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Trialkylsilyl(hydrido)(ethylene)pentamethylcyclopentadienylrhodium(m) 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).

$$[(C_5Me_5)Rh(H)_2(SiEt_3)_2] + C_2H_4 \rightleftharpoons HSiEt_3 + (1) \\ [(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)] \\ (2)$$
(1)

$$[(C_{5}Me_{5})Rh(H)(SiEt_{3})(C_{2}H_{4})] + C_{2}H_{4} \rightleftharpoons$$
(2)
$$HSiEt_{3} + [(C_{5}Me_{5})Rh(C_{2}H_{4})_{2}] \qquad (2)$$
(3)
$$[(C_{5}Me_{5})Rh(H)(SiEt_{3})(PPh_{3})]$$
(4)

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, $[{}^{2}H_{8}]$ toluene, -70 °C) by a resonance at δ 97.0 (C₅Me₅) 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_5 Me₅ resonance came at δ 94.5 (J 3.7 Hz). The hydride signal of (2) at $\delta - 13.75$ [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 ¹⁰³Rh 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 C₆D₅-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 ²⁹Si 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.