Communication

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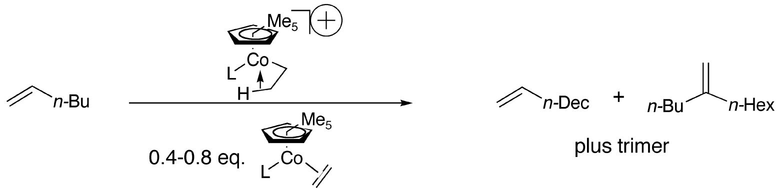

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Cobalt-Catalyzed Dimerization of α-Olefins to Give Linear α-Olefin Products

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Linear α-olefins in the C_6-C_{20} range have broad utility including use as comonomers in the production of linear low-density polyethylene and as precursors to detergents, synthetic oils, and plasticizers.[1] These olefins are commercially produced primarily through oligomerization of ethylene followed by fractionation of the resulting broad distribution of even-numbered carbon oligomers.[1] Catalyst systems have been developed which selectively trimerize ethylene to 1-hexene,[2] and more recently certain chromium systems have shown selectivity for forming the tetramer, 1-octene.[3] An alternate, attractive method for producing specific higher α-olefins would be the dimerization of low carbon number α-olefins, for example, conversion of 1-butene to 1-octene or conversion of 1-hexene to 1-dodecene.

Small[4] described the use of cobalt pyridine bis-imine catalysts that dimerize propene to 1-hexene as a major product through a cycle involving 1,2 insertion of propene into a metal hydride followed by 2,1 insertion to yield $L_nM(CH(CH_3)CH_2CH_2CH_2CH_3)$. β-Elimination of this species generated 1-hexene together with 2-hexene. Use of 1-butene as monomer led to internal olefin dimers with high linearity. Indeed, there are no reports of dimerization of α-olefins other than propene to linear *terminal* olefin dimers. Wasserschied reported Ni catalysts which convert 1-butene predominantly to linear octenes containing internal double bonds.[5,6] Small also reported iron pyridine bis-imine catalysts that convert 1-butene, 1-pentene, and 1-hexene to linear dimers with internal unsaturation.[7] Gibson described similar results for the dimerization of propene, 1-butene, and 1-hexene using a supported, electron-poor, cobalt pyridine bis-imine catalyst.[8] We report here cobalt-catalyzed oligomerization of 1-hexene and a mechanistically unique catalytic process wherein C_nH_{2n} α-olefins can be converted, in part, to $C_{2n}H_{4n}$ α-olefins.

Oligomerization of 1-hexene catalyzed by $[Cp^*CoP(OMe)_3Et]^+$ $BArF^-$ (**1**) [generated in situ by addition of 1 equiv of HBArF [HBArF = $(3,5\text{-}(CF_3)_2C_6H_3)_4B^-$ $(Et_2O)_2H^+$] to $Cp^*CoP(OMe)_3$-(ethene) (**2**)][9] was carried out in 1,2-difluorobenzene solutions (40 vol % 1-hexene) at 25 °C under argon. One dimer and two trimers along with minor amounts of tetramers were formed; the structures of the dimer and trimers are shown in Figure 1. After one turnover and loss of the ethyl group, the catalytic cycle can be described as illustrated with the hydride as chain carrier. Dimer **A** (66 mol % based on GC analysis using an internal standard) is the result of 1,2 insertion of 1-hexene into the Co-hexyl species **3** to give **4**. β-Elimination of **4** provides dimer **A**. A second 1,2 insertion of 1-hexene into **4** followed by β-elimination produces the minor trimer **B** (7 mol %). When **3** undergoes 2,1 insertion with 1-hexene, metal migration down the chain via β-elimination/readdition produces the terminal dodecyl agostic species **5** which apparently undergoes insertion faster than β-elimination. Insertion of hexene into **5** in a 1,2 manner followed by β-elimination produces the major trimer, **C** (27 mol %).[10−12] Dimer **A** and trimers **B** and **C** were identified by independent synthesis (see Supporting Information). The formation of the dimer and trimers is slow with turnover frequencies of about 0.65 h^{-1} over 12 h. Turnover numbers of about 80 are found after 10 days of reaction.

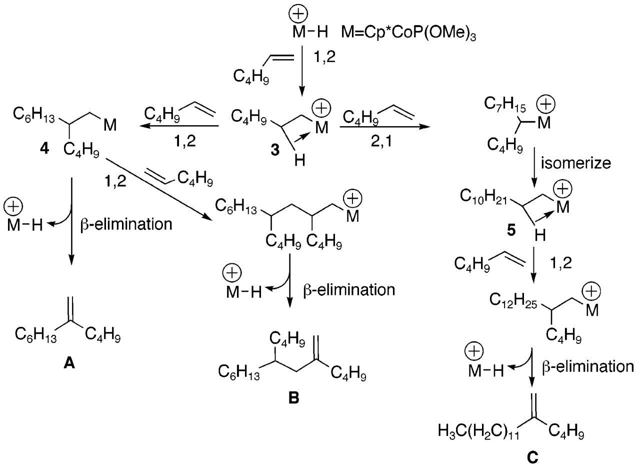

Figure 1. Catalytic oligomerization of 1-hexene initiated by **1** formed by protonation of **2** with HBArF. 1,2 and 2,1 refer to the olefin insertion modes.

Surprisingly, when a deficit of HBArF was used to protonate **2** in the presence of 1-hexene the oligomer distribution was altered; 1-dodecene was now formed at the expense of dimer **C**. For example, use of 0.82 equiv of HBArF yielded after 3.5 h 80% **A**, 5% **B**, only 1% **C**, and the formation of 14% 1-dodecene. After 12 h similar ratios of **A**, **B**, **C**, and dodecene were observed of which about 25% had isomerized to internal olefins.[13] Runs were carried out varying the HBArF between 40 and 85 mol %.[14] As expected higher turnover frequencies were observed with higher HBArF loadings. The turnover frequency was proportional to the concentration of 1-hexene, and productivity doubled with a doubling of the catalyst concentration. When a 4:1 ratio of isolated agostic ethyl salt $[Cp^*CoP(OMe)_3CH_2CH_3]^+[BArF]^-$ and neutral ethylene complex **2** was employed in catalysis, the same ratio of **A**/**B**/dodecene was observed as when 80 mol % HBArF was used. Similar reactivity was seen in the dimerization of 1-octene to 1-hexadecene and 1-butene to 1-octene.

A mechanism consistent with formation of 1-dodecene at the expense of trimer **C** is shown in Figure 2. Using less than 1 equiv of HBArF results in formation of a mixture of agostic hexyl complex **6** and neutral 1-hexene complex **7** after one turnover of the mixture of neutral and cationic C_2 starting complexes **1** and **2**. Following 2,1 insertion of 1-hexene into **6** and isomerization to the agostic dodecyl complex **5** (see Figure 1), proton exchange between **5** and the neutral 1-hexene complex **7** yields the agostic

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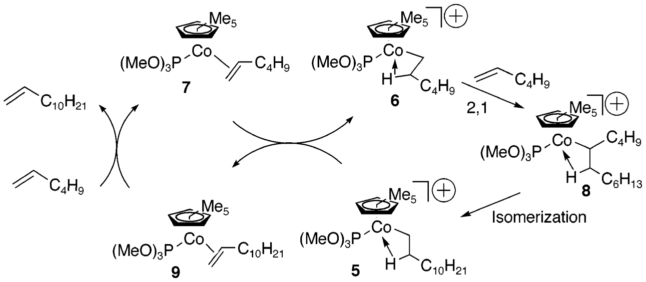
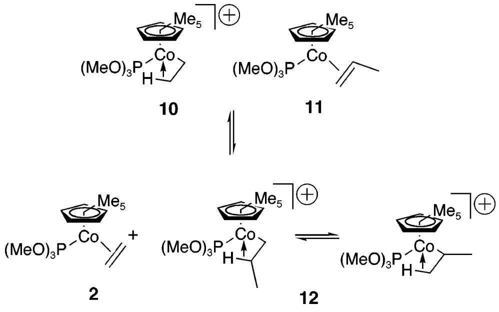


Figure 2. Formation of 1-dodecene via intermolecular agostic H transfer.

Scheme 1. Intermolecular Exchange of Agostic Hydrogen



hexyl complex **6** and neutral 1-dodecene complex **9**. Exchange of coordinated 1-dodecene in **9** by 1-hexene yields free 1-dodecene and neutral 1-hexene complex **7**, which reenters the catalytic cycle.

Two experiments provide evidence that this bimolecular process is a viable pathway for this transformation. Isolated cationic ethyl complex **10** was allowed to react with 1-hexene for 12 h at which time GC analysis showed a turnover frequency for 1-dodecene of 0.015 h^{-1}. At that time, the neutral complex **2** (ratio **10**/**2** = 4/1) was added, and another aliquot was taken after a further 12 h showing a TOF of 0.05 h^{-1}. As a comparison, the TOF for formation of dimer **A** decreased from 0.76 to 0.64 h^{-1} over the same period of time. Addition of 1-hexene to a solution of the neutral ethene complex in the absence of either HBArF or **10** gave no oligomerization. This clearly demonstrates that the addition of neutral **2** to **10** increases the rate of formation of 1-dodecene. In the second experiment, ethyl agostic complex **10** and propene complex **11** were mixed in C_6D_5Cl, and the reaction was monitored over time by ^1H NMR spectroscopy (Scheme 1). Within 50 min, signals for the propyl agostic complex **12**[9] and the neutral ethene complex **2** were observed. This shows that the transfer of an agostic H to a neutral species is possible. Over longer periods of time, $Cp^*CoH(P(OMe)_3)_2{}^+BArF^-$ formed and ultimately became the major species in solution.

In summary, this work demonstrates an unprecedented process, conversion of α-olefins to linear α-olefin dimers. Although this is a potentially valuable process, the catalyst reported here is not practical due to competitive formation of branched dimers and slow turnover frequencies. However, these studies suggest generally how chain-walking, proton transfer, and olefin exchange can be coupled to achieve this unique dimerization process. More efficient catalysts based on this scheme are being sought.

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Supporting Information Available: Full experimental procedures for the dimerization and oligomerization reactions and for the synthesis of reference compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Vogt, D. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W., Eds.; VCH: New York, 1996; Vol. 1, pp 245−257.

(2) For Cr catalysts: (a) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun*. **2002**, 858. (b) McGuinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552. (c) For Ta catalysis: Andes, C.; Harkins, S. B.; Murtuza, S.; Oyler, K.; Sen, A. *J. Am. Chem. Soc*. **2001**, *123*, 7423. (d) For Ti catalysis: Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Angew. Chem., Int. Ed*. **2001**, *40*, 2516.

(3) Bollmann, A. et al. *J. Am. Chem. Soc.* **2004**, *126*, 14712.

(4) Small, B. L. *Organometallics* **2003**, *22*, 3178.

(5) Ellis, B.; Keim, W.; Wasserscheid, P. *Chem. Commun*. **1999**, 337.

(6) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 1, pp 258−268.

(7) Small, B. L.; Marcucci, A. J. *Organometallics* **2001**, *20*, 5738.

(8) Tellmann, K. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Organometallics* **2005**, *24*, 280.

(9) Brookhart, M.; Lincoln, D. M.; Volpe, A. F.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212.

(10) Preliminary accounts of this work have appeared in (a) Brookhart, M.; Volpe, A. F.; DeSimone, J. M.; Lamanna, W. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 461. (b) Volpe, A. F., Jr. Olefin Polymerization Catalysts Based on Highly Electrophilic Co(III) Complexes: Mechanistic Studies and Catalyst Design. Ph.D. Thesis, University of North Carolina Chapel Hill, 1991. The structure of dimer **C** was reported incorrectly in (a).

(11) Replacement of $P(OMe)_3$ with PMe_3 results in a >20:1 ratio of the dimer **A** formed through 1,2 insertion relative to trimer **C**. Presumably the larger size of PMe_3 relative to $P(OMe)_3$ directs the insertion through the 1,2 mode. Use of ligands less sterically demanding than $P(OMe)_3$ should improve the regioselectivity of the insertion.

(12) Different batches of catalyst provide slightly different ratios of **A**/**B**/**C**. For instance, use of the same catalyst batch for the oligomerization as is used for the reaction shown in Figure 2 gives a ratio of 81:6:13.

(13) The isomerization of 1-dodecene is assumed to be metal catalyzed, but we have not yet identified the active species. No free HBArF was observed when a deficit was used to promote the reaction.

(14) Use of greater than 1 equiv of HBArF gave olefin isomerization to internal olefin products presumably through an acid-catalyzed process.

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