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Communications

The Role of Metallacycles in the Chromium-Catalyzed Trimerization of Ethylene

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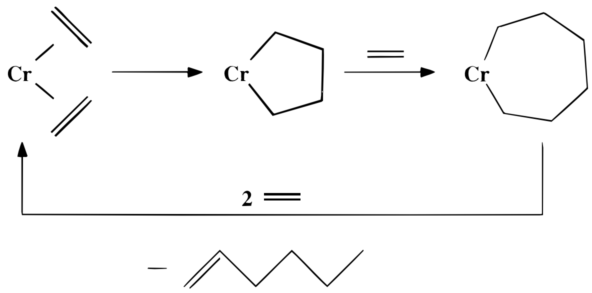
Summary: η^5-Cyclopentadienyl-stabilized metallacyclopentane and -cycloheptane derivatives of chromium have been isolated, and their chemical behavior lends support to a metallacyclic mechanism for the Cr-catalyzed selective trimerization of ethylene to 1-hexene. In the presence of MAO, the amino-substituted cyclopentadienyl−chromium derivatives show a remarkable activity for the catalytic polymerization of ethylene.

It has been suggested that metallacyclic intermediates might be involved in the chromium-catalyzed trimerization of ethylene to 1-hexene (Scheme 1).[1−4] The key to this mechanism lies in the relative stability toward intramolecular β-H-transfer of the metallacyclopentane ring compared to the metallacycloheptane ring, and this is consistent with the known behavior of metallacyclic derivatives of platinum.[5] The preparation and reactions of the metallacyclic derivatives of chromium reported below lend further support.

Scheme 1



The chromacyclopentane derivatives $Cp^*\overline{Cr(PR_3)CH_2C_2H_4CH_2}$ (**1**, R = Me; 2, R = Et) and $(Me_2NC_2H_4C_5Me_4)\overline{CrCH_2C_2H_4CH_2}$ (**3**) and the chromacycloheptane derivatives $Cp^*\overline{Cr(PMe_3)CH_2C_4H_8CH_2}$ (**4**) and $(Me_2NC_2H_4C_5Me_4)\overline{CrCH_2C_4H_8CH_2}$ (**5**) have been prepared in good yield by reacting the appropriate dichloride with either 1,4-dilithiobutane or 1,6-dichloromagnesiohexane.[6−8] This is illustrated in Scheme 2 for **3** and **5** along with their molecular structures (**3**: Cr−C(14) 2.080(1) Å, Cr−C(17) 2.103(1) Å, Cr−N(2) 2.169(1) Å, Cr−D 1.924 Å, C(14)−C(15) 1.527(2) Å, C(14)−Cr−C(17) 84.2(1)°. **5**: Cr−C(14) 2.102(2) Å, Cr−C(19) 2.092(2) Å, Cr−N(2) 2.188(2) Å, Cr−D 1.946 Å, C(14)−C(15) 1.527(3) Å, C(14)−Cr−C(19) 96.2(1)°.[9]

[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1997.

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(8) Satisfactory analytical and mass spectral data have been obtained for all compounds.

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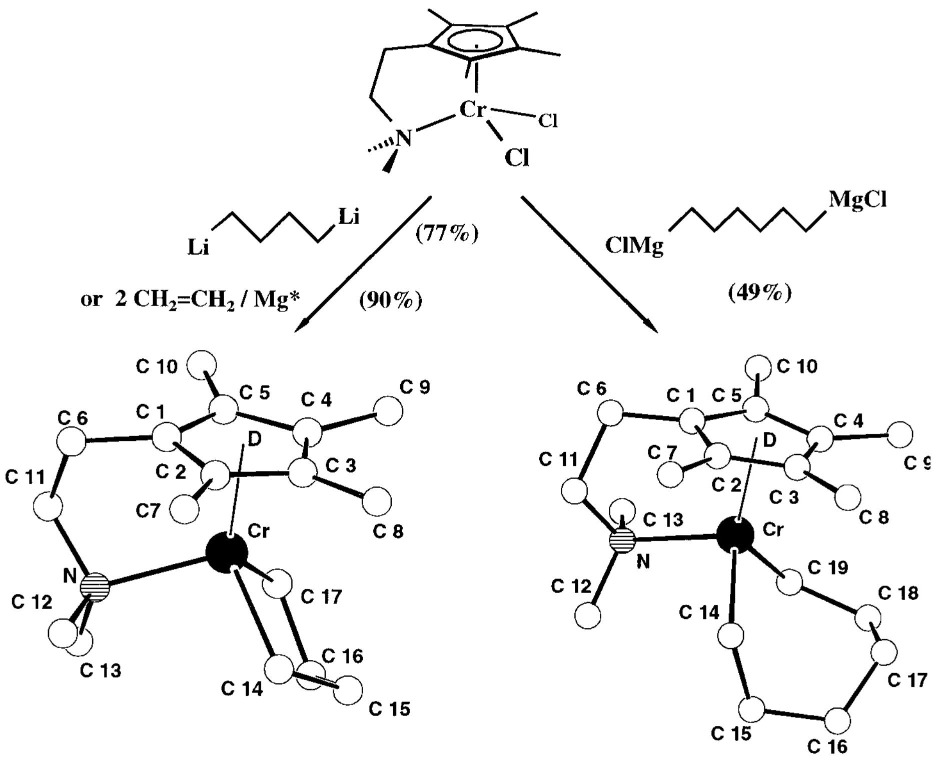
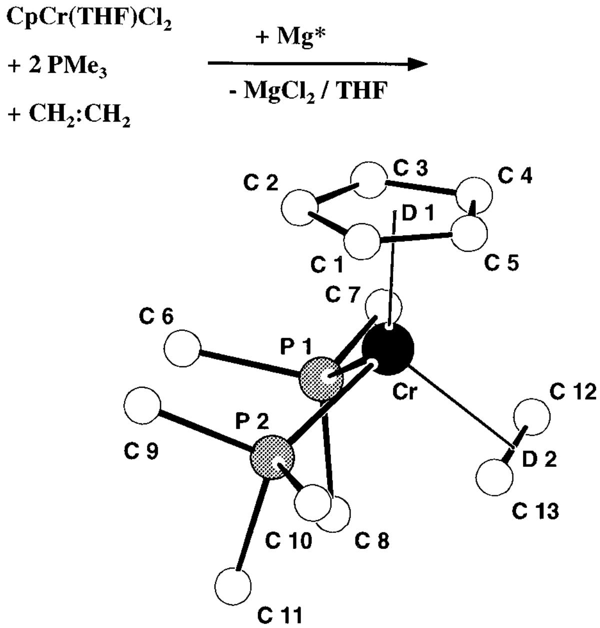
Scheme 2



3 **5**

Scheme 3



(1)

6

Particularly relevant to the mechanism shown in Scheme 1 are the following observations. (1) The metallacyclopentane derivatives are indeed more stable than the corresponding metallacycloheptane derivates: T_{dec} = 20 °C (**1**), 0 °C (**4**); (DSC) 151 °C (**3**), 56 °C (**5**). (2) The chromacycloheptane derivatives decompose with the expected liberation of 1-hexene.[10] (3) Protonolysis of the product of the reaction of the chromacyclopentane derivative **3** with ethylene (0.1 bar, room temperature, 2 weeks) leads to the liberation of hexane and butane (1:3). (4) The chromacyclopentane derivatives **1** and **3** can be prepared in high yield (70−90%) by reacting the appropriate dichloride with active Mg[11] *in the presence of ethylene* (Scheme 2).

Support for the intermediacy of an (η^2-CH_2:CH_2)Cr-species in this last reaction has been obtained by reducing $CpCr(THF)Cl_2$ with active Mg in the presence of ethylene and *excess* trimethylphosphine: the monoethylene complex **6** is formed in 57% yield. The molecular structure of **6**[9] is shown in Scheme 3 (**6**: Cr−D(1) 1.844 Å, Cr−D(2) 2.008 Å, Cr−P(1) 2.038(1) Å, Cr−P(2) 2.290(1) Å, C(12)−C(13) 1.415(3) Å, P(1)−Cr−P(2) 97.3°) and represents the first (CH_2:CH_2)Cr-species reported. The crystals of **6** are extremely labile, decomposing slowly even at −60 °C. Furthermore, **6** is active for the polymerization of ethylene at room temperature and 50 bar.

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(9) *Crystal data* for **3**: $C_{17}H_{30}CrN$, M_w = 300.43; monoclinic; space group $P2_1/c$; a = 8.232(2) Å; b = 23.050(6) Å; c = 9.159(1) Å; β = 111.10(1)°; V = 1621.3(6) Å^3; Z = 4; D_c = 1.23 Mg m^{-3}; μ = 6.77 cm^{-1}; T = 295 K; 4025 measured reflections; 3697 unique reflections; 3346 reflections with $I \geq 2\sigma(I)$ used in refinement; structure solved by direct methods; R = 0.026; R_w = 0.037 ($w = 1/\sigma^2(F_o)$); EOF = 1.84; residual electron density = 0.32 e Å^{-3}. For **5**: $C_{19}H_{34}CrN$, M_w = 328.47; monoclinic; space group $P2_1/c$; a = 17.726(1) Å; b = 14.450(1) Å; c = 15.561(1) Å; β = 114.227(1)°; V = 3634.9(4) Å^3; Z = 8 (two isomers); D_c = 1.200 Mg m^{-3}; μ = 6.25 cm^{-1}; T = 173 K; 6335 measured reflections; 6335 unique reflections; 5640 reflections with $I \geq 2\sigma(I)$ used in refinement; structure solved by direct methods; R = 0.0368; R_w = 0.0413 ($w = 1/\sigma^2(F_o)$); EOF = 2.44; residual electron density = 0.29 e Å^{-3}. For **6**: $C_{13}H_{27}CrP_2$, M_w = 297.30; monoclinic; space group $P2_1/c$; a = 13.396(1) Å; b = 8.802(1) Å; c = 13.438(1) Å; β = 92.397(1)°; V = 1583.1(2) Å^3; Z = 4; D_c = 1.247 Mg m^{-3}; μ = 9.01 cm^{-1}; T = 173 K; 6884 measured reflections; 2750 unique reflections; 2607 reflections with $I \geq 2\sigma(I)$ used in refinement; structure solved by heavy-atom method; R = 0.0291; R_w = 0.0383 ($w = 1/\sigma^2(F_o)$); EOF = 2.011; residual electron density = 0.363 e Å^{-3}. The data were collected using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) by the ω-2θ scan method in the range 2° < 2θ < 55°. The structure was solved by SHELX86 and refined anisotropically for non-hydrogen atoms with H-atoms isotropic, $\sum w(F_o - F_c)$ minimized. For the final refinement, the program GFMLX was used. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

Considerably more active catalysts for the polymerization of ethylene have been obtained by activating **3** (or the corresponding dichloride) with MAO (methylaluminoxane), and activities of 16.6 kg polyethylene/mmol Cr/h have been observed under ambient temperatures and 2 bar. Particularly remarkable, in addition to the mild reaction conditions, is the low Al:Cr ratio needed to obtain full activity (100:1), and this should be contrasted to the value of ca. 10^4:1 (Al:Zr) reported for the MAO-activated *ansa*-zirconocene catalysts[12] and amido-substituted cyclopentadienyl−titanium catalysts.[13] The same Cr catalysts also polymerize propene (to atactic polypropene) and copolymerize ethylene andnorbornene to an alternating copolymer.[14] Further details are reserved for an extensive publication.

Supporting Information Available: Text giving full experimental procedures and characterization data for compounds **1**−**3**, **5**, and **6** and ORTEP diagrams and tables of crystal data and collection parameters, bond distances, bond angles, atomic fractional coordinates, and thermal parameters for **3**, **5**, and **6** (29 pages). Ordering information is given on any current masthead page.

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(10) For example, thermolysis of **5** at 200 °C leads to the liberation (MS identification) of 1-hexene (23.4%) as well as hydrogen (34.2%) and small (<10%) amounts of propane, propene, methane, ethane, hexane, and 1,3-butadiene. The main organic products of the thermolysis of the chromacyclopentane derivatives are 1-butene and ethylene.

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