Phosphinimides as a Steric Equivalent to Cyclopentadienyl: An Approach to Ethylene Polymerization Catalyst Design

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Summary: *Complexes of the form* ($Cp^\dagger$)$TiCl_2$(NPR_3) *and the analogous dimethyl derivatives* ($Cp^\dagger$)$TiMe_2$(NPR_3) *have been prepared. These species in the presence of MAO,* $B(C_6F_5)_3$, *or* $[Ph_3C][B(C_6F_5)_4]$ *are active catalysts for ethylene polymerization.*

In developing new homogeneous olefin polymerization catalysts, a number of research groups are exploring the chemistry of novel early transition metal complexes.[1] Among the variety of species examined are Ti and Zr complexes containing diamido,[2−5] bidentate aryloxides,[6−8] borollide,[9,10] boratobenzene,[11,12] pendant boranecyclopentadienyl,[13] trimethylene,[14] cyclopentadienylborate,[15] and macrocyclic[16] ligands. Although appreciable catalytic activities have been achieved, the only system that truly competes with bis(cyclopentadienyl) systems is the cyclopentadienyl chelating amido complex, the so-called "constrained geometry catalyst" (CGC).[17−21] The high activity of CGC may in part be attributed to the exposure of the metal center precipitated by the constraint inherent in the chelating cyclopentadienyl−amide ligand.

In developing an approach to catalyst design, we noted the work of Wolczanski et al.,[22] who described the steric analogy between the tri-*tert*-butylmethoxide and cyclopentadienyl ligands. In related systems, Dehnicke et al.[23,24] have noted the electronic analogy between phosphinimide ligands and cyclopentadienyl. We have combined these approaches in our design of new titanium olefin polymerization catalysts. Complexes of bulky phosphinimide ligands are expected to provide titanium environments that sterically and electronically mimic metallocenes. Herein we describe our initial implementation of this strategy. Complexes of the form ($Cp^\dagger$)$TiCl_2$(NPR_3) are shown to act as precursors to effective cationic ethylene polymerization catalysts. In addition, the first X-ray structural data for a cationic single-site titanium olefin polymerization catalyst is presented.

Complexes of the form ($Cp^\dagger$)$TiCl_2$(NPR_3) are readily prepared via the reaction of $CpTiCl_3$ with the appropriate trimethylsilylphosphinimine $R_3PNSiMe_3$.[25,26] Among the complexes we have prepared and characterized are ($Cp^\dagger$)$TiCl_2$(NPR_3) where $Cp^\dagger = C_5H_5$, R = Cy **1**, *i*-Pr **2**, *t*-Bu **3**, and $Cp^\dagger = C_5H_4$-*t*-Bu, R = Cy **4**, *i*-Pr **5**, *t*-Bu **6**.[27] The analogous dimethyl derivatives ($Cp^\dagger$)$TiMe_2$(NPR_3), **7**−**12**, were also readily isolated in high yields. See Scheme 1.

In preliminary polymerization experiments,[28] compounds **1**−**6** and **12** in the presence of MAO were found to rapidly effect the catalytic polymerization of ethylene (Table 1). The tri-*tert*-butylphosphimide complexes **3**, **6**, and **12** show activity comparable to Cp_2ZrCl_2 and CGC and significantly higher than Cp_2TiCl_2 or $CpTiCl_3$ under similar conditions. GPC data reveal that these systems generate polyethylene (MW: 55−90 000) with polydispersities of 1.6−2.4. These data are consistent with

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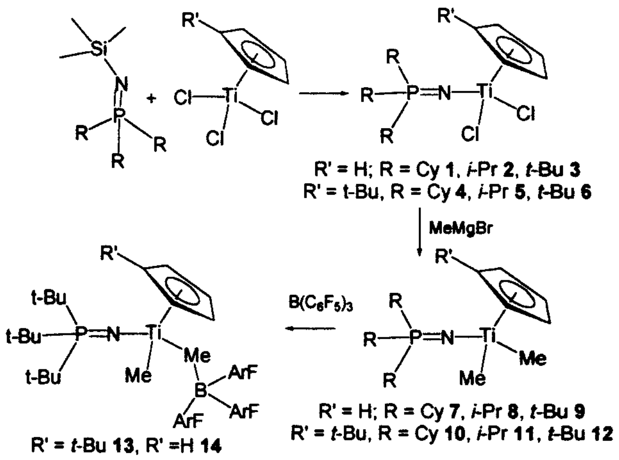
Scheme 1



single-site catalysis. In contrast, the complexes **1**, **2**, **4**, and **5** give rise to polymers that have bimodal molecular weight distributions, suggesting the presence of more than one active species. It is noteworthy that in these cases although these catalysts have reduced activity, molecular weights of PE as high as 1.6×10^6 g/mol were observed.

The dimethyl complexes **7**−**12** also act as catalyst precursors for the polymerization of ethylene. In the presence of $Ph_3C[B(C_6F_5)_4]$, these phosphinimide-based catalysts rapidly generate high molecular weight, highly linear (by NMR) polyethylene. The polymer generated from complexes **7**−**9** range in molecular weight from 135 to 165 000 g/mol with polydispersities in the range of 2.4−3.8. The analogous *tert*-butylcyclopentadienyl complexes **10**−**12** give even higher molecular weight polyethylene (260−320 000) at a rate substantially higher than observed with MAO activation.

The nature of the active species in the above polymerizations was probed via stoichiometric reactions. The reaction of **12** with $Ph_3C[B(C_6F_5)_4]$ resulted in the formation of an unstable species, whereas the reaction of **12** with $B(C_6F_5)_3$ yielded the stable product $[(C_5H_4$-*t*-Bu)TiMe(NP-*t*-Bu_3)(μ-Me)$B(C_6F_5)_3$, **13**.[27] ^{1}H NMR data for **13** reveal a single broad resonance attributable to the Ti- and B-methyl groups, inferring a rapid exchange process. This process was not slowed even on cooling to −80 °C. Similar facile exchange of borane between the methyl groups has been observed in related metallocene systems,[29] although such exchange was not seen in the monocyclopentadienyl complex $(C_5Me_5)TiMe_2(\mu\text{-Me})B(C_6F_5)_3$.[30,31] This observation suggests that the CpTi(NPR_3) fragment mimics Cp_2M. It is interesting to note that the ^{1}H NMR data affirm the absence of a plane of molecular symmetry in **13** despite the rapid exchange process of the borane. This is in contrast to that observed for **6** and **12**. Presumably, steric interactions between the *tert*-butyl group on the cyclopentadienyl ring and the arene substituents on the boron in **13** preclude a symmetric disposition, whereas this is not the case for less hindered **6** or **12**.

In the case of the reaction of **9** with $B(C_6F_5)_3$, a few X-ray quality crystals of **14** were isolated. Crystallographic study[32] revealed **14** to be (C_5H_5)TiMe(NP-*t*-Bu_3)(μ-Me)$B(C_6F_5)_3$ (Figure 1), in which there is ion pairing between the borate and the Ti cation with a Ti−B separation of 4.04 Å. The Lewis acidity of the Ti center in **14** is evidenced by the proximity of the borate methyl group, although the Ti−C(19) distance of 2.404(4) Å is significantly longer than the terminal Ti−C(18) distance of 2.123(5) Å. The Ti−C−B angle in **14** is 167.2(3)°, which lies between the Zr−C−B angles of 161.8(2)° and 170.5(3)° found in $(C_5H_3Me_2)_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$[33] and $(C_5H_3(SiMe_3)_2)_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$,[34] respectively. Agostic interactions between Ti and two of the hydrogen atoms of the abstracted methyl group H(19A) and H(19B) are evidenced by the close Ti−H approach (2.197(3) Å, 2.257(3) Å). In contrast, the Ti−H(19C) distance is 2.435(3) Å. Bond distances and angles within the phosphinimide ligand in **14**,[27] while consistent with Ti−N π-bonding, are essentially un-

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[27] Sample synthetic methodologies are described for **3**, **6**, and **14**. Synthesis of **3**: To a solution of titanium tetrachloride (1.900 g, 10 mmol) in toluene (5 mL) was added a toluene (1.5 mL) solution of trimethylsilylcyclopentadiene (1.532 g, 11.1 mmol). The reaction was heated to 60 °C for 30 min, and then a toluene (3 mL) solution of trimethylsilyl tri-*tert*-butylphosphinimine (2.895 g, 10 mmol) was added. The reaction was allowed to cool and was stirred at room temperature overnight. A yellow crystalline solid had formed, and heptane (50 mL) was added to the reaction mixture. The product was filtered, washed with heptane (2×10 mL), and dried in vacuo. Yield = 3.774 g, 94%. The product was pure by ^{1}H NMR spectroscopy. The product could also be prepared by the reverse addition of phosphinimine and trimethylsilylcyclopentadiene to $TiCl_4$. Synthesis of **6**: Methylmagnesium bromide (0.80 mL; 3.0 M; 2.40 mmol) in ether was added to a benzene solution (5 mL) of complex **3** (0.250 g; 0.70 mmol) at room temperature. The solution was stirred for 12 h. The solvent was removed under vacuum and the residue extracted with hexane (3×10 mL) and filtered. The hexane was removed under vacuum to yield a pure pale yellow solid (0.395 g; 0.95 mmol; 87%). Synthesis of **14**: To a stirring solution of $B(C_6F_5)_3$ (119 mg 0.232 mmol) in 3 mL of hexane was added **6** (63 mg, 0.231 mmol) in 2 mL of hexane. This mixture, which became immediately cloudy, was stirred for 30 min, resulting in a yellow precipitate. The clear, pale yellow supernatant was decanted, and the precipitate was washed with 3×10 mL hexane. The residue was pumped dry to yield the pale yellow solid product **14** (170 mg, 85%).

[28] In these preliminary screenings of the polymerization activities, the reactions at 1 atm pressure of ethylene and 25 °C, typically used 0.01−0.03 mmol of catalyst. The length of time the reaction was allowed to proceed was limited to preclude diffusion-controlled kinetics.

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[32] Crystal data for $C_{37}H_{38}BF_{15}NPTi$: M = 871.36; monoclinic, space group $P2_1/n$, $a = 11.7511(2)$ Å, $b = 18.32420(10)$ Å, $c = 18.1505(3)$ Å, $\beta = 100.5090(10)°$, $V = 3842.78(9)$ Å^3, $Z = 4$, $\rho_{calc} = 1.51$ mg m^{-3}. Diffraction experiments were performed on a Siemens Smart systems CCD diffractometer employing graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and collecting a hemisphere of data in 1329 frames with 10 s exposure times. Of 17 871 data, 6002 were unique and 5581 ($>2\sigma(I)$) were used to refine the structure employing 517 parameters. The atom positions were determined using direct methods employing SHELX-TL93 and successive difference Fourier map calculations. The full-matrix least-squares refinement were carried out by using techniques on *F*. All non-hydrogen atoms were assigned anisotropic temperature factors. Empirical absorption corrections ($\mu = 0.399$ mm) were applied to the data sets employing SADABS. Most hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. In the case of the bridging hydrogens, these atoms were located and the positions refined ($R = 0.0551$; $R_w = 0.2209$, GOF = 0.472). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-10360. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Rd., Cambridge CB21EZ, U.K. (fax (+44)1223-336-033; e-mail *deposit@ccdc.cam.ac.uk*).

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Table 1. Polymerization Data

catalyst precursor	mmol of catalyst	cocatalyst[a]	time (min)	productivity (g mmol^{-1} h^{-1})	M_w[b]	M_w/M_n
1	0.0385	MAO	3.00	42	3590	1.8
					336 000	2.2
2	0.0265	MAO	3.00	49	18 700	2.8[e]
					578 500	2.4[e]
3	0.0310	MAO	3.00	500	89 900	1.6
4	0.0258	MAO	3.00	46	7410	2.1[e]
					893 500	3.4[e]
5	0.0372	MAO	3.00	16	7580	1.9[e]
					910 200	2.5[e]
6	0.0219	MAO	3.00	881	65 400	2.4
7	0.0251	TB	3.00	231	134 600	2.8
8	0.0333	TB	3.00	225	163 800	3.9
9	0.0214	TB	3.00	401	165 800	3.4
10	0.0276	TB	0.50	1807	310 200	7.5[c]
11	0.0332	TB	0.50	1193	259 200	9.9[c]
12	0.0181	TB	0.50	1296	321 300	12.3[c]
12	0.0181	MAO	3.00	853	55 600	2.3
Cp_2ZrCl_2	0.0246	MAO	2.00	895	116 353	2.8
14	0.0175	none	2.00	459		
CGC[d]	0.0195	MAO	2.00	630		
Cp_2TiCl_2	0.0253	MAO	2.00	415		
$CpTiCl_3$	0.0260	MAO	2.00	<20		

[a] MAO: methylalumoxane (500 equiv); TB: trityl tetrakis(pentafluorphenyl)borate(2 equiv). All polymerizations were run at 1 atm pressure of ethylene and 25 °C. [b] Molecular weight data were recorded against polyethylene standards. [c] The high activity of these systems together with the observation of polydispersities in the range of 7−12 suggest that these polymerizations rapidly become diffusion-controlled reactions. [d] CGC = [($C_5Me_4SiMe_2N$-*t*-Bu)$TiCl_2$. [e] GPC curves were clearly bimodal, and the quoted polydispersities were derived from a computational fit. Overall polydispersities, ignoring this bimodal nature, were **1** (14.9), **2** (44.4), **4** (59.0)**,** and **5** (56.7).

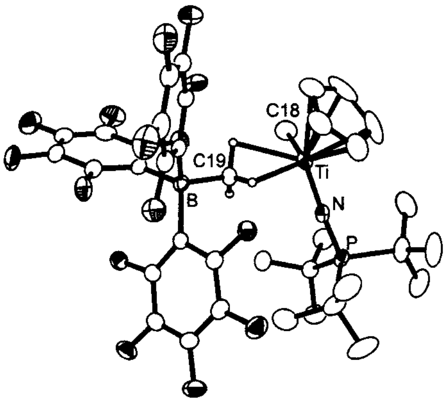

Figure 1. ORTEP drawing of **14**, 30% thermal ellipsoids are shown, all but the bridging methyl hydrogen atoms are omitted for clarity: Ti−N 1.765(3) Å, Ti−C(18) 2.123(5) Å, Ti−C(19) 2.404(4) Å, P−N 1.612(4) Å, B−C(19) 1.655(5) Å, N−Ti−C(18) 101.1(2)°, N−Ti−C(1103.53(15)°, P−N−Ti 176.0(2)°, B−C(19)−Ti 167.2(3)°.

changed from those seen in **3**.[35] The Cp−Ti−N angle in **14** of 131.2° is comparable to the Cp−Ti−Cp angle of 130.96° in Cp_2TiCl_2.[36] Moreover, this is significantly larger than Cp−M−N angles of 107.6° and 107.9° found in the "constrained geometry" complexes [($C_5Me_4SiMe_2N$-*t*-Bu)$TiCl_2$[37] and [($C_5Me_4CH_2CH_2N$-*t*-Bu)$TiCl_2$[37] and non-constrained cyclopentadienyl−amide complexes (115−120°).[38] Furthermore, the Cp−Ti−N angle in **14** is significantly greater than the Cp−Ti−O angle found in CpTi(OC_6H_2-*i*-Pr_3)$_2$Cl (119.2°, 113.1°).[35] These data indicate that while these phosphinimide derivatives contain Cp and N ligation, structurally they emulate bis(cyclopentadienyl) complexes rather than constrained geometry catalysts. It is also noteworthy that the structural data for **14** represent the first to be reported for a cationic single-site Ti olefin polymerization catalyst.

In summary, the feasibility of an approach to catalyst design based on the steric analogy between phosphinimide and cyclopentadienyl ligands is supported by the family of titanium phosphinimide complexes (Cp†)TiX_2(NPR_3). Both the demonstrated activity of these species in ethylene polymerization and the metric parameters of the titanium−phosphinimide catalyst **14** affirm that such ligands provide a metal environment that mimics metallocenes. While the application of this approach to the design of catalysts for olefin polymerization continues to be a focus of our efforts, this strategy suggests the potential for the application of related compounds in a variety of other processes. These aspects are also the subjects of ongoing efforts.

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Supporting Information Available: Spectroscopic, elemental analyses, and crystallographic information tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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