2**) was identified (^{13}C n.m.r. at 100.62 MHz, $[^2H_8]$toluene, −70 °C) by a resonance at δ 97.0 (C_5Me_5) and two doublets, arising from the inequivalent ends of co-ordinated ethylene, at δ 36.0 [J(Rh–C) 10.2 Hz] and 37.6 [J(Rh–C) 13.4 Hz]. Upon warming, these two latter resonances coalesced to one doublet (30 °C, δ 38.7, J 12.2 Hz) owing to rotation of the co-ordinated ethylene.[3] As expected, even at −70 °C, the carbon resonances for the two ethylenes in (**3**) were seen as one doublet at δ 42.9 [J(Rh–C) 13.9 Hz]; the C_5Me_5 resonance came at δ 94.5 (J 3.7 Hz). The hydride signal of (**2**) at δ −13.75 [d, J(Rh–H) 35 Hz] in the ^1H n.m.r. spectrum was quite distinct from that of (**1**) (δ −13.85, J 36.9 Hz).[1] Observation of such a normal hydride resonance rules out any significant contribution to agostic bonding to the structure of (**2**), in contrast to the situation in $[(C_5H_5)Co(C_2H_4)H(L)]^+$ and its analogues.[4]

The ^{103}Rh n.m.r. spectrum of an irradiated solution of (**3**) and triethylsilane in cyclohexane was recorded using the INEPT pulse sequence [J(Rh–H) 35 Hz]. This showed two signals. One, at δ −1374.8 (with respect to Ξ 3.16 MHz = 0 p.p.m.) was an out-of-phase doublet with separation of 35 Hz, due to the mono-hydride (**2**). The separation of 35 Hz was in agreement with J(Rh–H) found from the ^1H spectrum. The other resonance, at δ −1714,[1] was also an out-of-phase doublet, but this time of separation 74 Hz. This was due to the dihydride (**1**), which has J(Rh–H) 36.9 Hz.†

Mixtures containing (**2**) by n.m.r. analysis were formed by either heating (85 °C) or irradiating the bis-ethylene complex (**3**) and triethylsilane, or by heating (85 °C) or irradiating a mixture of (**1**) and (**3**). Heating (**1**) and ethylene under pressure (60—70 °C, 50 atm) gave (**3**); (**2**) could not be detected but the volatiles showed the presence (g.c.–mass spectrometry) of vinyltriethylsilane and tetraethylsilane in the ratio 3 : 1.

It was not convenient to measure rates of reaction of (**1**) with ethylene, but the thermal reaction of (**1**) with either triphenylphosphine [to give (**4**)] or non-1-ene showed the same rates over molar ratios of (**1**) to reagent of 1 : 1—1 : 3 and 1 : 6—1 : 25 respectively. This suggests strongly that the rate-determining step in the substitution reactions of (**1**) is a unimolecular reductive elimination of triethylsilane and that a co-ordinatively unsaturated species, $[(C_5Me_5)Rh(H)(SiEt_3)]$, is an intermediate. The trimethylsilyl analogue of (**1**), $[(C_5Me_5)Rh(H)_2(SiMe_3)_2]$, underwent reaction with triphenylphosphine to give the trimethylsilyl analogue of (**4**), at only about 10% of the rate of (**1**). This emphasises the importance of steric factors in the dissociation process, as would be expected for a unimolecular reaction.

Complex (**1**) underwent H/D exchange in *all* positions on heating in C_6D_6, as shown by ^2H n.m.r. spectroscopy; we presume that this also occurs *via* initial dissociation of one triethylsilane and the η^2-co-ordination of the benzene, followed by oxidative addition of C_6D_5–D,[5] and redistribution of the label.

The fact that complexes such as (**2**) are reasonably stable makes them unlikely to be the transition states in the olefin hydrosilylation and related reactions,[2] but it makes their participation in such reactions quite plausible.

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† *Added in proof*: The ^{29}Si n.m.r. spectrum of a solution containing (**2**) showed a doublet at δ 38.2 [J(Rh–Si) 17.2 Hz] confirming the existence of a direct Rh–Si bond in this complex.

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