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Homologation of α-Olefins with Ethene by a Neutral Zirconium Alkyl Complex

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A prime aspect of the organoaluminium chemistry developed by K. Ziegler and his group in the 1950s is the insertion of ethene into the Al-C bonds of AlEt₃ to give Al₂{(CH₂CH₂)₃Et}, derivatives with a narrow (Poisson) distribution of chain lengths. Chain growth takes place under rather drastic conditions (100-120 °C, ≥200 bar) and may be followed by a displacement reaction with ethene or other olefins at high temperature (≥200 °C) and low pressure to release a narrow distribution of linear α-olefins. This principle has been the basis of commercial syntheses of linear α-olefins and alcohols. While investigating the chemistry of the neutral 14-electron organoaluminium species Al₃{C₆H₅C₂H₅}₄, we predicted the occurrence of homologation of linear α-olefins with ethene to give higher linear α-olefins.

A subtle structural difference between the Zr and Hf alkyl complexes is revealed by comparison of the NMR spectra of the n-Bu derivatives. The Zr ethyl complex Cp*Zr(CH₃)₂Et was known from NMR and IR data to have a β-agostic structure (especially noticeable in the upfield shift for the β-protons and the relatively large 1JCH coupling on the α-carbon). We found these features to be absent in the Hf n-Bu derivative I. Such a difference between ethyl and higher alkyl derivatives has been observed in other systems as well (e.g., for Cp*Sn alkyl). For Zr, the n-Bu derivative 2 still has the upfield β-proton resonance (δ -0.82 ppm), and this feature appears to be present for all other n-alkyl derivatives (vide infra). It suggests a difference in relative stability of the ethyl derivative (agostic for both metals) versus the higher alkyl derivatives (nonagostic for Hf only).

The zirconium complex Cp*Zr(CH₃)₃(n-Bu) (2) reacts with 3 equiv of ethene (C₆D₆ solvent, 20 °C) within 15 min to give a mixture of Cp*Zr(CH₃)(CH₂CH₂)Bu species. A broad 1H NMR resonance around δ -0.7 ppm is indicative of β-agostic interaction in these compounds. By GC⁶ it is seen that a Poisson-type distribution of Zr alkyl chains is formed (Figure 1a). Only a small fraction (5%) of α-olefins results from chain transfer with ethene. Addition of new portions of ethene (each of 2 equiv) to the mixture shifts the center of the alkyl group distribution towards higher chain lengths (Figure 1b,c). This shows that the Zr-alkyl species are still capable of further olefin insertion and that the alkyl groups show virtually living growth with ethene at ambient temperature. With each portion of ethene added some additional α-olefin is produced, but by NMR no significant accumulation of the Zr ethyl species is seen.

The Cp*Zr(C₆H₅)(n-alkyl) species react with α-olefins at slightly elevated temperatures to give displacement of the alkyl group, rather than insertion into the Zr alkyl bond. Thus, Cp*Zr(C₆H₅)(n-Bu) (2) reacts with excess propene at 50 °C (C₆D₆ solvent) to give Cp*Zr(C₆H₅)(n-Pr) and 1-butene. This combination, with the observed “living” growth of the alkyl groups with ethene, allows the performance of Aufbau homologation of α-olefins with ethene via sequential chain growth (A) and chain transfer (B) to give a narrow distribution of higher α-olefins (Scheme 1).

This possibility was demonstrated with a simple experiment. A solution of Cp*Zr(C₆H₅)(n-Bu) (2) and 10 equiv of 1-pentene in C₆D₆ solvent was subjected to four consecutive cycles of (a) reaction with 1.5 equiv of ethene (10 min at 20 °C) to effect chain growth and (b) warming to 50 °C for 10 min to effect chain transfer. The resulting α-olefin distribution after each cycle is shown in Figure 2. After the first cycle, a distribution of C-even olefins is observed (Figure 2a). After the second cycle an additional distribution of C-odd olefins is produced (Figure 2b), essentially mimicking the first but with one additional carbon per chain (now starting from a ZrC₃ instead of a ZrC₂ species). The two subsequent cycles essentially add to the C-odd olefin distribution (Figure 2c,d). It shows that the stepwise homologation of 1-pentene with ethene can be performed with this system under conditions unusually close to ambient. The amount of branching introduced in the olefinic

homologation product is small (<1%). However, slow concomitant dimerization of the excess 1-pentene and olefin isomerization are also observed. This appears to occur mainly during the displacement step.

The reactivity of the Hf n-butyl complex I is quite different. At ambient temperature and pressure, reaction with ethene is slow (approximately 40 times slower than that for Zr), producing a mixture of Cp*Hf(C₆H₁₀)Et (>70%), Cp*Hf(C₆H₁₀)-(CH₂CH₃)₃H (<30%), and linear α-olefins. It shows that for Hf the rates of ethene insertion and chain transfer are much more closely matching than for Zr and that the Hf ethyl species (stabilized relative to the other alkyl species by a β-agostic interaction) accumulates as “resting state”. Under 39 bar of ethene at 100 °C (benzene solvent), Cp*Hf(C₆H₁₀)Et catalyzes the oligomerization of ethene to a Flory-Schultz distribution ([C₆]+2/[C₆] = 0.31) of linear α-olefins with high selectivity (C₆ fraction is >99.6% 1-hexene) but low productivity (16.8 g of 1-hexene (g Hf)⁻¹ h⁻¹ over 3 h).

Preliminary investigations into the rates of propagation versus chain transfer in these systems suggest that the main difference in observed reactivity between the Zr and Hf complexes is due to a much greater rate of insertion of ethene into the Zr alkyl bond (approximately by at least a factor of 40). In contrast, the intrinsic rate of β-elimination as determined from the rate of isomerization of Cp*Zr(C₆H₁₀)(i-Pr) to the corresponding n-Pr derivatives for Zr was only about 4 times faster than that for Hf. This gives the Zr alkyl system under the applied conditions virtually living character in its reaction with ethene.

“Living” growth of transition metal alkyls with ethene and “living” polymerization of ethene with cationic transition metal complexes has been observed in a number of cases, usually at low (-80 to -0 °C) temperatures, To our knowledge, Cp*Zr(C₆H₁₀)(alkyl) is the first transition metal alkyl system that shows Aufbau-type chemistry under ambient conditions.

In this respect it may be noted that in the recently reported system Cp*Zr(C₆H₁₀)Me₂/MAO (M = Nb, Ta), which polymerizes ethene to give polyethylene with unusually narrow polydispersities, the proposed active cationic species [Cp*Zr-(C₆H₁₀)Me]⁺ is isoelectronic with the diene-alkyl complexes discussed here.

Supporting Information Available: Experimental procedures and spectroscopic data for reported compounds (7 pages). See any current masthead page for ordering and Internet access instructions.