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We have shown that the complex $[Rh(PPh_3)_2SnCl_3]$ (I), which was first described by Wilkinson al., [1], is an active catalyst for the isomerization of 1-hexene to a mixture of cis- and trans-2-hexenes and cis- and trans-3-hexenes in CH_2Cl_2 at 25°C in the absence of molecular hydrogen. The addition of gaseous HCl or excess PPh₃ sharply lowers the catalyst activity. The observed reaction presumably proceeds through a π -allylhydride mechanism (i.e., though the $[(\eta^3-ally1)RhH(PPh_3)_2SnCl_3]$ intermediate). This is indicated by 1,3 deuterium migration leading to a random deuterium distribution between C¹ and C³ in 3-propene-D₁ upon its reaction with (I) in CH_2Cl_2 studied using ¹³C NMR spectroscopy.

In the absence of HCl, $[Rh(PPh_3)_3Cl]$ (II), in contrast to (I), does not catalyze the isomerization of olefins. The isomerization of 1-hexene in a system consisting of (II) and HCl in CH_2Cl_2 (the optimal HCl:Rh ratio is 1) proceeds with a lower reaction order than when using complex (I) in the absence of HCl. ¹H and ³¹P NMR spectroscopy indicates that $[HCl_2Rh(PPh_3)_3]$ is the catalytically active complex.

Complex (I) was synthesized by the insertion of SnCl₂ into the Rh-Cl bond in complex (II). The composition and structure of (I) were confirmed by elemental analysis and ³¹P-{¹H} NMR spectroscopy in CH₂Cl₂ at -90°C. The spectrum obtained is an A₂BX spin system with 117/ 119 Sn satellites. ($\delta(P_A) = 31.1$, $\delta(P_B) = 27.3$ ppm; ¹J_{PA}-Rh = 124, ¹J_{PB}-Rh = 197, ²J_{PA}-P_B = 35, ²J_{PA}-IIISR = 453, ²J_{PA}-IIISR = 2516 Hz.

LITERATURE CITED

1. J. F. Young, R. D. Gillard, and G. Wilkinson, J. Chem. Soc., 5176 (1964).

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