Homogeneous Chromium Model Chemistry for the Phillips Catalyst

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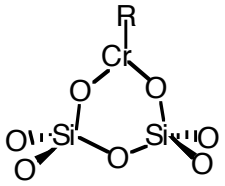
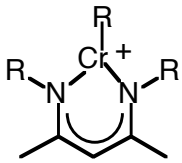
We have constructed a homogeneous model system for the Phillips catalysts for ethylene polymerization (i. e. inorganic Cr/SiO_2, see **A** below). To mimic the coordinatively unsaturated chromium on a hard oxide support, we have chosen N, N'-disubstituted diketiminate ligands ("$(R)_2$nacnac", as in **B**), i. e. bidentate nitrogen ligands that confer variable steric protection upon the chromium.



A



B

We have prepared a series of neutral and cationic chromium alkyls supported by $(Ar)_2$nacnac ligands (Ar = Ph, 2,6-Me_2Ph, 2,6-$^i Pr_2$Ph). These paramagnetic complexes feature chromium in a range of formal oxidation states (II – V). Structurally characterized cationic Cr(III) alkyls of the general type $[(Ar)_2nacnacCr(R)(OEt_2)]^+BARF^-$ (Ar = 2,6-Me_2Ph, 2,6-$^i Pr_2$Ph; R = Me, CH_2SiMe_3) catalyze the polymerization of ethylene and the copolymerization of ethylene with α-olefins in the absence of any cocatalysts.[1]

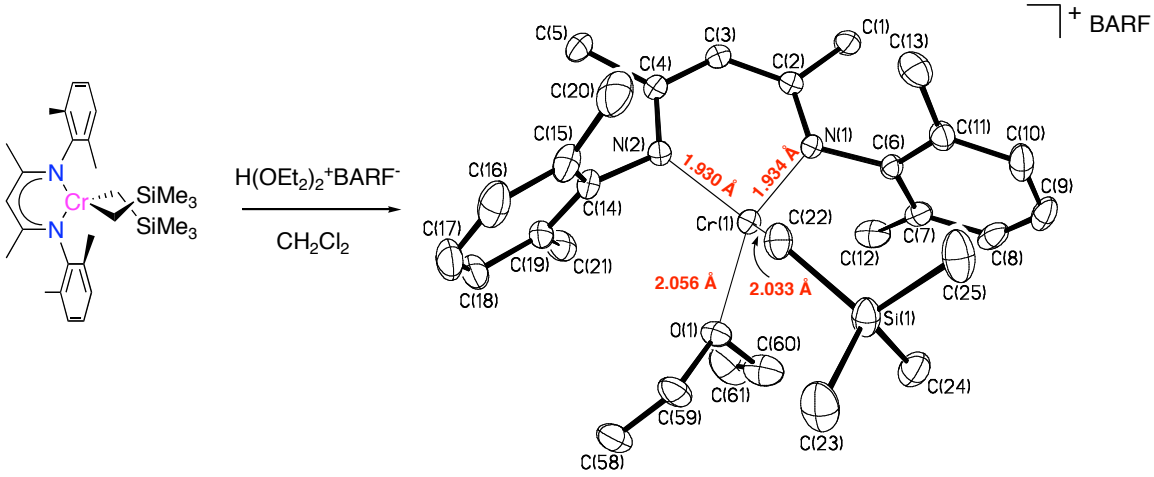


Figure 1. Synthesis of representative cationic chromium olefin polymerization catalyst $[(2,6\text{-}Me_2Ph)_2nacnacCr(OEt_2)CH_2SiMe_3]BARF$

Extraordinarily low polydispersities (M_w/M_n = 1.1 – 1.4) provide evidence for "living" polymerization catalysis, and the polymer microstructure of polyethylene produced with the more sterically encumbered [(2,6-^{i}Pr$_2$Ph)$_2$nacnac Cr(OEt$_2$)Me]BARF shows evidence for "chain walking".[2]

Recent attempts to create an entirely base free catalysts of the type [nacnacCrR]$^+$ protected by even more congested nacnac ligands will be described, as will be the reactivity of isostructural Cr(II) alkyls – i. e. three-coordinate nacnacCrR.

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References:

1. A chromium catalyst for the polymerization of ethylene as a homogeneous model system for the Phillips catalyst, Leonard A. MacAdams, Gerald P. Buffone, Christopher D. Incarvito, Arnold L. Rheingold, and Klaus H. Theopold, *J. Am. Chem. Soc.* **2005**, *127*, 1082.

2. Nacnac Metal Alkyls as Homogeneous Polymerization Catalysts, K. H. Theopold, L. A. Mac Adams, C. Puttnual, G. P. Buffone, and A. L. Rheingold, *Polymeric Materials Science and Engineering*, **2002**, *86*, 310.