Homologation of α-Olefins with Ethene by a Neutral Zirconium Alkyl Complex
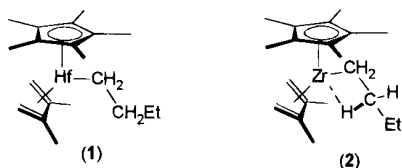
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A prime aspect of the organoaluminium chemistry developed by K. Ziegler and his group in the 1950s is the insertion of ethene into the Al-C bonds of AlEt$_3$ to give Al[(CH$_2$CH$_2$)$_n$Et]$_3$ derivatives[1] with a narrow (Poisson) distribution[2] 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[3] to release a narrow distribution of linear α-olefins. This principle has been the basis of commercial syntheses of linear α-olefins and alcohols.[4] While investigating the chemistry of the neutral 14-electron alkyl complexes Cp*M(C$_6$H$_{10}$)(alkyl) (Cp* = *h*^{5}-C$_5$Me$_5$; C$_6$H$_{10}$ = 2,3-dimethyl-1,3-butadiene; M = Hf,[5] Zr), we observed subtle yet significant differences in structure and reactivity between the Zr and Hf congeners. The Zr alkyl derivatives were found to react with ethene at ambient temperature and pressure to give virtually living growth of the alkyl group. This allows Ziegler-type "Aufbau" chemistry to occur under unusually mild conditions. We used this to perform the stepwise 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.[6] The Hf ethyl complex Cp*Hf(C$_6$H$_{10}$)Et was known from NMR and IR data to have a *b*-agostic structure (especially noticeable in the upfield shift for the *b*-protons and the relatively large $^1J_{CH}$ coupling on the α-carbon).[5b] We found these features to be absent in the Hf *n*-Bu derivative **1**. Such a difference between ethyl and higher alkyl derivatives has been observed in other systems as well (e.g., for Cp*$_2$Sc alkyl[7]). For Zr, the *n*-Bu derivative **2** still has the upfield *b*-proton resonance (*d* -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(C$_6$H$_{10}$)(*n*-Bu) (**2**) reacts with 3 equiv of ethene (C$_6$D$_6$ solvent, 20 °C) within 15 min to give a mixture of Cp*Zr(C$_6$H$_{10}$)[(CH$_2$CH$_2$)$_n$Bu] species. A broad
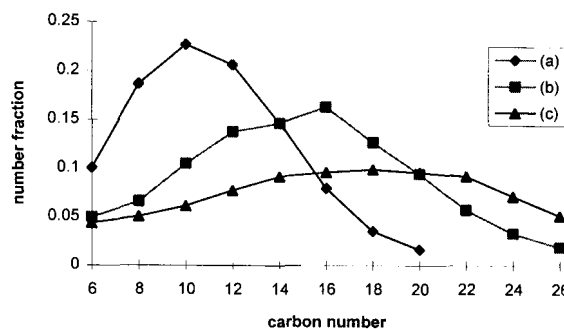

Figure 1. Alkyl chain length molar distributions from the reaction of **2** with (a) 3 equiv of ethene, (b) with an additional 2 equiv, and (c) with a second additional 2 equiv.

^{1}H NMR resonance around *d* -0.7 ppm is indicative of *b*-agostic interaction in these compounds. By GC[8] 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 to higher chain lengths (Figure 1b,c). This shows that the Zr-alkyl species are still capable of further ethene 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(C$_6$H$_{10}$)(*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-(C$_6$H$_{10}$)(*n*-Bu) (**2**) reacts with excess propene at 50 °C (C$_6$D$_6$ solvent) to give Cp*Zr(C$_6$H$_{10}$)(*n*-Pr) and 1-butene. This feature, combined 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).
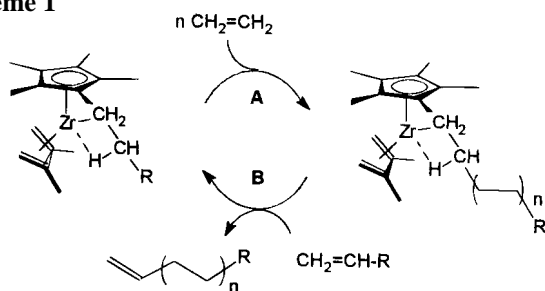
This possibility was demonstrated with a simple experiment. A solution of Cp*Zr(C$_6$H$_{10}$)(*n*-Bu) (**2**) and 10 equiv of 1-pentene in C$_6$D$_6$ solvent was subjected to four consecutive cycles of (a) reaction with 1.5 equiv of ethene (10 min at 20 °C) to effect chain growth and (b) warming to 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 Zr-C$_5$ instead of a Zr-C$_4$ 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

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(4) (a) Chauvel, A.; Lefebvre, G. *Petrochemical Processes*; Editions Technip: Paris, 1989; Vol. 1, p 180. (b) *Ibid.*; Vol. 2, p 95. (c) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*; VCH: Weinhem, 1993; p 75. (d) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992; p 69.

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(6) NMR data (C$_6$D$_6$ solvent, *J* values given in hertz) of the alkyl group in Cp*M(C$_6$H$_{10}$)(*n*-Bu). For M = Zr (**2**): ^{1}H NMR (300 MHz) *d* 1.35 (ps sextet, 7 Hz, 2H, *g*-CH$_2$), 0.94 (t, 7.3 Hz, 3H, *d*-CH$_3$), 0,30 (m, 2H, α-CH$_2$), -0.82 (m, 2H, *b*-CH$_2$); ^{13}C NMR (75.4 MHz) *d* 15.14 (q, 125 Hz, *d*-CH$_3$), 20.37 (t, 114 Hz, *b*-CH$_2$), 27.19 (t, 125 Hz, *g*-CH$_2$), 53.94 (t, 128 Hz, α-CH$_2$). For M = Hf (**1**): ^{1}H NMR *d* 1.34 (ps sextet, 7.1 Hz, 2H, *g*-CH$_2$), 0.94 (t, 7.2 Hz, 3H, *d*-CH$_3$), 0.17 (m, 2H, *b*-CH$_2$), -0.03 (m, 2H, α-CH$_2$); ^{13}C NMR *d* 14.65 (q, 124 Hz, *d*-CH$_3$), 22.37 (t, 120 Hz, *b*-CH$_2$), 28.13 (t, 124 Hz, *g*-CH$_2$), 64.25 (t, 117 Hz, α-CH$_2$).

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(8) GC samples were drawn from the reaction tube through a septum and injected into the GC sample port. Under these conditions, alkyl groups bound to the metal are liberated as alkanes and are readily distinguished from olefins formed via chain transfer with ethene.
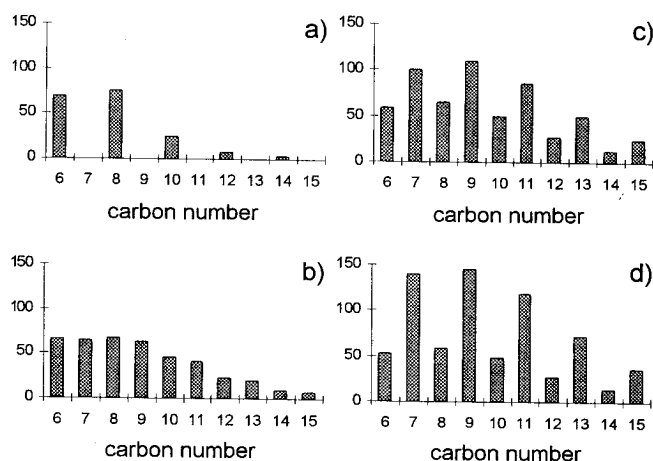
Scheme 1

Figure 2. Molar distribution of α-olefins from the reaction of **2** and 10 equiv of 1-pentene in C_6D_6 with sequential portions of 1,5 equiv of ethene at 20 °C followed by warming to 50 °C: after 1 (a), 2 (b), 3 (c), and 4 (d) cycles, respectively,

homologation product is small (<1 %). However, slow concomitant dimerization of the excess 1-pentene and olefin isomerization are also observed.[9] This appears to occur mainly during the displacement step.

The reactivity of the Hf *n*-butyl complex **1** 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(C_6H_{10})Et (>70%), Cp*Hf(C_6H_{10})-$(CH_2CH_2)_nH$ (<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 ***b***-agostic interaction) accumulates as "resting state". Under 39 bar of ethene at 100 °C (benzene solvent), Cp*Hf(C_6H_{10})Et catalyzes the oligomerization of ethene to a Flory-Schultz distribution ($[C_{n+2}]/[C_n]$ = 0.31) of linear α-olefins with high selectivity (C_6 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 ***b***-elimination as determined from the rate of isomerization of Cp*M(C_6H_{10})(*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[7b,10] and "living" polymerization of ethene with cationic transition metal complexes[11,12] has been observed in a number of cases, usually at low (-80 to -0 °C) temperatures, To our knowledge, Cp*Zr(C_6H_{10})(alkyl) is the first transition metal alkyl system that shows Aufbau-type chemistry under ambient conditions.[13]

In this respect it may be noted that in the recently reported system Cp*M(C_6H_{10})Me$_2$/MAO (M = Nb, Ta), which polymerizes ethene to give polyethylene with unusually narrow polydispersities,[12] the proposed active cationic species [Cp*M-(C_6H_{10})Me]$^+$ is isoelectronic with the diene-alkyl complexes discussed here.

(9) After four cycles, the amount of 2-propyl-1-heptene is comparable to that of linear C_{10} product from the first cycle (GC); 11 % of total olefins are internal (NMR) and the homologation products contain about 5% internal olefins (GC).

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(13) Catalytic oligomerization of ethene in the presence of α-olefins has in some cases been observed to lead to homologation of the α-olefins. Doyle, M. J. Eur. Pat. Appl. EP 596553 (1994, to Shell).