Nondissociative Mechanism for Decomposition of Dialkylzirconocenes to produce Alkene–Zirconocene–Phosphine Complexes

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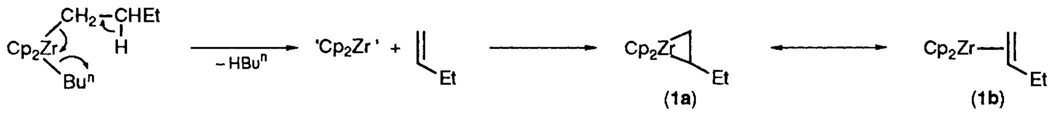
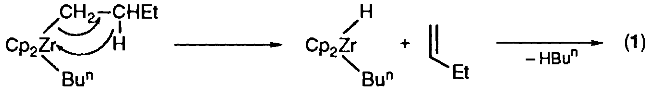
Examination of the reaction of $[Cp_2Zr(n\text{-}octyl)_2]$(**2**) with $D_2C{=}CH$–n-hexyl or styrene in the presence of PMe_3 by NMR spectroscopy rules out dissociative mechanisms for the conversion of (**2**) into alkene–$ZrCp_2$–PMe_3 complexes involving free $ZrCp_2$ and supports non-dissociative mechanisms (Cp = cyclopentadienyl).

We have recently reported that thermal decomposition of dialkylzirconocenes, such as $[Bu^n{}_2ZrCp_2]$ (Cp = cyclopentadienyl), provides the corresponding (alkene)zirconocenes, which can serve as convenient '$ZrCp_2$' sources and can be isolated and characterised as their complexes with phosphines, such as PMe_3.[1,2] This transformation can, in principle, proceed *via* dissociative mechanisms involving the intermediacy of free $ZrCp_2$, such as those shown in equations (i) and (ii), or *via* non-dissociative mechanisms, such as that shown in equation (iii). To date, however, no experimental data allowing the distinction between the two mechanistic types have been available.

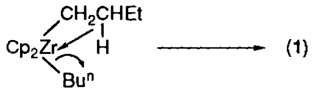
We now present experimental data which rule out dissociative mechanisms as defined above. Specifically, $[Cp_2Zr(Oct^n)_2]$ (**2**) (Oct^n = n-octyl) was generated *in situ* by addition of 2 equiv. of Oct^nLi in tetrahydrofuran (THF)[3] to solid $[Cp_2ZrCl_2]$ placed in a flask cooled at −78 °C. After the reaction mixture had been stirred for 30 min at −78 °C 1 equiv. of $CD_2{=}CHHex^n$ (Hex^n = n-hexyl) and 1.05 equiv. of PMe_3 were added at −78 °C, and the thermal decomposition process was monitored by ^{13}C NMR spectroscopy at −10 °C. Conversion of (**2**) into $[(oct\text{-}1\text{-}ene)ZrCp_2(PMe_3)]$ (**3**) was conveniently monitored by quantitative analysis of the Cp signal for (**2**) at δ 110.62 and those for (**3**) at δ 99.65 and 99.85. The decomposition reaction displayed first-order kinetics, $k_1 = (5.8 \pm 0.4) \times 10^{-3}\ min^{-1}$. This and three additional rate constants observed at −5, 0, and 5 °C yielded the following activation data: $\Delta H^{\ddagger} = 11.8 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -'24 \pm 1.5$ cal $mol^{-1}\ K^{-1}$ (1 cal = 4.184 J). Simultaneously, scrambling between oct-1-ene derived from (**2**) and 1,1-dideuteriooct-1-ene added externally was monitored also by ^{13}C NMR analysis. The internal olefinic carbon signal for



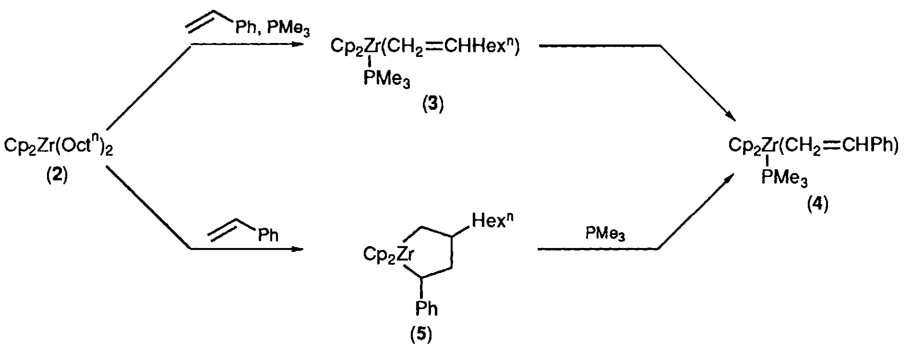
(i)



(ii)



(iii)



oct-1-ene appeared at δ 139.14, while that for the 1,1-dideuterio derivative appeared at δ 138.92. Significantly, the alkene scrambling process lagged far behind conversion of (**2**) to (**3**). Thus, at 50% conversion of (**2**) to (**3**), <5% of oct-1-ene had been freed from (**3**) by displacement with 1,1-dideuteriooct-1-ene, even though an essentially 50:50 mixture of free oct-1-ene and its 1,1-dideuterio derivative was eventually obtained upon warming the reaction mixture to 25 °C. To rule out the possibility that the observed results might be a consequence of some kinetic deuterium isotope effects, we prepared $[Cp_2Zr(CD_2C_7H_{15}{}^n)_2]$ and monitored its decomposition in the presence of 1 equiv. of oct-1-ene and 1.05 equiv. of PMe_3 in the same manner at −10 °C by ^{13}C NMR spectroscopy. Both the rate of decomposition, $k_1 = (5.5 \pm 0.5) \times 10^{-3}\ min^{-1}$, and the rate of alkene exchange were comparable to those presented above for the reaction of (**2**).

The reaction of $[Cp_2Zr(Oct^n)_2]$ (**2**) with 1 equiv. of styrene in the presence of 1.05 equiv. of PMe_3 at 25 °C produced within a few hours styrene–$ZrCp_2$–PMe_3 (**4**) as a 70:30 mixture of two stereoisomers in 90% NMR yield, the yield of (**3**) being <2%. We have previously shown that the reaction of (**2**) with 1 equiv. of styrene in the absence of PMe_3 predominantly produces (**5**).[3] Interestingly, subsequent treatment of (**5**) with 1.05 equiv. of PMe_3 at 25 °C for 1 h cleanly produced (**4**) in 90% yield. These results not only indicate that, under thermodynamic conditions, (**4**) is strongly favoured over (**3**), but also provide an additional clear-cut example which points to the chemical lability of the C(3)–C(4) bond of the zirconacyclopentane ring.[2,4,5] To probe further the mechanism of the reaction of (**2**) with styrene in the presence of PMe_3, it was monitored by ^1H NMR spectroscopy at −10 °C. Significantly, the initially formed product at this temperature was (**3**), and the yield of (**4**) at the time of 50% conversion of (**2**) into (**3**) was <5%. An authentic sample of (**4**) was prepared by decomposition of $[Cp_2Zr(CH_2CH_2Ph)_2]$ in the presence of PMe_3, for which the first-order rate constant of $k_1 = (1.4 \pm 0.1) \times 10^{-2}\ min^{-1}$ at −20 °C was obtained.

The experimental results herein presented rule out, for the first time, any dissociative mechanisms involving the intermediacy of free $ZrCp_2$ and firmly support non-dissociative mechanisms, of which that shown in equation (iii) is a plausible example.

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