

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

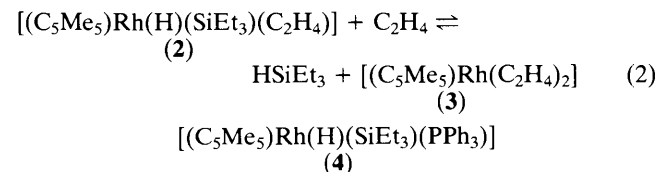
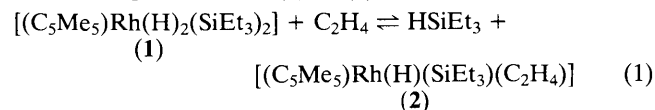
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The equilibria  $[(C_5Me_5)Rh(H)_2(SiEt_3)_2] + C_2H_4 \rightleftharpoons HSiEt_3 + [(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)]$ , and  $[(C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)] + C_2H_4 \rightleftharpoons HSiEt_3 + [(C_5Me_5)Rh(C_2H_4)_2]$ , can be induced either thermally 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**)<sup>1</sup> 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.<sup>2</sup>

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).



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 (<sup>13</sup>C n.m.r. at 100.62 MHz, [<sup>2</sup>H<sub>8</sub>]toluene, -70 °C) by a resonance at δ 97.0 (C<sub>5</sub>Me<sub>5</sub>) 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.<sup>3</sup> 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<sub>5</sub>Me<sub>5</sub> 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 <sup>1</sup>H n.m.r. spectrum was quite distinct from that of (1) (δ -13.85, *J* 36.9 Hz).<sup>1</sup> 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.<sup>4</sup>

The <sup>103</sup>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 <sup>1</sup>H spectrum. The other resonance, at δ -1714,<sup>1</sup> was also an out-of-phase

doublet, but this time of separation 74 Hz. This was due to the dihydride (**1**), which has  $J(\text{Rh-H})$  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,  $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{H})(\text{SiEt}_3)]$ , is an intermediate. The trimethylsilyl analogue of (**1**),  $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{H})_2(\text{SiMe}_3)_2]$ , 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  $\text{C}_6\text{D}_6$ , as shown by  $^2\text{H}$  n.m.r. spectroscopy; we presume that this also occurs *via* initial dissociation of one

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

triethylsilane and the  $\eta^2$ -co-ordination of the benzene, followed by oxidative addition of  $\text{C}_6\text{D}_5\text{-D}$ ,<sup>5</sup> 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,<sup>2</sup> but it makes their participation in such reactions quite plausible.

We thank Dr. R. Perutz for disclosing results on the photolysis of  $[(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2]$  and the formation of  $[(\text{C}_5\text{H}_5)\text{Rh}(\text{SiEt}_3)\text{H}(\text{C}_2\text{H}_4)]$ <sup>6</sup> prior to publication, and the S.E.R.C. and the City of Murcia, Spain, for support of this work.

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