Selective Skeletal Rearrangement by Carbon–Carbon Bond Activation

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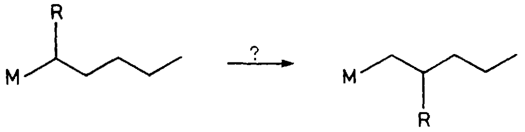
Skeletal rearrangement of α-substituted organometallic compounds to give β-substituted compounds by carbon–carbon bond activation was performed with bis(η^5-cyclopentadienyl)-2,5-dimethyl-zircona- or -hafna-cyclopentane, which were regio- and stereo-selectively converted into the corresponding 3,4-dimethylmetallacyclopentanes in high yield.

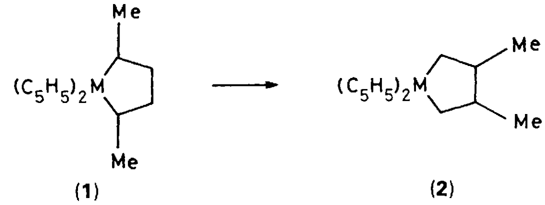
Selective skeletal rearrangement by carbon–carbon bond activation is a potentially attractive methodology in organic synthesis. Reaction (1) for organometallic compounds can be considered to be representative. We now describe a novel selective rearrangement by carbon–carbon bond activation using organozirconium or organohafnium compounds (Scheme 1).

The zirconium complex (**1a**) with methyl groups on the α- and α′-carbon atoms was prepared *in situ* from $(C_5H_5)_2ZrCl_2$ and the corresponding Grignard reagent (**3**), and underwent selective skeletal rearrangement during 1 h at room temperature by carbon–carbon activation to give 2,3-dimetylbutane after hydrolysis in 98% yield based on the metal. Bromination of the reaction mixture instead of hydrolysis gave (±)-1,4-dibromo-2,3-dimethylbutane selectively [(±):*meso* 99:1] (Scheme 2). 2,5-Dibromohexane was totally absent.

The hafnium derivative (**1b**) reacted similarly, at higher temperature. The rearrangement product 2,3-dimethylbutane was obtained in 53 and 98% yield during 1 h at 50 and 80 °C, respectively, after hydrolysis. The reaction was monitored by ^{1}H NMR spectroscopy. Reaction of $(C_5H_5)_2HfCl_2$ with the Grignard reagent (**3**) quantitatively afforded (**1b**), the ^{1}H NMR spectrum of which showed a C_5H_5 signal at δ 5.89. At 50 °C three new singlets assignable to the C_5H_5 groups of (**2b**) and two intermediates, 2,4-dimethylhafnacyclopentane isomers, emerged at δ 5.93, 5.90, and 5.87, respectively, and grew at the expense of that of (**1b**) at δ 5.89. This process obeyed first-order kinetics, $k_1 = (6.5 \pm 0.2) \times 10^{-3}$ min^{-1} at 50 °C. The final spectrum revealed only one singlet peak for



(1)

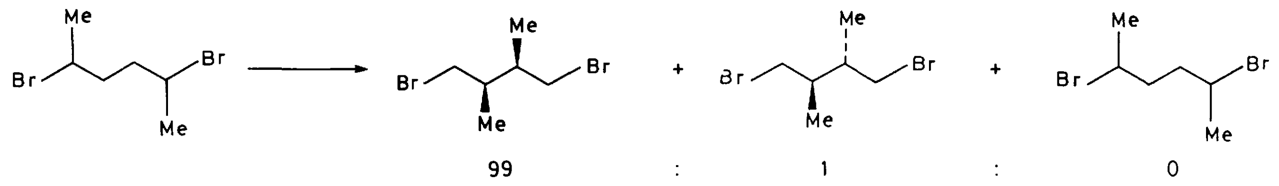


(**1**) (**2**)

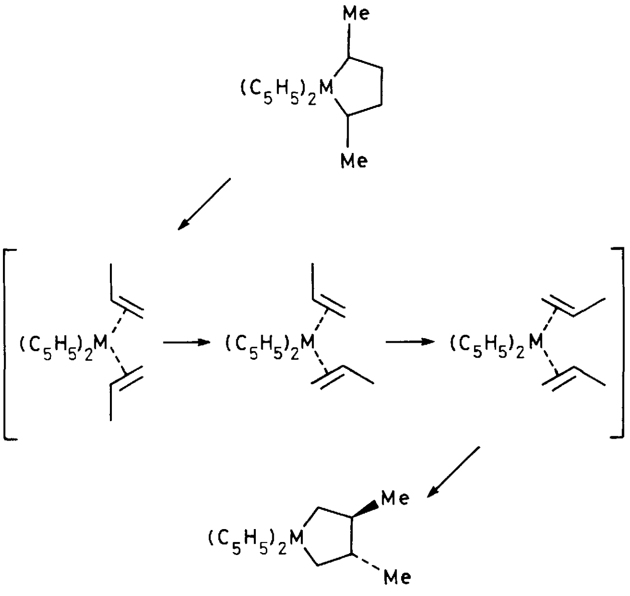
MeCH(MgBr)CH_2CH_2CH(MgBr)Me
(**3**)

a; M = Zr
b; M = Hf

Scheme 1



Scheme 2. *Reagents*: Mg, then $(C_5H_5)_2ZrCl_2$, then Br_2.



Scheme 3

the C_5H_5 group of (**2b**) at δ 5.93, signals due to the C_5H_5 groups of the starting material and the two intermediates having completely disappeared.

Zircona- and hafna-cyclopentane complexes undergo carbon–carbon bond cleavage to give zirconium and hafnium ethylene complexes,[1—3] respectively. Similar transformations of some other metallacyclopentanes have been reported.[4] As expected, addition of an excess of PMe_3 to bis(η^5-cyclopentadienyl)dimethylzirconacyclopentane prepared *in situ* led to carbon–carbon bond cleavage to produce the zirconocene–propene complex which was identified by its characteristic ^1H, ^{13}C, and ^{31}P NMR spectra, which were the same as those of an authentic sample obtained from dipropylzirconocene complex.[5]

Furthermore, a cross-over experiment using bis(η^5-cyclopentadienyl)zirconacyclopentane and (**2a**) gave 1,4-dibromo-2-methylbutane in 10% yield after bromination of the mixture.

These results strongly suggest a β,γ-carbon–carbon bond activation of (**1**). Bis(alkene)complexes have been proposed as chemical species after β,γ-carbon–carbon bond fission of metallacyclopentane systems.[3,4] Although the determination of the structure of the actual intermediate species of the rearrangement reactions must await further investigations, the skeletal rearrangements can be explained by the mechanism in Scheme 3 involving β,γ-carbon–carbon bond activation, followed by formation of a bis(alkene) complex, rotation of the alkenes due to steric hindrance, and selective coupling of two alkenes on the metal.

Recently we have found regio- and stereo-selective alkene coupling reactions on zirconium or hafnium compounds.[6] The reaction of propene with $(C_5H_5)_2Zr(MeCH{=}CH_2)^5$ prepared *in situ* from $(C_5H_5)_2ZrPr_2$ afforded, after bromination, 1,4-dibromo-2,3-dimethylbutane, displaying a very similar regio- and stereo-selectivity pattern as the skeletal rearranged product.

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