Synthesis of and Olefin Polymerization Using Tethered, *ansa*-Metallocene Complexes

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Introduction. There is considerable interest in the development of supported versions of metallocene and other single-site olefin polymerization catalysts, particularly in the context of their application to commercial processes for poly(olefin) manufacture. A variety of approaches have been developed for supporting metallocene complexes on silica, including direct reaction of silica with a metallocene complex, followed by activation with a cocatalyst (e.g., MAO), reaction of MAO-modified silica with a metallocene complex, or similar conceptual approaches where other cocatalysts are supported on silica.[1] Recently, considerable attention has focused on covalent anchoring of metallocene complexes on silica through either metallocene synthesis on the support or reaction of a suitably functionalized, metallocene complex with e.g. silica.[2]

In general, supported catalysts are frequently much less active than their soluble counterparts, and even optimal formulations are anywhere from $^1/_4$ to $^1/_2$ the activity of their soluble counterparts (based on total metal) when examined under the same conditions.[1] We report here a novel approach to the synthesis of covalently anchored, *ansa*-metallocene complexes and demonstrate that these supported catalysts have comparable or even superior activity in olefin polymerization to their soluble counterparts when compared under the same conditions.

Results and Discussion. We were interested in developing a general route to "tethered" *ansa*-metallocene complexes in that these complexes are exceedingly useful in both ethylene and α-olefin polymerization[3] and where the structure of the *ansa*-metallocene complex or the nature and length of the tether could be easily varied prior to supporting it, i.e., a convergent synthetic approach. Also, we were interested in developing supporting chemistry that was chemically clean and unambiguous so that the polymerization behavior of these supported catalysts might be meaningfully interpreted and compared. Our approach is summarized in Scheme 1.[4]

We relied on hydrosilylation chemistry,[5] using either a Me_2SiHCl-treated, hydroxylated silica and a *ansa*-metallocene bearing a $(CH_2{=}CH)SiMe$ bridge (route A, Scheme 1) or, more usefully, a *ansa*-metallocene complex bearing a MeSiH bridge, with a suitably functionalized silica (route B, Scheme 1) in that the length and nature of the tether can be readily varied using the latter approach.[6] In solution, these hydrosilylation reactions are clean and reasonably rapid at room temperature in the presence of $[^nBu_4N]_2[PtCl_6]$[7] (see Supporting Information); it seems that *ansa*-metallocene complexes bearing a MeSiH bridge have hydrosilylation reactivities toward terminal alkenes that are comparable to chlorosilanes! The required *ansa*-metallocene dichloride complexes **1a,b** and *rac*-**2a,b** were readily prepared by amine elimination reactions between $Zr(NMe_2)_4$ and the appropriate *ansa*-ligand, followed by metathesis with Me_3SiCl (see Supporting Information for details).[8]

A variety of different, "tethered" *ansa*-metallocene complexes were prepared which differed in (a) the Zr loading on the support, (b) the length/identity of the tether, and/or (c) metallocene structure (i.e., **1** or **2**, Scheme 1), and the designations of these supported catalysts (**A**−**E**, respectively) along with their Zr contents (by neutron activation analysis) are summarized in Table 1. Although not optimized or studied in a systematic fashion, supported catalysts having Zr contents from ca. 1 to 5 wt % can be readily obtained by this approach. A CP-MAS $^{13}C\{^1H\}$ NMR spectrum of catalyst **B,** which featured the highest Zr loading and shortest tether, was consistent with the proposed structure (see Supporting Information).

These supported catalysts were tested in ethylene polymerization in the presence of MAO (1000:1 Al:Zr) at 70 °C and 75 psi C_2H_4, and the results are summarized in Table 1. Under identical conditions, a conventional, SiO_2·MAO supported catalyst prepared from $Me_2Si(Cp)_2ZrCl_2$ (**3**), a model for the metallocene complex tethered to the other supports, and commercially available SiO_2·MAO (24 wt % Al from Witco GMBH), at two different Zr contents, were significantly less active than the best tethered formulations (entries 1−3 vs 7 and 8). Some of these tethered catalysts have activities, based on Zr, that rival or even *exceed* those of a soluble analogue [i.e., **3**, Table 1, entries 1−3 vs 10 in toluene and 4 vs 11 in hexane slurry] when compared under the same activation conditions (i.e., 1000:1 Al:Zr).

It is important to note that comparisons of this sort should be conducted with the same absolute amount of Zr present, particularly as the activity (but not the average MW or MWD of the polymer formed), of *soluble* metallocene complex **3** shows a strong dependence on [Zr] (at *constant* Al:Zr; see Table 1, entries 9 vs 10). This interesting behavior may be due to increased formation of dormant, dinuclear μ-alkyl Zr complexes at higher [Zr];[9] the proportion of cationic alkylzirconocene [Zr*] present at equilibrium should be sensitive to absolute Zr concentration at constant Al:Zr ratios (eq 1).

$$[Cp_2ZrR][X] + Cp_2ZrR'_2 \overset{K>1}{\rightleftharpoons} [Cp_2ZrR(\mu\text{-}R')R'ZrCp_2][X] \quad (1)$$

Although we do not have enough systematic data, it seems that a principal variable affecting supported catalyst activity in ethylene polymerization is the Zr loading (i.e., a lower Zr loading leading to higher

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Scheme 1

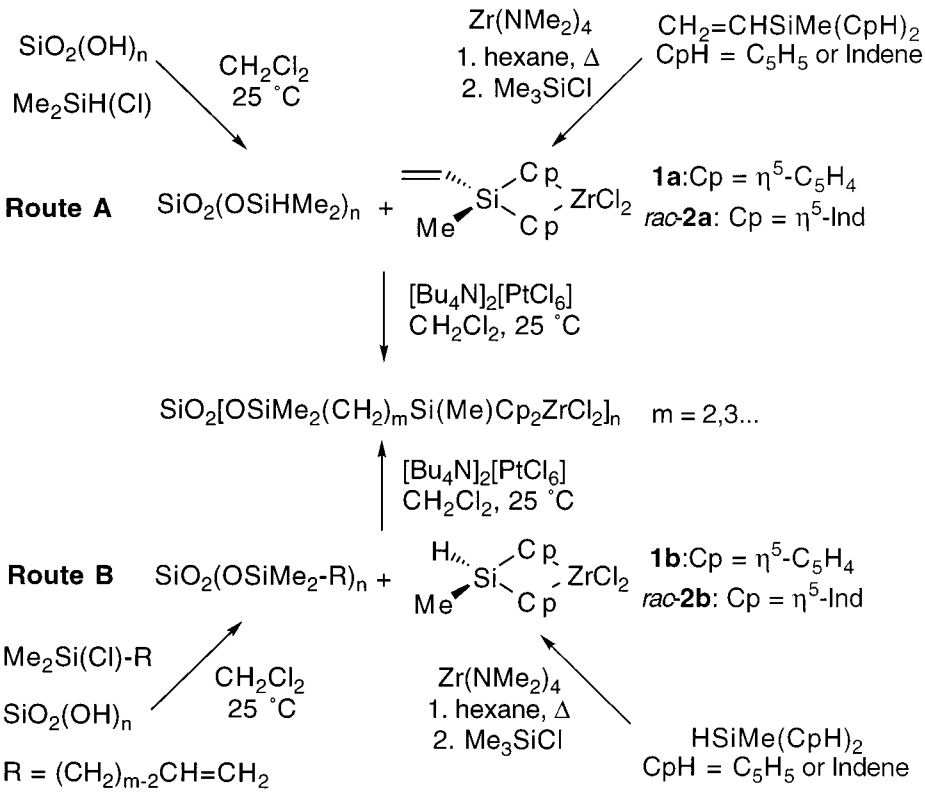

Table 1. Olefin Polymerization Using Supported *ansa*-Metallocene Catalysts[a]

entry (code)	route[b]	Met.[c]	m[d]	Zr (wt %)[e]	Zr (μmol)	*A*[f]	M_w (K)	PDI	% mmmm
1 (**A**)	B	**1b**	8	0.79	0.86	50.0	43	2.1	
2 (**A**)	B	**1b**	8	1.14	0.72	33.0	52	3.1	
3 (**A**)	B	**1b**	8	1.14	1.46	36.0	53	3.3	
4 (**A**)	B	**1b**	8	1.14	3.42	13.1[g]	34	3.0	
5 (**B**)	A	**1a**	2	2.62	3.42	3.9	47	3.4	
6 (**C**)	B	**1b**	3	0.43	1.72	21.5	43	2.8	
7	C[h]	**3**		3.45	3.74	21.0	24	2.9	
8	C	**3**		0.21	0.58	20.0	29	3.1	
9		**3**			5.96	16.0	28	2.5	
10		**3**			0.86	40.0	26	2.9	
11		**3**			0.86	11.4[g]	42	3.1	
12 (**D**)	A	*rac*-**2a**	2	2.11	1.00	8.80	50	2.1	86.2
13 (**E**)	B	*rac*-**2b**	8	2.85	1.00	23.4	56	2.0	85.3
14	C[h]	**4**		4.32	1.00	11.0	53	1.9	87.2
15		**4**			1.00	30.6	49	1.8	85.7

[a] In a typical procedure, the supported catalyst (in amounts so as to give the amount of Zr indicated in μmol) was precontacted with MAO (640 equiv) in ca. 10 mL of toluene (unless otherwise noted) for less than 5 min at 25 °C, prior to injection into a reactor containing ca. 490 mL of toluene (unless otherwise noted) and 360 equiv of MAO, presaturated with monomer at 70 °C and 75 psi (ethylene) or 40 °C and 45 psi (propylene). [b] Synthetic route employed in catalyst preparation; see Scheme 1 or footnote *h*. [c] Metallocene complex used; for structures of **1a,b** and **2a**,**b** see Scheme 1, **3** = $Me_2SiCp_2ZrCl_2$ and **4** = *rac*-$Me_2SiInd_2ZrCl_2$. [d] Length of tether; see Scheme 1. [e] Weight fraction Zr on the support (in %) as measured by neutron activation analysis. [f] Polymerization activity in 10^6 g of polymer/(mol of Zr h). [g] Polymerization in hexane slurry using PMAO−IP. [h] Complex **3** or **4** was precontacted with SiO_2·MAO (24 wt % Al, Witco GMBH) in toluene slurry at room temperature and the resulting supported catalyst was used after washing with toluene and drying in vacuo.

productivity based on Zr, entries 1 vs 2 and 5 vs 6), although the length of the tether also seems to have an influence, long being better than short (entries 3 vs 6). In most cases, the polymer formed has a significantly higher average MW (ca. 50% higher) than that produced using its soluble counterpart and a comparable MWD. Note that the activity of the supported catalyst at a given loading is independent of total Zr present (entries 2 vs 3) unlike the situation for the soluble analogue.

The isospecific, "tethered" metallocene complexes (i.e., complexes **2a,b**, Scheme 1) were evaluated in propylene polymerization at 40 °C and 45 psi of C_3H_6, and the results are also summarized in Table 1. Here it seems that the length of the tether is quite important, supported catalyst **E** being about 2.5 times more active than **D** despite having similar Zr content (entries 13 vs 12). The former catalyst is about 2 times more active than a conventional SiO_2·MAO/$Me_2Si(Ind)_2ZrCl_2$ (**4**) formulation (entry 14). The polymer MWD and microstructure in all cases are quite comparable to that observed using soluble complex **4** at this lower temperature (entry 15).[10]

Although reactor fouling was not noticeable in either hexane or toluene suspension, preliminary evidence suggests that these supported catalysts are susceptible to leaching by MAO at least in toluene solution at elevated temperatures in the *absence* of monomer. For example, prior exposure of catalyst **A** to MAO (640 equiv) at 70 °C for 30 min, filtration through a 7.5 μm stainless steel frit, and polymerization with the filtrate (total Al:Zr = 1000:1) revealed that nearly 50% of the observed activity might be accounted for by catalyst leaching during polymerization. At lower temperatures and for shorter time periods, leaching during the precontacting period is less problematic—≤10% of the observed activity at 70 °C for periods ≤5 min at 25 °C.

On the other hand, precontacting this same catalyst with MAO using the normal procedure (640 equiv, <5 min at 25 °C), followed by prepolymerization with ethylene (initially at 25 °C but *strongly* exothermic) in toluene for ∼3 min, filtration, and use of the filtrate indicated minimal leaching (i.e., <2%) once the support has been coated/encapsulated with PE. It seems that

the short precontact time with MAO results in efficient activation of the supported catalyst (and may be essential for development of high activity using MAO as cocatalyst),[11] but once the support is covered in polymer, the material behaves like a supported catalyst from a practical perspective.[1]

We also briefly investigated the utility of "single-component" coinitiators as activators for these supported catalysts. Use of either prealkylated catalysts, e.g. catalyst **A** (Table 1, entry 1) + Me_2Mg in THF, followed by washing and removal of THF to give catalyst **F** (Zr content by NAA = 0.69 wt %) or in-situ alkylation (e.g., catalyst **A** + excess Bu_2Mg in toluene), followed by activation with $[Ph_3C][B(C_6F_5)_4]$ (~2 equiv) prior to polymerization in the presence of $^iBu_3Al$ (=10:1 Al:Zr) was successful; polymerization activities under these conditions (ca. $(35-55) \times 10^6$ g of PE/(mol of Zr h) in toluene and ca. 25×10^6 g of PE/(mol of Zr h) in hexane) were gratifyingly comparable to those observed using MAO (at much higher levels).

Future work will concentrate on exploring the utility of these tethered metallocene catalysts in gas-phase polymerization processes[12] and for elucidating/optimizing the fundamental chemistry involved with activation and use of these supported catalysts.

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Supporting Information Available: Preparative and characterization data for *ansa*-metallocene complexes **1** and **2**, supported catalyst preparation and characterization, representative polymerization procedure, NMR spectra, and SEM photographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Kaminsky and co-workers have obtained some evidence (see e.g. Kaminsky, W.; Bark, A.; Steiger, R. *J. Mol. Catal.* **1992**, *74*, 109) that there is a deactivation process that is bimolecular in Zr which may limit activity and polymer MW using a soluble complex (dinuclear species such as that shown in eq 1 may be intermediates in this process[9]). If the same complex is "site-isolated" on a support and this deactivation process is kinetically significant under the reaction conditions studied (e.g., elevated temperatures and higher catalyst concentrations), one would expect to obtain higher activity and possibly higher MW polymer using a supported catalyst. The results obtained here are not totally consistent with this interpretation, and further work is indicated.

(11) GC-MS evidence suggests that MAO is effective and selective in cleaving the $SiO_2-\mathbf{O}SiMe_2R$ bond in these supported catalysts: Metcalfe, R., unpublished results.

(12) Unfortunately, the bulk density of the PE prepared using these supported catalysts was generally quite low (<0.30 g/cm^3). SEM photos reveal that this may be due to extensive mechanical fracture of the spherical silica (average particle diameter ~ 75 μm) during chemical modification (i.e., average particle size ~ 15 μm).

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