Constrained Geometry Chromium Catalysts for Olefin Polymerization

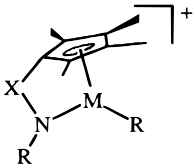
Yuanfeng Liang, Glenn P. A. Yap, Arnold L. Rheingold, and
Klaus H. Theopold*,†

*Department of Chemistry and Biochemistry, Center for Catalytic Science and Technology,
University of Delaware, Newark, Delaware 19716*

Received September 9, 1996⊗

Summary: Chromium(III) alkyls featuring an amido ligand tethered to a permethylcyclopentadienyl ring (i.e. [η^5-$Me_4C_5SiMe_2$-η^1-N^tBu]CrR) have been prepared and structurally characterized. They catalyze the polymerization of ethylene and the dimerization and isomerization of α-olefins.

Among the metallocene catalysts currently revolutionizing the field of Ziegler− Natta catalysis,[1] so-called constrained geometry molecules (see **A**)—i.e. metal complexes containing an amide ligand tethered to a cyclopentadienyl group—play a special role as copolymerization catalysts.[2] The sterically unencumbered nature of the catalytic site is thought to facilitate incorporation of various α-olefins into growing polymer chains. Extension of this structural feature to chromium, one of the metals employed commercially in coordination polymerization,[3] might thus be expected to generate a new family of Cr-based copolymerization catalysts. Herein we report the synthesis and characterization of the first constrained geometry chromium alkyls and an investigation of their reactivity with olefins.



M = Ti, Zr, Hf
X = SiR_2, C_2H_4, etc.

A

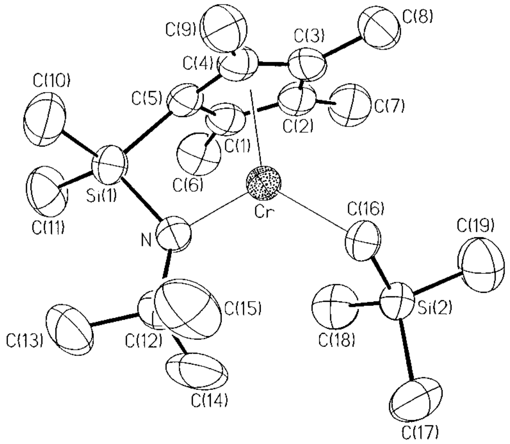


Figure 1. Molecular structure of (Cp*SiNR)$CrCH_2SiMe_3$ (**4**). Selected interatomic distances and angles: Cr−N, 1.920(4) Å; Cr−C(16), 2.092(5) Å; Cr−$C_{Cp,av}$, 2.23 Å; N−Cr−C(16), 113.8(2)°; $Cp_{centroid}$−Cr−N, 115.9°; Cr−C(16)−Si(2), 119.6(3)°.

Slow addition of $Li_2(THF)_n[Me_4C_5SiMe_2N^tBu]$[4] to a suspension of $CrCl_3(THF)_3$ in THF at low temperature afforded dark green (Cp*SiNR)CrCl(THF) (**1**) in 68% yield. Alkylation of this starting material with various lithium alkyls yielded a new class of chromium(III) alkyls (see Scheme 1). Depending on the steric bulk of the alkyl group, the complexes either retained or lost the THF ligand; in the latter case (e.g. when R = CH_2SiMe_3) a coordinativley unsaturated metal alkyl akin to **A** was isolated. Figure 1 shows the result of a crystal structure determination of (Cp*SiNR)$CrCH_2SiMe_3$ (**4**),[5] a brown solid that is freely soluble in hydrocarbon solvent. The molecule has approximate mirror symmetry; the idealized mirror plane bisects the chelating ligand, and the alkyl carbon directly bonded to chromium deviates only very little from it (0.26 Å). The three-coordinate nitrogen is planar (sum of angles: 359.2°), and the Cr−N (1.92 Å) distance is considerably shorter than the Cr−C(16) bond (2.09 Å), the latter an entirely normal chromium(III)−carbon single-bond distance.[6] Both observations are consistent with some degree of ligand-to-metal π-donation involving the amide ligand, albeit not sufficient for a full Cr═N double bond (ca 1.65 Å).[7] The effective magnetic moment of the complex measured $\mu_{eff}(RT) = 4.0(1)\ \mu_B$, consistent with three unpaired electrons. Thus the π-acceptor orbital on the metal must be singly occupied, and the N−Cr π-bond is a three-electron interaction of attenuated strength. The $Cp_{centroid}$−Cr−N angle of 115.9° is an indication of the "openness" of the structure adjacent to the Cr−C bond, i.e. the anticipated site of catalytic activity. Despite its coordinative and electronic unsaturation, **4** exhibited no indication of an agostic interaction,[8] e.g. with one of the methyl hydrogen atoms of the

---

† E-mail: theopold@udel.edu.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.

[1] (a) Thayer, A. M. *Chem. Eng. News* **1995**, Sept 11, 15. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

[2] Stevens, J. C. Constrained Geometry and Other Single Site Metallocene Polyolefin Catalysts: A Revolution in Olefin Polymerization. In *11th International Congress on Catalysis-40th Anniversary*; Hightower, J. W., Delgass, W. N., Iglesia, E., Bell, A. T., Eds.; Elsevier: Amsterdam, 1996; pp 11−20.

[3] McDaniel, M. P. *Adv. Catal.* **1985**, *33*, 47.

[4] (a) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.

[5] **4**: $C_{19}H_{38}CrNSi_2$, triclinic $P\bar{1}$, a = 9.186(1) Å, b = 9.678(1) Å, c = 13.745(1) Å, α = 94.803(9)°, β = 100.434(8)°, γ = 102.05(1)°, Z = 2, T = 297 K, R = 5.30%, R_w = 6.24%.

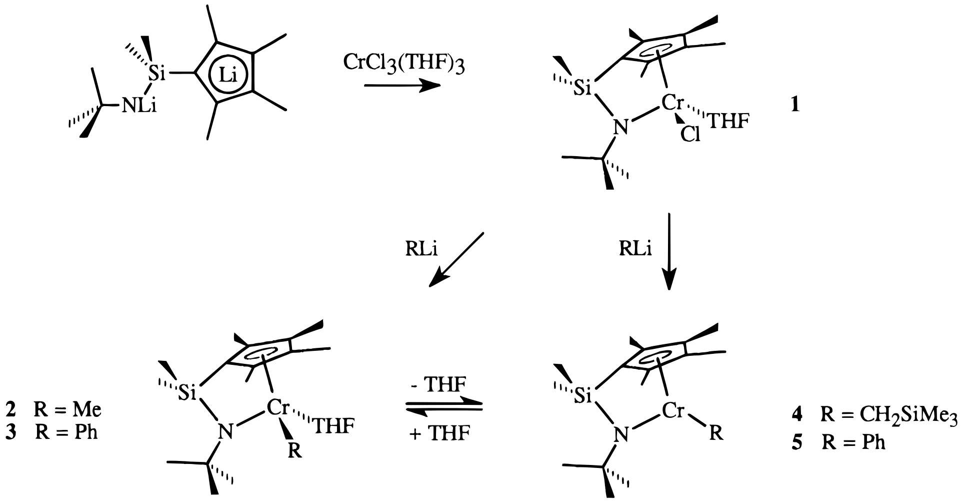
[6] Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263.

[7] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; p 180.

[8] (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

S0276-7333(96)00774-1 CCC: $12.00

Scheme 1



(trimethylsilyl)methyl ligand. Such interactions—at least in the ground state—would not appear to be important in chromium catalysis.[9]

We have previously established the minimum requirements for ethylene polymerization activity of organochromium catalysts, namely a chromium(III)−carbon σ-bond and coordinative unsaturation (i.e. pseudo-five-coordination in a cyclopentadienyl complex).[10] Complex **4** fits this description, and accordingly it catalyzed the polymerization of ethylene. Exposure of a toluene solution (50 mL, 3.0 mM) at room temperature to ethylene (500 psi) for 3.5 h yielded 2.6 g of polyethylene. When the same polymerization reaction was carried out in a 1:1 mixture of toluene and 1-hexene, 2.1 g of polymer was formed.[11] By ^{13}C NMR, this material showed no evidence for incorporation of the α-olefin! Despite the great concentration advantage of the hexene the catalyst selectively polymerized only ethylene. Attempts to polymerize propene, using **4** as a catalyst, were unsuccessful. However, when the reaction of **4** with propene at room temperature was monitored by ^{1}H NMR, complete conversion to 2-methyl-1-pentene was observed over the course of several hours (the product was identified by ^{1}H and ^{13}C NMR). While "constrained geometry" chromium catalysts can apparently bind and insert α-olefins, the latter do not compete effectively with ethylene for incorporation into a growing polymer chain, and chain transfer by β-hydrogen elimination must be very facile for chromium alkyls featuring tertiary C−H bonds at the β-carbon atom.

Several observations are relevant to a consideration of the mechanism for the olefin dimerization reaction noted above. The isotropically shifted resonances of **4** remained constant during this transformation, and no new paramagnetic compounds were observed by ^{1}H NMR; furthermore, no organic compounds containing (trimethylsilyl)methyl groups were observed by NMR. Reaction of 1-hexene with **4** yielded not only the expected product of head-to-tail dimerization, i.e. 2-butyl-1-octene, but also a mixture of isomeric internal hexenes. Thus **4** catalyzes the isomerization of olefins as well. Finally, both the dimerization and isomerization were accelerated by the addition of hydrogen (e.g. 300 Torr H_2). On the basis of these observations, we suggest that the actual catalyst may be the hydride $[(Cp^*SiNR)CrH]_n$, small quantities of which may be formed by β-elimination from $(Cp^*SiNR)CrCH_2CHRCH_2SiMe_3$, i.e. the product of insertion of an olefin in the chromium−carbon bond of **4**. Indeed, prolonged exposure of **4** to H_2 yielded $SiMe_4$ and at least one new, and as yet unidentified, paramagnetic compound. Efforts to characterize this species fully are under way.

The catalytic regiospecific head-to-tail dimerization of olefins may have applications in organic synthesis,[12] and we have tested a number of substrates to begin to delineate the scope of this transformation. Styrene or 3,3-dimethyl-1-butene did not react under these conditions. 1,5-Hexadiene yielded solely methylenecyclopentane, and 1,6-heptadiene gave methylenecyclohexane and 1-methyl-2-methylenecyclopentane in a 3:1 ratio. We are currently exploring the utility of **4** and its analogues for cyclizations of more complex organic substrates.

Our understanding of organochromium chemistry related to olefin polymerization has reached the stage where molecular design of catalysts is feasible. However, simple extrapolation of design principles from group 4 chemistry to the later metal fails, and a homogeneous chromium-based copolymerization catalyst remains elusive. The available evidence suggests that cyclopentadienylchromium(III) complexes feature

---

(9) For the role of such interactions in metallocene catalysis with earlier metals, see: Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85.

(10) (a) Thomas, B. J.; Noh, S.-K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893. (b) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738.

(11) (a) Toluene: $M_w = 85720$, $M_w/M_n = 52$. (b) Toluene/1-hexene: $M_w = 102\,300$, $M_w/M_n = 37$. Note that these numbers reflect bimodal product distributions with most of the samples being of low molecular weight ($M_w = 1000-10\,000$). A possible explanation for this observation (suggested by a reviewer) is the presence of small amounts of a chromium alkyl resulting from cleavage of the Cp*−Si bond during the synthesis (i.e. a compound containing a C_5HMe_4 ligand); such fragmentation has been noted in group 4 chemistry, and low levels of contaminants would be hard to detect in paramagnetic Cr complexes.

(12) (a) Christoffers, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 4715. (b) Shaughnessy, K. H.; Waymouth, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 5873. (c) Negishi, E.; Jensen, M. D.; Kondakov, D. Y.; Wang, S. *J. Am. Chem. Soc.* **1994**, *116*, 8404. (d) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123. (e) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74. (f) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610.

highly disparate rates of chain growth for ethylene and α-olefins.[13] Our results militate against a steric origin of this selectivity; the relevant electronic factors may influence both olefin binding and/or the migratory insertion step. That chromium is capable of copolymerization is demonstrated by the Phillips catalyst (inorganic Cr/SiO2).[3] Homogeneous complexes more closely related to its active site are reasonable synthetic targets in our quest for novel chromium catalysts.

Acknowledgment. This research was supported by research grants from the NSF (CHE-9421802) and Chevron Chemical Co.

Supporting Information Available: Tables giving a summary of the crystal structure determination, positional and thermal parameters, and bond distances and angles of **4** and text providing syntheses and spectroscopic data for all complexes (10 pages). Ordering information is given on any current masthead page.

OM960774H

---

[13] White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics*, in press.