Reviews

The Road to Early-Transition-Metal Phosphinimide Olefin Polymerization Catalysts

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This paper chronicles our work examining early-transition-metal systems incorporating phosphinimide ligands for use as olefin polymerization catalysts. Incorporation of these ancillary ligands affords unique deactivation pathways which are readily overcome by specific activation procedures and contrived ligand modification. In these ways, a new family of highly active olefin polymerization catalysts was successfully developed.

Introduction

The early finding that metallocenes could be activated for olefin polymerization catalysis has been a major stimulus for research in organometallic chemistry. For more than 25 years, research around the globe has been motivated by the potential of developing a new commercially viable homogeneous early-transition-metal olefin polymerization catalyst. A variety of strategies have been employed to this end.[1−8] While much attention has focused on the modification of cyclopentadienyl ligands to provide stereoselective catalysts,[9−12] other efforts have sought new catalyst systems by the inclusion of noncyclopentadienyl ancillary ligands about titanium or zirconium.[4] The first examples of nonmetallocene catalysts to be put into commercial practice were the so-called “constrained geometry catalysts” (CGC).[13−16] These titanium complexes incorporate ligands introduced by Bercaw et al., in which a bulky amide group is linked to a cyclopentadienyl unit.[17] These catalysts exhibit high polymerization activity, which is believed to result from increased availability of the metal center to the incoming substrate. Over the last two decades, a large variety of systems based on various ancillary ligands have been prepared and evaluated. Much of this work has been previously reviewed.[1−8] As examples of these efforts, we cite two specific systems. In landmark work in the 1990s McConville and coworkers developed titanium complexes containing bulky bis-amido-chelate ligands, $[ArN(CH_2)_3NAr]TiMe_2$ (Figure 1), which were effective “nonmetallocene” catalysts for olefin polymerization.[18−20] Moreover, they also showed that these systems afforded “living catalysts”. More recently, the development of the “FI” catalysts by researchers at Mitsui has drawn considerable attention.[21−25] These Zr complexes, containing phenoxy-imine chelate ligands (Figure 1), display very high ethylene polymerization activity upon activation by methylalumoxane (MAO) at 25 °C. Even higher activity was seen when the $[Ph_3C][B(C_6F_5)_4]/i\text{-}Bu_3Al$ system was used in place of MAO.

A large number of other systems have been developed and evaluated for olefin polymerization activity. In this review, we describe our successful efforts to develop a

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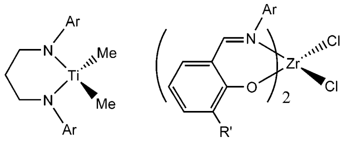


Figure 1. McConville and FI olefin polymerization catalysts.

new ligand scaffold for olefin polymerization catalysts based on phosphinimide ligands. Previous reviews have described portions of this work.[26,27]

Ligand Design Strategy

During a sabbatical leave in Münster, Germany, in 1995, we began to develop our own ideas about new ligands for catalysis and organometallic chemistry in general. There were a number of features we considered desirable if these "new" ligands were to be widely applicable. They must be readily available, or at least easy to prepare. The preparative route should be amenable to substituent modification for tuning of both the electronic and steric characteristics. The resulting ligands must be stable on storage and easily handled. Also, they must be cheap.

Considering catalyst systems that had been described in the literature at the time, we noted several teachings. The CGC system clearly exhibits high activity because the metal center is exposed to the incoming substrate as a result of the short link between the cyclopentadienyl ligand and the amide donor. On the other hand, McConville's work illustrates the need to employ sterically demanding substituents when using heteroatom donors to ensure that the chemistry occurs at the metal and not at the ligand.

To augment our "academic" perspective, discussions with industrial colleagues offered other viewpoints on ligand design. While cheap and easy syntheses were seen as desirable, it was perhaps not unexpected that industrial concerns focused on the activity of the resulting catalysts. However, it is important to note that the industrial standard of activity is limited to temperatures between 70 and 160 °C, as this is the range at which commercial olefin polymerization typically is performed. This is a serious limitation for most systems developed in academic laboratories. Clearly, this aspect could not be assessed a priori; however, it does imply that, for commercial success, thermal stability of both the ligand and the catalyst will be of paramount importance. This suggests that systems which offer strong ligand–metal bonds may offer the best opportunities, thus casting a shadow of doubt on systems derived from neutral donor ligands. Finally, perhaps the most important limitation from an industrial perspective is one not routinely considered by academics: patent position. Efforts in the development of a new ligand set with all of the attributes above that yields highly active polymerization catalysts under industrial conditions are for naught if the system is covered by competitors' patents.

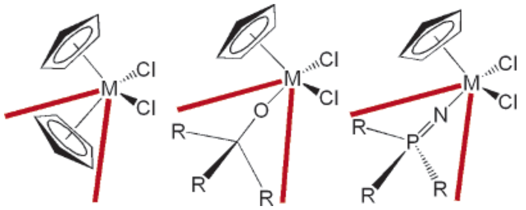
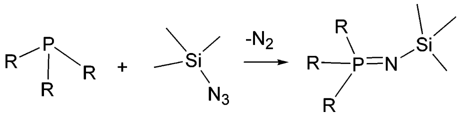


Figure 2. Sterically analogous ligand complexes.

Scheme 1. Synthesis of Phosphinimines



In the distillation of these academic and industrial considerations, we noted a further teaching from Wolczanski and co-workers in which the concept of steric analogy between cyclopentadienyl ligands and bulky alkoxides[28] and siloxides[29−34] was put forth. It was demonstrated that such systems mimicked the chemistry of metallocenes. While bulky alkoxides and siloxides did not have a number of the attributes we sought, the metric similarity of a P–N bond to a Si–O bond suggested that phosphinimide ligands (R_3PN^-) offered very attractive possibilities. Literature precedent showed that these ligands are readily synthesized[35] and bind to metals offering a linear geometry at nitrogen,[36,37] thus providing a conical ligand. Although this mimics the steric demands of cyclopentadienyl ligands, the steric bulk is somewhat removed from the metal center by the intervening nitrogen atom (Figure 2). This offers a second-sphere environment similar to that of the cyclopentadienyl ligand, while offering a more open first coordination sphere: a situation that augurs well for the reactivity of the resulting complexes.

The preparation of phosphinimines is straightforward. It is achieved in high yield by simple azide oxidation (Staudinger reaction[38]) of ubiquitous phosphine ligands (Scheme 1). A range of such phosphinimines had been reported previously, suggesting that access to a variety of such ligands with varying steric and electronic properties would be facile.[36,37,39,40] Finally, as these ligands contain phosphorus, ^{31}P NMR spectroscopy is a convenient spectroscopic handle for monitoring reactions. In terms of the industrial criteria, high-oxidation-state P-based ligands are expected to be thermally stable, but, perhaps most importantly, phosphinimide-based olefin polymerization catalysts were

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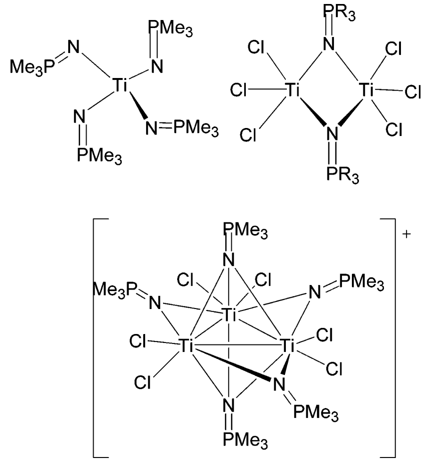
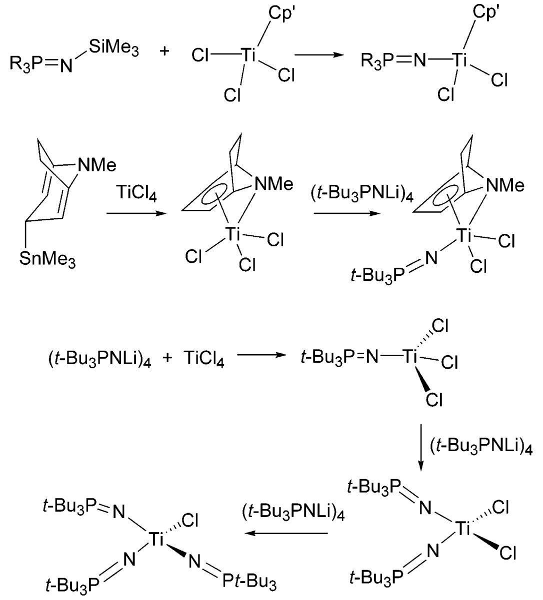


Figure 3. Examples of early-metal phosphinimide complexes.

Scheme 2. Syntheses of Ti Phosphinimide Complexes



not covered by prior art in the patent literature of the day.

Synthesis and Chemistry of Group 4 and 5 Phosphinimide Complexes

Examples of early-transition-metal phosphinimide complexes known at the time are depicted in Figure 3. While these examples demonstrate that a variety of transition-metal phosphinimide complexes are accessible, they suggest that a judicious choice of substituents is required to control the degree of aggregation. In this section, we describe our studies designed to synthesize specifically monometallic phosphinimide complexes of titanium, zirconium, vanadium, and tantalum.

Titanium. Elimination of Me_3SiCl in the reaction of (trimethylsilyl)phosphinimines with $CpTiCl_3$ gave the complexes $CpTi(NPR_3)Cl_2$ in high yields (Scheme 2).[41,42] This general synthetic route can be applied to prepare a range of systems providing access to complexes with various substituents on phosphorus or the cyclopentadienyl rings.[41,43] Alternatively, replacement of the Cp ligand as in the tropidinyl complex $(trop)(R_3PN)TiCl_2$

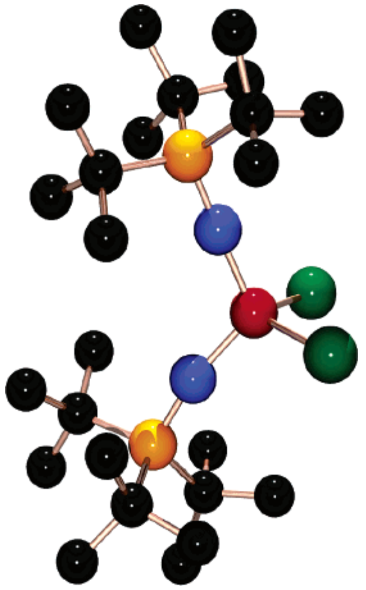
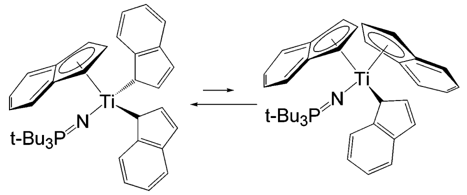


Figure 4. POV-ray depiction of $(t\text{-}Bu_3PN)_2TiCl_2$: Ti, red; Cl, green; N, blue; P, orange; C, black.

Scheme 3. $\eta^5-\eta^1$ Exchange in an Indenyl Ti Phosphinimide Complex



(Scheme 2) also can be achieved in a similar fashion.[44] These reactions are readily scaled up to give multigram quantities. Alternatively, metathesis reactions of the lithium phosphinimides $[t\text{-}Bu_3PNLi]_4$[45] and $TiCl_4$ afforded $(t\text{-}Bu_3PN)TiCl_3$, $(t\text{-}Bu_3PN)_2TiCl_2$ (Figure 4), and $(t\text{-}Bu_3PN)_3TiCl$ (Scheme 2).[46, 47]

The CpTi and cyclopentadienyl-free titanium complexes are readily alkylated with alkyllithium or Grignard reagents. Alkylation of $(t\text{-}Bu_3PN)_3TiCl$ was limited to methylation, presumably as a result of the steric crowding in this compound.[46] Similarly, $LL'Ti(NP\text{-}t\text{-}Bu_3)Cl$ and $L_2L'Ti(NP\text{-}t\text{-}Bu_3)$ (L, L′ = Cp, indenyl) were prepared by reaction of $((CH_2OMe)_2)NaCp$ or Li(indenyl) with the appropriate precursors. In these cases, the cyclopentadienyl and indenyl rings adopt either an η^5 or η^1 bonding mode, depending on temperature and steric crowding. When VT NMR spectra could be measured, an $\eta^5-\eta^1$ exchange process with a barrier of 8−9 kcal/mol was indicated (Scheme 3).[43]

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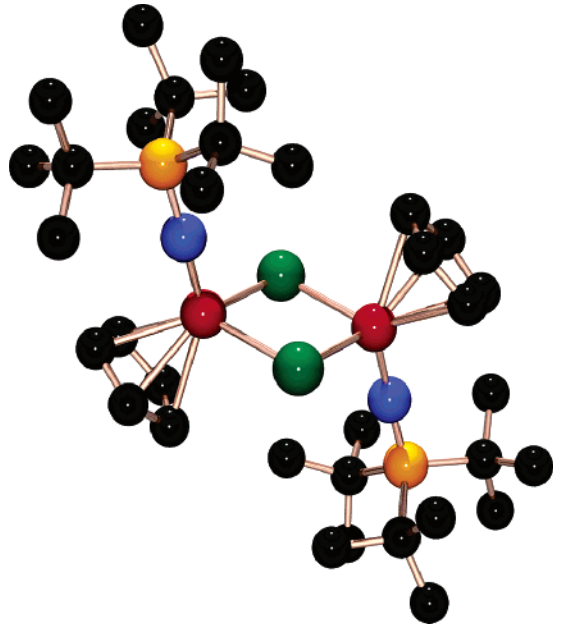
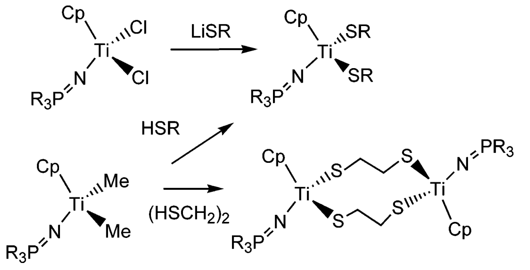


Figure 5. POV-ray depiction of $[CpTi(NP\text{-}t\text{-}Bu_3)(\mu\text{-}Cl)]_2$: Ti, red; Cl, green; N, blue; P, orange; C, black.

Scheme 4. Synthesis and Reactivity of Ti Phosphinimide Thiolate and Sulfur Derivatives



Related titanium phosphinimide thiolate complexes are easily prepared by thiolate-for-chloride metathesis or by protonolysis of metal−carbon bonds by thiols. Thus, $CpTi(NPR_3)(SR')_2$ ($R = i\text{-}Pr$, t-Bu; $R' = CH_2Ph$; Ph, t-Bu) and $[CpTi(NP\text{-}i\text{-}Pr_3)(S_2(CH_2)_2)]_2$ (Scheme 4) and $CpTi(NP\text{-}i\text{-}Pr_3)(S_2R)$ ($R = (CH_2)_3$, $(CH_2)_2C_6H_4$) were prepared.[48,49] The dimeric nature of the ethanedithiolate complex stands in contrast to the monomeric form of the propanedithiolate derivative and is a reflection of subtle steric effects. $CpTi(NP\text{-}t\text{-}Bu_3)Me(SPh)$ and $(t\text{-}Bu_3PN)_2Ti(Me)(St\text{-}Bu)$ are isolable. The related compound $(t\text{-}Bu_3PN)_2Ti(Me)(SCH_2Ph)$ was unstable, evolving CH_4 to give $(t\text{-}Bu_3PN)_2Ti(\eta^2\text{-}SCHPh)$. Reaction of $(t\text{-}Bu_3PN)_2TiMe_2$ with S_8 did not result in S insertion into the Ti−C bond, but the methyl groups were lost and $(t\text{-}Bu_3PN)_2Ti(\eta^2\text{-}S_5)$ was produced.[48]

The reduction of $CpTi(NP\text{-}t\text{-}Bu_3)Cl_2$ with Mg powder in benzene proceeded slowly to give the reddish brown product $[CpTi(NP\text{-}t\text{-}Bu_3)(\mu\text{-}Cl)]_2$ (Figure 5).[50] This Ti(III) complex has been characterized in detail by X-ray crystallography as well as by a solid single-crystal X-band EPR study. The **g** matrix and zero-field parameters are consistent with EHMO calculations, which show a HOMO comprised principally of metal d orbitals that are approximately orthogonal to the Ti−Ti vector. This illustrates that while phosphinimide ligands are sterically analogous to cyclopentadienyl ligands, they are electronically distinct.

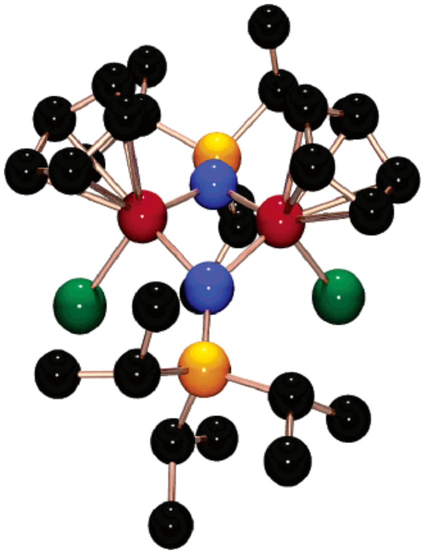
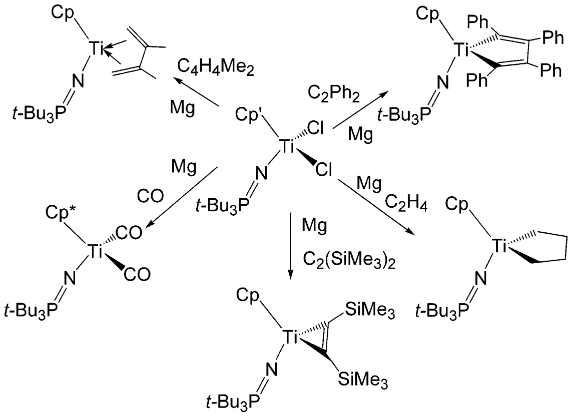


Figure 6. POV-ray depiction of $[CpTi(\mu\text{-}NP\text{-}i\text{-}Pr_3)Cl]_2$: Ti, red; Cl, green; N, blue; P, orange; C, black.

Scheme 5. Trapping of Ti(II) Intermediate with Diphenylacetylene, Ethylene, and CO



Further studies of the reduction of Ti phosphinimides were carried out. Treatment of $CpTi(NPR_3)Cl_2$ (R = Me, i-Pr) with Mg in THF gave the Ti(III) phosphinimide bridged dimers $[CpTiCl(\mu\text{-}NPR_3)]_2$ (R = Me, i-Pr) (Figure 6).[51] This structure is similar to that of the known $[TiBr_2(\mu\text{-}NPPh_3)]_2$[52] but distinct from that of the above $t\text{-}Bu_3PN$ analogue,[50] presumably a result of steric demands. In contrast, reduction of $CpTi(NP\text{-}t\text{-}Bu_3)Cl_2$ by Mg in THF generates a transient Ti(II) intermediate which could be intercepted with 2,3-dimethyl-1,3-butadiene, diphenylacetylene, phenylacetylene, ethylene, and propylene to give $CpTi(NP\text{-}t\text{-}Bu_3)(CH_2CMe)_2$, $CpTi(NP\text{-}t\text{-}Bu_3)(C_2Ph_2)_2$, $CpTi(NP\text{-}t\text{-}Bu_3)(CPhCH)_2$, $CpTi(NP\text{-}t\text{-}Bu_3)(CH_2)_4$, and $CpTi(NP\text{-}t\text{-}Bu_3)(CH_2CHMe)_2$, respectively (Scheme 5). Several of these complexes were structurally characterized by X-ray crystallography and shown to be titanacyclopentadienes and titanacyclopen-

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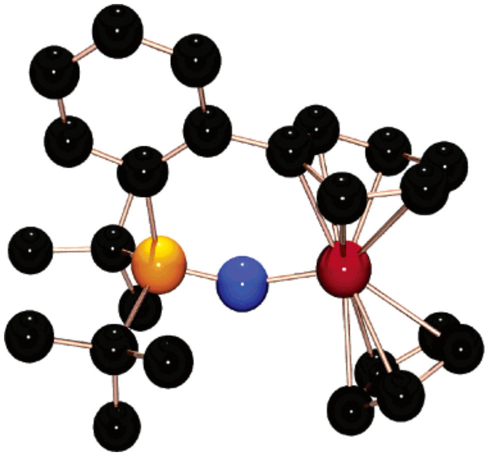


Figure 7. POV-ray depiction of [CpTi(NP-*t*-Bu_2(2-C_6H_4Ph))]: Ti, red; N, blue; P, orange; C, black.

tanes. In the case of the analogous reaction with bis(trimethylsilyl)acetylene, the molecule CpTi(NP-*t*-Bu_3)(η^2-$C_2(SiMe_3)_2$) was isolated (Scheme 5).[51] In this case, the steric demands of the acetylene limited the product to a titanacyclopropene structure. The analogous complexes Cp*Ti(NP-*t*-Bu_3)$(CH_2)_4$ and (indenyl)Ti(NP-*t*-Bu_3)$(CH_2)_4$ were prepared using ethylene to trap the Ti(II) intermediates. The unequivocal role of Ti(II) intermediates in this chemistry was confirmed by the isolation of Cp*Ti(NP-*t*-Bu_3)$(CO)_2$ upon reduction of Cp*Ti(NP-*t*-Bu_3)Cl_2 in the presence of CO (Scheme 5).[51]

Related complexes of the type Cp′Ti(NP-*t*-Bu_2(2-C_6H_4Ph))Cl_2 (Cp′ = Cp, Cp*) were readily prepared, although the initial oxidation with Me_3SiN_3 of the precursor phosphine required prolonged reflux (2 weeks). NMR data showed formation of a 3:1 ratio of two isomers attributable to restricted rotation about the P−C(biphenyl) bond. Reduction of these complexes gave [Cp′Ti(NP-*t*-Bu_2(2-C_6H_4Ph))] (Cp′ = Cp, Cp*), in which the Ti interacts with the pendant phenyl substituents. Metric parameters are consistent with a Ti(IV) cyclohexadiene dianion formulation (Figure 7).[51]

Computational studies of phosphinimide-based catalyst systems were performed by the Ziegler group at the University of Calgary. These DFT calculations predict that the cation $[(R_3PN)_2TiMe]^+$ has a lower ion separation energy than $[CpTi(NCR_2)Me]^+$, $[(CpSiR_2NR')TiMe]^+$, $[CpOSiR_3TiMe]^+$, and $[Cp(R_3PN)TiMe]^+$. This energy is decreased further with increasing size of the R group.[53] Thus, bulky phosphinimide complexes should be active polymerization catalysts.

Zirconium. Zr phosphinimide complexes of the forms CpZr(NPR_3)Cl_2 and Cp*Zr(NPR_3)Cl_2 also were readily prepared, although this required the use of the appropriate trialkylphosphinimide lithium salt, since Me_3SiCl elimination on treatment of zirconium halides with silyl-phosphinimines proved unsuccessful.[54,55] Similarly, the “mixed-ring” complexes Cp*Zr(NPR_3)(Cp)Cl (R = *i*-Pr, *t*-Bu) also were prepared cleanly by the reaction of sodium cyclopentadienide with the precursor dihalide. Alkylation and arylation of the above dihalide compounds as well as of Cp_2Zr(NP-*t*-Bu_3)Cl also were straightforward, affording CpZr(NP-*t*-Bu_3)R_2, Cp*Zr(NP-*t*-Bu_3)R_2, and Cp_2Zr(NP-*t*-Bu_3)R (R = Me, CH_2Ph) in high yield. The butadiene derivatives Cp*Zr(NPR_3)(CH_2CMe_2) (R = *i*-Pr, *t*-Bu) (Figure 8) were prepared by reduction of Cp*Zr(NPR_3)Cl_2 with Mg powder in the presence of 2,3-dimethyl-1,3-butadiene.[54] The structural data revealed that the butadiene fragment is oriented with the open end toward the Cp* ligand. This so-called *supine* orientation is determined by the minimization of steric interactions between methyl groups on the Cp* and butadiene ligands.

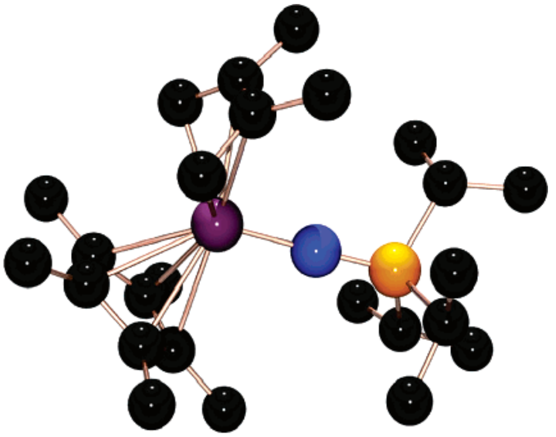
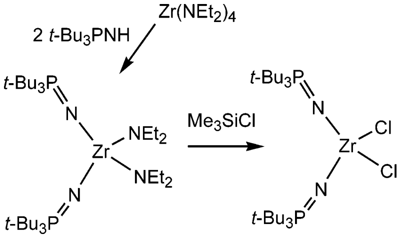


Figure 8. POV-ray depiction of [Cp*Zr(NP*i*-Pr_3)(CH_2CMe)$_2$]: Zr, violet; N, blue; P, orange; C, black.

Scheme 6. Synthesis of Zr Bis-Phosphinimide Complexes



The Zr bis(phosphinimide) complex Zr(NP-*t*-Bu_3)$_2Cl_2$ was not obtained in the reaction of the Li phosphinimide salt with $ZrCl_4$, Zr(NP-*t*-Bu_3)$_3$Cl being isolated instead.[54] However, protonolysis of $Zr(NEt_2)_4$ with 2 equiv of HNP-*t*-Bu_3 afforded Zr(NP-*t*-Bu_3)$_2(NEt_2)_2$. The latter reacted with Me_3SiCl to give Zr(NP-*t*-Bu_3)$_2Cl_2$ in an overall 72% isolated yield (Scheme 6). Attempts to alkylate this product to give Zr(NP-*t*-Bu_3)$_2Me_2$ employing a number of methods were unsuccessful, affording a mixture of unresolved compounds.

Reaction of CpZr(NP-*t*-Bu_3)Me_2 with $B(C_6F_5)_3$ in the presence of the donor THF afforded the salt [CpZr(NP-*t*-Bu_3)Me(THF)][$MeB(C_6F_5)_3$].[54] Similarly, reaction with [$HNMe_2Ph$][$B(C_6F_5)_4$] generated the salt [CpZr(NP-*t*-Bu_3)Me(NMe_2Ph)][$B(C_6F_5)_4$], while reaction of CpZr(NP-*t*-Bu_3)$_2$(CH_2Ph) with $B(C_6F_5)_3$ gave [CpZr(NP-*t*-Bu_3)$_2$][($PhCH_2$)$B(C_6F_5)_3$].[54] Insertion into the Zr−Me bond was effected by reaction of the Zr−dimethyl precursor with the borane and carbodiimide, affording [Cp*Zr(NP-*t*-Bu_3)((*i*-PrN)$_2$CMe)][$MeB(C_6F_5)_3$] and [CpZr(NP-*t*-Bu_3)((*i*-PrN)$_2$CMe)][$MeB(C_6F_5)_3$] (Scheme 7).[54] In an analogous manner, the reaction of Cp*Zr(NP-*t*-Bu_3)(CH_2CMe)$_2$ with $B(C_6F_5)_3$ gave the betaine complex Cp*Zr(NP-*t*-Bu_3)($CH_2C(Me)C(Me)CH_2B(C_6F_5)_3$) (Figure 9).[54]^{19}F NMR

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(53) Xu, Z.; Vanka, K.; Firman, T.; Michalak, A.; Zurek, E.; Zhu, C.; Ziegler, T. *Organometallics* **2002**, *21*, 2444−2453.

(54) Hollink, E.; Wei, P.; Stephan, D. W. *Organometallics* **2004**, *23*, 1562−1569.

(55) Yue, N.; Hollink, E.; Guerin, F.; Stephan, D. W. *Organometallics* **2001**, *20*, 4424−4433.

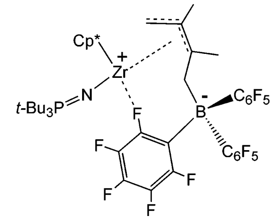
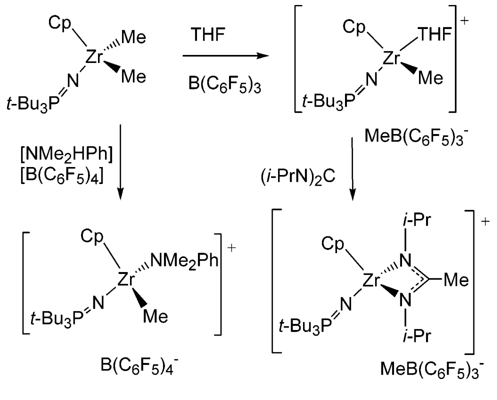
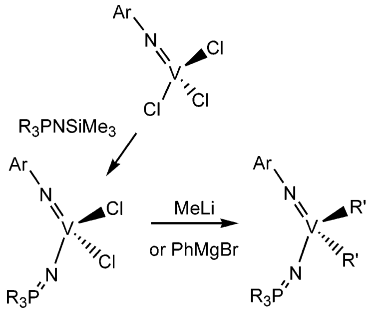


Figure 9. Structure of $Cp^*Zr(NP\text{-}t\text{-}Bu_3)(CH_2C(Me)C(Me)CH_2B(C_6F_5)_3)$.

Scheme 7. Cationic Zr Phosphinimide Complexes



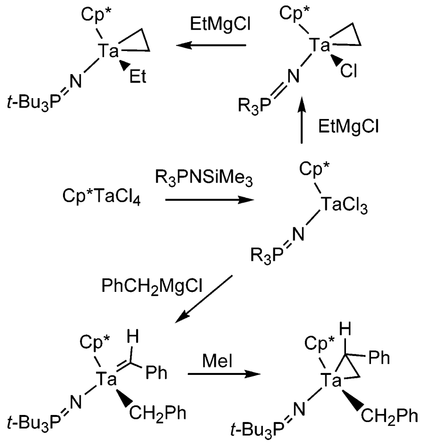
Scheme 8. Synthesis of V Phosphinimide Complexes



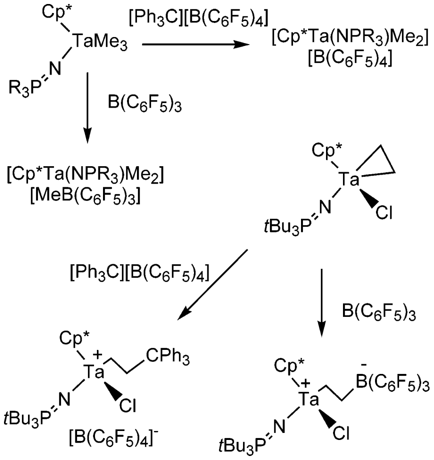
data revealed a stabilizing interaction of the cationic Zr center with an ortho fluorine of one of the arene rings.

Vanadium. The synthesis of vanadium phosphinimide complexes was unsuccessful when procedures that were successful in the case of titanium were used. For example, reactions of $VOCl_3$ with Me_3SiNPR_3 or $Li[NPR_3]$ led to unresolvable mixtures of products. In one such effort, a few crystals of $VCl_2(NPPh_3)_3$ were isolated and shown to be the salt $[VCl(NPPh_3)_3]Cl$. When other synthetic methods were explored, reactions of $VCl_3(NAr)$ (Ar = Ph, C_6H_3-2,6-*i*-Pr_2) with $R_3PNSiMe_3$ (R = Ph, *i*-Pr, *t*-Bu) resulted in the straightforward syntheses of $VCl_2(NAr)(NPR_3)$ (Scheme 8). These products could be alkylated or arylated to give the related compounds $VR_2(NAr)(NP\text{-}t\text{-}Bu_3)$ (R = Me, Ph).[56] Alternatively, the chlorides could be replaced with other ligands to afford compounds such as $VCl(N(SiMe_3)_2)(NPh)(NP\text{-}t\text{-}Bu_3)$ and $V(SCH_2Ph)_2(NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(NP\text{-}t\text{-}Bu_3)$. All preliminary tests of vanadium phosphinimide complexes showed poor catalytic activities and afforded polyethylene with broad polydispersities.[56] This implies complex instability, even under mild polymerization conditions.

Scheme 9. Synthesis of Ta Phosphinimide Complexes



Scheme 10. Synthesis of Cationic Ta Phosphinimide Complexes



Tantalum. Complexes of the type $Cp^*Ta(NPR_3)Cl_3$ were readily prepared by the stoichiometric reactions of Cp^*TaCl_4 with $R_3PNSiMe_3$.[57] It is interesting that, for $Cp^*Ta(NP\text{-}t\text{-}Bu_3)Cl_3$, variable-temperature ^1H NMR studies revealed restricted rotation about the Ta−N bond at low temperature, inferring a "cogwheel" effect. These chlorides are readily alkylated sequentially to give $Cp^*Ta(NPR_3)RCl_2$ (R = Me, CH_2Ph) and $Cp^*Ta(NP\text{-}t\text{-}Bu_3)(CH_2Ph)Me_2$.[57] When en excess of benzyl-Grignard reagent was used in the synthesis, the alkylidene complex $Cp^*Ta(NPR_3)(CHPh)(CH_2Ph)$ was formed (Scheme 9). The latter reacted with methyl iodide to form the styrene−Ta metallacycle $Cp^*Ta(NP\text{-}t\text{-}Bu_3)(\eta^2\text{-}CHPhCH_2)(CH_2Ph)$ (Scheme 9). Alkylation of the trichloride with EtMgCl resulted in β-hydrogen elimination and formation of the complex $Cp^*Ta(NP\text{-}t\text{-}Bu_3)(\eta^2\text{-}C_2H_4)Cl$, while addition of an excess of EtMgCl gave $Cp^*Ta(NP\text{-}t\text{-}Bu_3)(\eta^2\text{-}C_2H_4)(CH_2Me)$.[57]

Tantalum zwitterions and salts are readily formed. For example, $Cp^*Ta(NP\text{-}t\text{-}Bu_3)Cl_3$ reacted with $B(C_6F_5)_3$ to give the salt $[Cp^*Ta(NP\text{-}t\text{-}Bu_3)Cl_2][ClB(C_6F_5)_3]$, while the analogous reaction with $Ph_3C[B(C_6F_5)_4]$ afforded $[Cp^*Ta(NP\text{-}t\text{-}Bu_3)Cl_2][B(C_6F_5)_4]$.[57] The zwitterionic complexes $Cp^*Ta(NPR_3)Me_2(MeB(C_6F_5)_3)$, $[Cp^*Ta(NPR_3)Me_2][B(C_6F_5)_4]$ (R = *i*-Pr, *t*-Bu), and [Cp*Ta(NP-*t*-

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(56) Hawkeswood, S. B.; Stephan, D. W. *Inorg. Chem.* **2003**, *42*, 5429−5433.

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Table 1. Selected Activities of Ethylene Polymerization Catalysts (MAO Activation)[a]

cat.	act.[c]	M_w	PDI	cat.	act.	M_w	PDI
$CpTi(NPCy_3)Cl_2$	42	3 590	1.8	t-$BuCpTi(NPCy_3)Cl_2$	46	7 410	2.1
		336 000	2.2			893 500	3.4
$CpTi(NP$-i-$Pr_3)Cl_2$	49	18 700	2.8	t-$BuCpTi(NP$-i-$Pr_3)Cl_2$	16	7 580	1.9
		578 500	2.4			910 200	2.5
$CpTi(NP$-t-$Bu_3)Cl_2$	652	89 900	1.6	t-$BuCpTi(NP$-t-$Bu_3)Cl_2$	881	65 400	2.4
$CpTi(NPPh_3)Cl_2$	34	109 200	2.6	n-$BuCpTi(NP$-t-$Bu_3)Cl_2$	2000		

[a] Conditions: MAO = methylalumoxane (500 equiv); 1 atm pressure of ethylene, 25 °C, 5 min. [b] Conditions: Schlenk line, 1 atm pressure of ethylene, 25 °C, 30 min. [c] Activity units are g of PE $mmol^{-1}$ h^{-1} atm^{-1}.

Table 2. Selected Activities of Ethylene Polymerization Catalysts ($[Ph_3C][B(C_6F_5)_4]$ Activation)[a]

cat.	act.[b]	M_w[c]	PDI	cat.	act.	M_w	PDI
$CpTi(NPCy_3)Me_2$	231	134 600	2.8	t-$BuCpTi(NPCy_3)Me_2$	1807	310 200	7.5
$CpTi(NP$-i-$Pr_3)Me_2$	225	163 800	3.9	t-$BuCpTi(NP$-i-$Pr_3)Me_2$	1193	259 200	9.9
$CpTi(NP$-t-$Bu_3)Me_2$	401	165 800	3.4	t-$BuCpTi(NP$-t-$Bu_3)Me_2$	1296	321 300	12.3

[a] Conditions: 1 atm ethylene, 25 °C, cocatalyst trityl tetrakis(perfluorophenyl)borate. [b] Activity units are g of PE $mmol^{-1}$ h^{-1} atm^{-1}. [c] Molecular weight data were recorded against polyethylene standards.

$Bu_3)(CH_2Ph)Cl][ClB(C_6F_5)_3]$ were formed in a similar manner. Treatment of $Cp^*Ta(NP$-t-$Bu_3)(\eta^2$-$C_2H_4)Cl$ with $[Ph_3C][B(C_6F_5)_4]$ gave $[Cp^*Ta(NP$-t-$Bu_3)(Cl)(CH_2CH_2CPh_3)][B(C_6F_5)_4]$ (Scheme 10), while reaction with $B(C_6F_5)_3$ resulted in formation of the zwitterionic complex $[Cp^*Ta(NP$-t-$Bu_3)(Cl)(CH_2CH_2B(C_6F_5)_3)]$. None of these cationic or zwitterionic complexes showed ethylene polymerization activity.[57]

First-Generation Phosphinimide Olefin Polymerization Catalysts

Titanium. Cyclopentadienyltitanium phosphinimide dichloride derivatives were evaluated as catalysts for ethylene polymerization activity by activation with 500 equiv of methylalumoxane (MAO) using 1 atm of ethylene at 25 °C (Table 1).[41,42] These screening data suggested that the activity is markedly dependent on the substituents on the ligands. For example, the catalysts derived from $CpTi(NPCy_3)Cl_2$ and $CpTi(NP$-i-$Pr_3)Cl_2$ exhibit relatively low activity when activated by MAO (Table 1), while $CpTi(NP$-t-$Bu_3)Cl_2$ gave rise to a catalyst with an activity of 652 g of PE $mmol^{-1}$ h^{-1} atm^{-1}, approaching that observed with Cp_2ZrCl_2 under the same conditions (895 g of PE $mmol^{-1}$ h^{-1} atm^{-1}). The latter phosphinimide catalyst gave polyethylene of molecular weight 89 000 with a polydispersity of 1.6, consistent with single-site catalysis.[41,42]

Encouraged by these initial screening data, we investigated other activation procedures. The zwitterionic complex $CpTiMe(NP$-t-$Bu_3)(\mu$-$MeB(C_6F_5)_3)$ was shown to be a single-component catalyst.[42] Addition of ethylene to its solution in hexane initiated polymerization, although the resulting activity of 459 g of PE $mmol^{-1}$ h^{-1} atm^{-1} was not exceptional. In the same vein, activation of dialkyl precursors of the type $CpTi(NPR'_3)R_2$ with $[Ph_3C][B(C_6F_5)_4]$ resulted in generally much higher activity, yielding higher molecular weight PE (135 000−321 000) than the analogous catalysts generated with MAO (Table 2). For example, the catalysts derived from $CpTi(NPCy_3)Me_2$ and $CpTi(NP$-i-$Pr_3)Me_2$ showed a substantially increased activity, giving 231 and 225 g of PE $mmol^{-1}$ h^{-1} atm^{-1}, respectively, upon activation by $[Ph_3C][B(C_6F_5)_4]$. Perhaps more importantly, systems with additional steric bulk resulting from larger substituents on the phosphorus atom and in the cyclopentadienyl ligand such as t-$BuC_5H_4Ti(NPR_3)Me_2$ (R = Cy, i-Pr, t-Bu) showed a dramatic increase in activity, giving 1807, 1193, and 1296 g of PE $mmol^{-1}$ h^{-1} atm^{-1}, respectively (Table 2). In these initial screening tests, the thermal spike resulting from the high activity resulted in polydispersities in the range of 7−12.[42] However, in subsequent tests under more controlled thermal conditions, the polydispersities were near 2.0, typical for single-site catalysts. This suggested that our strategy of cyclopentadienyl ligand replacement was credible, as several of these systems provided activities that were 2−3 times those of the metallocenes under similar conditions.[42,58−61] Addition of donor ligands to $CpTi(NP$-t-$Bu_3)Me(\mu$-$MeB(C_6F_5)_3)$ led to the displacement of the methylborate anion and isolation of a series of salts of the form $[CpTi(NP$-t-$Bu_3)Me(L)][MeB(C_6F_5)_3]$.[62] In a similar fashion, the salts $[CpTiMe(NP$-t-$Bu_3)(L)][B(C_6F_5)_4]$ were prepared in the reaction of $CpTiMe_2(NP$-t-$Bu_3)$ and $[Ph_3C][B(C_6F_5)_4]$ in the presence of a donor ligand.

Screening tests for catalysts derived from $(t$-$Bu_3PN)_2TiX_2$ using MAO activation showed rather poor activity, but activation with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ provided more active catalysts.[47] In collaboration with industrial researchers, several of these systems were probed under the more demanding conditions of higher temperatures (160 °C) and pressures of ethylene. Catalysts derived from Cp_2ZrMe_2, the constrained-geometry catalyst (CGC) $(C_5Me_4SiMe_2N$-t-$Bu)TiMe_2$, and $(t$-$Bu_3PN)_2TiMe_2$, all activated by $[Ph_3C][B(C_6F_5)_4]$, were tested under conditions used in commercial solution polymerization for the production of polyethylene (Table 3). The reagent and activator flow rates were optimized for each evaluated catalyst. It is noteworthy that under

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(61) Stephan, D. W.; Stewart, J. C.; Harrison, D. G. Supported phosphinimine-cyclopentadienyl catalysts for polymerization of olefins. EP 890581, 1999.

(62) Cabrera, L.; Hollink, E.; Stewart, J. C.; Wei, P.; Stephan, D. W. *Organometallics* **2005**, *24*, 1091−1098.

Table 3. Selected Activities of Ethylene Polymerization Catalysts under Industrially Relevant Conditions ($[Ph_3C][B(C_6F_5)_4]$ Activation)[a]

cat.	act.[b]	M_w[c]	PDI
$(t\text{-}Bu_3PN)_2TiMe_2$	62 310	77 500	1.9
$(t\text{-}BuNSiMe_2C_5Me_4)TiMe_2$	16 130	134 500	2.5
Cp_2ZrMe_2	8 850	12 300	3.8

[a] Conditions: 160 °C, flow conditions. [b] Activity units are g of PE $mmol^{-1}$ h^{-1} atm^{-1}. [c] Molecular weight data were recorded against polyethylene standards.

Table 4. Selected Activities of Ethylene Polymerization Zr Catalysts[a]

cat.	cocat.	act.[b]	M_n	M_w	PDI
$Cp^*Zr(NP\text{-}t\text{-}Bu_3)Cl_2$	MAO	170	3 070	5 930	1.9
			783 900	1 261 000	1.6
$CpZr(NP\text{-}t\text{-}Bu_3)Cl_2$	MAO	100	3 450	234 300	67.9
$Cp^*Zr(NP\text{-}t\text{-}Bu_3)Me_2$	MAO	70			
$Cp^*Zr(NP\text{-}t\text{-}Bu_3)Me_2$	$B(C_6F_5)_3$	270	59 900	161 300	2.7
$CpZr(NP\text{-}t\text{-}Bu_3)Me_2$	$B(C_6F_5)_3$	400	6 640	94 900	14.3
$Cp^*Zr(NP\text{-}t\text{-}Bu_3)Me_2$	$[Ph_3C][B(C_6F_5)_4]$	1010	54 200	177 000	3.3
$CpZr(NP\text{-}t\text{-}Bu_3)Me_2$	$[Ph_3C][B(C_6F_5)_4]$	1270	7 450	24 400	3.3

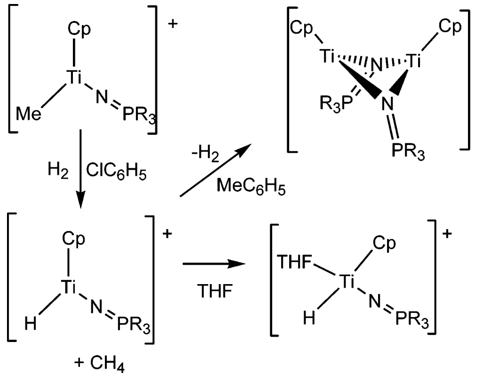
[a] Conditions: toluene, 30 °C, 1.82 atm of C_2, 50 μM catalyst, 30 min. MAO activation: Zr:Al ratio 1:500. $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$ activation: Zr:Al ratio 1:20 ($i\text{-}Bu_3Al$), 10 min. [b] Activity units are g of PE $mmol^{-1}$ h^{-1} atm^{-1}.

these commercial conditions the activity of the zirconocene catalyst (8800 g of PE $mmol^{-1}$ h^{-1} atm^{-1}) is roughly 1 order of magnitude greater than that observed under typical academic laboratory screening protocols. The CGC/$[Ph_3C][B(C_6F_5)_4]$ catalyst exhibited an activity that was about double that of the zirconocene/$[Ph_3C][B(C_6F_5)_4]$ catalyst, whereas the catalyst derived from $(t\text{-}Bu_3PN)_2TiMe_2$ afforded activities approximately 4 times that of the CGC catalyst.[47] In addition, it continued to act as a single-site ethylene polymerization catalyst under these stringent conditions, giving PE with a polydispersity of 1.9. The molecular weight of the polymer was, however, slightly lower than that produced by the constrained-geometry catalyst.[47]

Zirconium. The synthesis of zirconium zwitterionic complexes and salts suggested that Zr phosphinimides also might be effective polymerization catalysts. However, screening of some of these Zr complexes as catalysts for ethylene polymerizations employing MAO as the activator showed only moderate polymerization activities relative to zirconocene standards and analogous Ti compounds (Table 4).[55] This was attributed to interactions of the phosphinimide ligand with the Lewis acidic Al centers, leading either to ligand abstraction or C−H activation processes. This notion is consistent with single-point Gaussian calculations on $CpZr(NP\text{-}t\text{-}Bu_3)Cl_2$ and $Zr(NP\text{-}t\text{-}Bu_3)_2Cl_2$ which showed that the HOMO, HOMO-1, and HOMO-2 are comprised of significant N−Zr character and are accessible to sterically unencumbered Lewis acids.[55]

In marked contrast, high polymerization activities were obtained with Zr phosphinimide complexes using $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ as cocatalyst and $Al(i\text{-}Bu)_3$ as a scavenger for trace impurities in the solvent and ethylene. No evidence for the formation of $CpZr(NP\text{-}t\text{-}Bu_3)(C_6F_5)_2$ was observed. Thus, olefin insertion is rapid in comparison to methyl-for-C_6F_5 exchange. For all Zr catalysts tested, use of $[Ph_3C][B(C_6F_5)_4]$ as the cocatalyst led to significantly higher polymerization activities.[55] It is noteworthy that these Zr catalysts showed significantly better activity upon activation by $[Ph_3C][B(C_6F_5)_4]$ than with MAO activation, a situation also observed for Ti phosphinimide catalysts.

Scheme 11. Reactions of a Cationic Ti Hydride Complex



Deactivation Pathways

Hydrogen Transfer. Transfer of a β-hydrogen atom to the incoming olefin is known to terminate polymerization and result in the formation of a metal hydride complex. The mechanism of this process has been studied by DFT calculations.[63] These studies show that the steric bulk and electron-donating nature of the phosphinimide ligands in the cations $[(R_3PN)_2TiR]^+$ and $[CpTi(NPR_3)R]^+$ suppress hydrogen transfer reactions, although these cations undergo more facile hydrogen transfer than the corresponding zirconium systems.[63] In related synthetic chemistry, Piers and co-workers recently have shown that reaction of the cation $[CpTi(NPR_3)Me]^+$ with H_2 in ClC_6H_5 results in reduction of Ti(IV) to Ti(III), affording the dimeric dication $[CpTi(NPR_3)]_2^{2+}$. The analogous reaction in toluene followed by addition of THF provided the hydride cation $[CpTi(NPR_3)H(THF)]^+$ (Scheme 11).[64]

C−H Activation. The promise of "single-site catalysts" derived from phosphinimide complexes demonstrated by the results described above is qualified to some extent by the need for a specific activation strategy. The early results revealed generally poor activity with MAO activation[47,55,61] and significantly better reactivity with C_6F_5−B-based activators. Efforts to probe these observations present a challenge, as MAO is a complex reagent. However, interactions of phosphinimide complexes with MAO were modeled by reactions with $AlMe_3$. These reactions reveal C−H activation products and suggest that C−H bond activation may be a degradation pathway for phosphinimide catalysts in the presence of MAO. Alternatively, it may be that the dative interaction of the Ti-bound phosphinimide ligand with an Al center is sufficient to suppress catalyst activity. The C−H activation products are described below.

Reactions of $CpTi(NPR_3)Me_2$ or (indenyl)$Ti(NP\text{-}i\text{-}Pr_3)Me_2$ with $AlMe_3$ proceed smoothly at room temperature to effect triple C−H bond activation, giving the Ti−Al−carbide complexes $Cp'Ti(\mu_2\text{-}Me)(\mu_2\text{-}NPR_3)(\mu_4\text{-}C)(AlMe_2)_3$

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[63] Wondimagegn, T.; Vanka, K.; Xu, Z.; Ziegler, T. *Organometallics* **2004**, *23*, 2651−2657.

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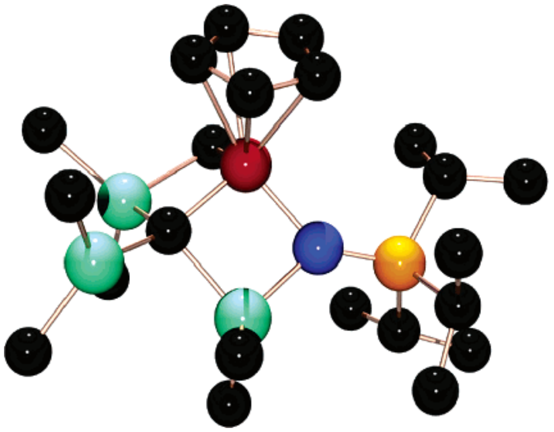


Figure 10. POV-ray depiction of CpTi(μ_2-Me)(μ_2-NP-*i*-Pr$_3$)(μ_4-C)(AlMe$_2$)$_3$: Ti, red; Al, light green; N, blue; P, orange; C, black.

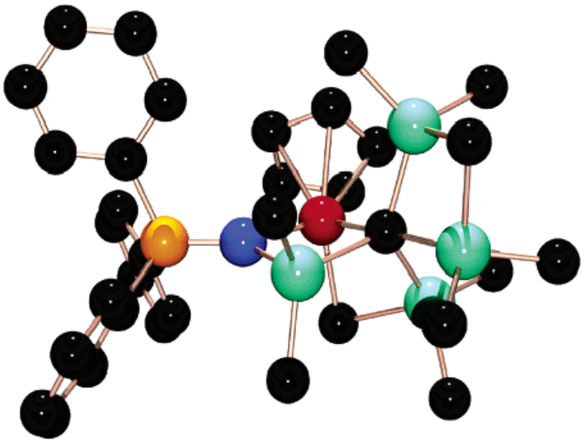
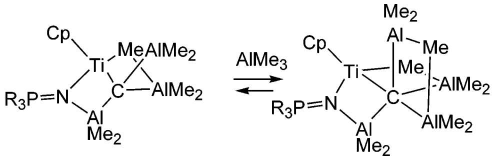
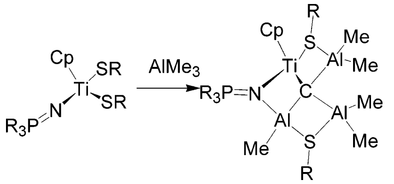


Figure 11. POV-ray depiction of CpTi(μ_2-Me)(μ_2-NPPh$_3$)(μ_5-C)(AlMe$_2$)$_3$(AlMe$_3$): Ti, red; Al, light green; N, blue; P, orange; C, black.

Scheme 12. Interconversion of Four- and Five-Coordinate Carbide Complexes



Scheme 13. Synthesis of Thiolate-Carbide Complexes



(Cp′ = Cp, indenyl) (Figure 10).[65] These complexes establish equilibria with an excess of AlMe$_3$, forming Cp′Ti(μ_2-Me)(μ_2-NPR$_3$)(μ_5-C)(AlMe$_2$)$_3$(AlMe$_3$) (Figure 11) in a facile interconversion of carbide complexes with distorted-tetrahedral and five-coordinate, pseudo-trigonal-bipyramidal geometries.[65] This was confirmed with X-ray crystallographic studies of CpTi(μ_2-Me)(μ_2-NP-*i*-Pr$_3$)(μ_4-C)(AlMe$_2$)$_3$ and CpTi(μ_2-Me)(μ_2-NPPh$_3$)(μ_5-C)(AlMe$_2$)$_3$(AlMe$_3$) (Scheme 12).[66] The equilibrium constant was determined by NMR spectroscopy to be 129 M^{-1} at 260 K. The corresponding thermodynamic parameters were found to be ΔG(260 K) = −10.5 kJ mol^{-1}, ΔH = −57.9 kJ mol^{-1}, and ΔS = −0.183 kJ mol^{-1} K^{-1}.[65]

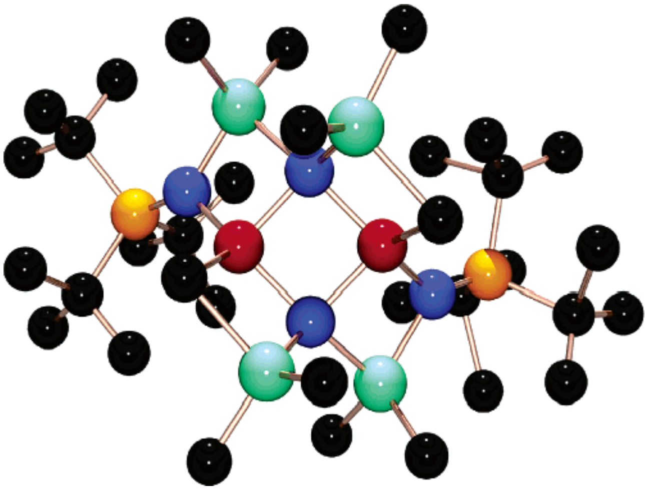


Figure 12. POV-ray depiction of [(μ_2-*t*-Bu$_3$PN)Ti(μ-Me)(μ_4-C)(AlMe$_2$)$_2$]$_2$: Ti, red; Al, light green; N, blue; P, orange; C, black.

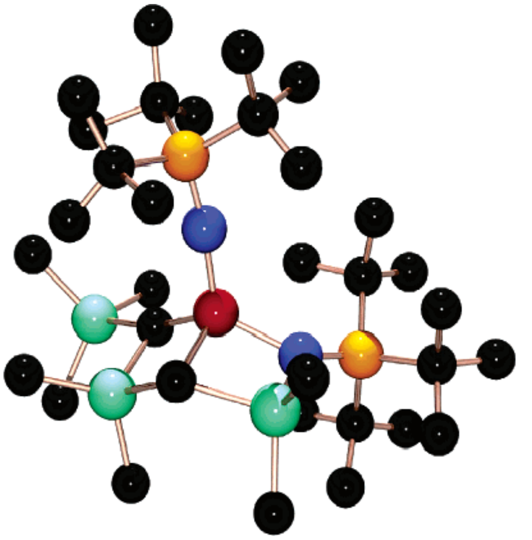


Figure 13. POV-ray depiction of (*t*-Bu$_3$PN)Ti(μ_2-NP-*t*-Bu$_3$)(μ_3-CH$_2$)$_2$(AlMe$_2$)$_2$(AlMe$_3$): Ti, red; Al, light green; N, blue; P, orange; C, black.

In a similar experiment, the compounds CpTi(NPR$_3$)(SR)$_2$ reacted with AlMe$_3$ to give the carbide complex CpTi(μ-NP-*i*-Pr$_3$)(μ-SR)(μ_4-C)(AlMe$_2$)$_2$(μ-SR)AlMe (R = CH$_2$Ph, Ph, *t*-Bu) (Scheme 13).[49] These reactions proceed via methyl-for-thiolate exchange. Such processes are precluded by chelating dithiolates, forming adducts of the form [CpTi(NP-*i*-Pr$_3$)(SRS)]·3AlMe$_3$ (R = (CH$_2$)$_3$, 1,2-(CH$_2$)$_2$(C$_6$H$_4$)).[48] In similar reactions, sterically crowded analogues limited the degree of C−H activation. For example, reaction of CpTi(NP-*i*-Pr$_3$)(CH$_2$SiMe$_3$)$_2$ with AlMe$_3$ gave CpTi(μ_2-Me)(μ_2-NP*i*-Pr$_3$)(μ_3-CSiMe$_3$)(AlMe$_2$)$_2$, while in the reaction of Cp*Ti(NP-*i*-Pr$_3$)Me$_2$ with AlMe$_3$ Cp*Ti(μ_2-Me)(μ_2-NP-*i*-Pr$_3$)(μ_3-CH)(AlMe$_2$)$_2$ was produced.[65]

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(65) Kickham, J. E.; Guerin, F.; Stewart, J. C.; Urbanska, E.; Ong, C. M.; Stephan, D. W. *Organometallics* **2001**, *20*, 1175−1182.

(66) Kickham, J. E.; Guerin, F.; Stewart, J. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3263−3266.

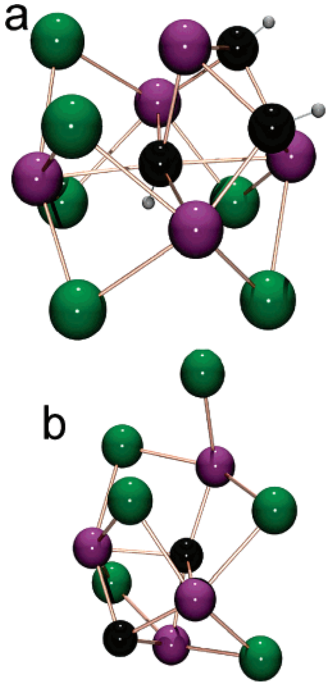

Figure 14. POV-ray depiction of core structures of the clusters $(Cp^*Zr)_4(\mu\text{-}Cl)_5(Cl)(\mu\text{-}CH)_2$ and $(Cp^*Zr)_5(\mu\text{-}Cl)_6(\mu\text{-}CH)_3$: Zr, violet; Cl, green; C, black.

In a similar vein, $(t\text{-}Bu_3PN)_2TiMe_2$ reacted with $AlMe_3$ to give the two Ti-based products $[(\mu_2\text{-}t\text{-}Bu_3PN)Ti(\mu\text{-}Me)(\mu_4\text{-}C)(AlMe_2)_2]_2$ (Figure 12) and $(t\text{-}Bu_3PN)Ti(\mu_2\text{-}NP\text{-}t\text{-}Bu_3)(\mu_3\text{-}CH_2)_2(AlMe_2)_2(AlMe_3)$ (Figure 13).[67] The latter compound reacted further with excess $AlMe_3$ at 60 °C to effect further C−H activation and give $[Ti(\mu_2{-}NP\text{-}t\text{-}Bu_3)_2(\mu_3\text{-}CH_2)(\mu_3\text{-}CH)(AlMe_2)_3]$.

Detailed mechanistic studies performed on the above reaction revealed that the two products were formed by competitive pathways involving initial methyl-for-phosphinimide metathesis and C−H activation.[67] Metathesis generated $(t\text{-}Bu_3PN)TiMe_3$, which underwent a series of three sequential C−H activations with rate constants $k_1 = [3.9(5)] \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_2 = [1.4(2)] \times 10^{-3}\ s^{-1}$, and $k_3 = [7(1)] \times 10^{-3}\ s^{-1}$ to give the carbide complex $[(\mu_2\text{-}t\text{-}Bu_3PN)Ti(\mu\text{-}Me)(\mu_4\text{-}C)(AlMe_2)_2]_2$.[67] In the competitive reaction leading to the formation of $(t\text{-}Bu_3PN)Ti(\mu_2\text{-}t\text{-}Bu_3PN)(\mu_3\text{-}CH_2)_2(AlMe_2)_2(AlMe_3)$, the rate constants of the initial C−H activation and ligand metathesis were found to be similar, at $[6(1)] \times 10^{-5}\ s^{-1}$ and $[6.1(5)] \times 10^{-5}\ s^{-1}$, respectively.[67] Consideration of the transient concentrations of the intermediates in these reactions is consistent with nonproductive equilibria involving intermediates in each pathway with $AlMe_3$. This was supported by stochastic−kinetic simulations.[67]

Analogous model reactions of Zr phosphinimide complexes with $AlMe_3$ led to complex mixtures of products, two of which were identified as the clusters $(Cp^*Zr)_4(\mu\text{-}Cl)_5(Cl)(\mu\text{-}CH)_2$ and $(Cp^*Zr)_5(\mu\text{-}Cl)_6(\mu\text{-}CH)_3$ (Figure 14).[55] The characterization of these products demonstrates that both ligand metathesis and C−H bond activation are involved in the formation of the mixture of products. This suggests that such reactions may also account for the generally poor activity of Zr phosphinimide complexes with Al-based activators.

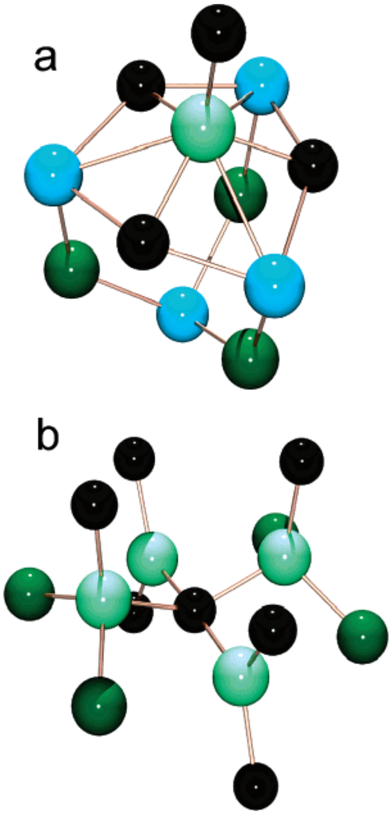

Figure 15. POV-ray depiction of core structures of the (a) cation and (b) anion of $[(Cp^*Cr)_4(\mu\text{-}Cl)_3(i\text{-}CH_2)_3AlMe][(Me_2Al)_2(\mu\text{-}CH)(AlCl_2Me)_2]$: Cr, green-blue; Al, light green; Cl, green; C, black.

In related chromium chemistry, $Cp^*Cr(HNP\text{-}i\text{-}Pr_3)Cl_2$ reacted with $AlMe_3$ to give crystals of $[(Cp^*Cr)_4(\mu\text{-}Cl)_3(\mu\text{-}CH_2)_3AlMe][(Me_2Al)_2(\mu\text{-}CH)(AlCl_2Me)_2]$ in low yield (Figure 15).[68] The Cr_4Al cation contains three bridging chlorides and three bridging methylene groups that bridge the Cr atom and the AlMe fragment. The anion contains four Al atoms about a central methine group in a pseudo-trigonal-bipyramidal arrangement. Mechanistically, it seems that chemistry similar to that occurring in the related Ti and Zr systems may account for ligand abstraction and C−H bond activation.

Ligand Exchange and Degradation. The above examples of phosphinimide ligand exhange clearly account for diminished catalyst activity. Ligand exchange reactions also are observed in reactions of Zr phosphinimides with $B(C_6F_5)_3$. For example, reaction of $CpZr(NP\text{-}t\text{-}Bu_3)Me_2$ with $B(C_6F_5)_3$ resulted in immediate formation of $CpZr(NP\text{-}t\text{-}Bu_3)(C_6F_5)_2$. Similar reactions were reported for the McConville diamide complexes $[ArN(CH_2)_3NAr]TiMe_2$.[69] While it was initially thought that such exchange processes could account for low activities of borane-activated catalysts, it was subsequently shown that methyl for C_6F_5 exchange is not significant in the presence of donor ligands, including ethylene. Computational studies showed that aryl group transfer from $[MeB(C_6F_5)_3]^-$ to the metal in $[(R_3PN)_2MMe]^+$ or $[CpM(NPR_3)Me]^+$ to produce $L_2MMe(C_6F_5)$ and $MeB(C_6F_5)_2$ is more facile for Zr than for Ti.

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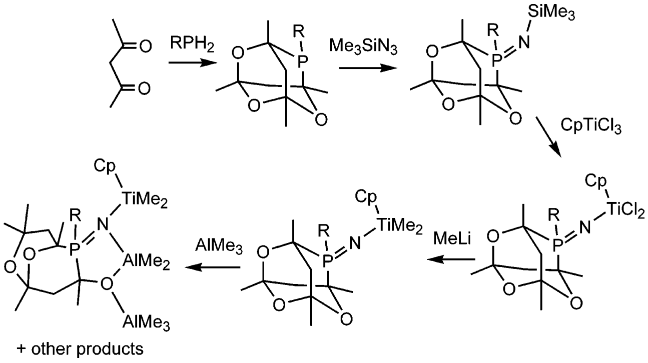
[67] Kickham, J. E.; Guerin, F.; Stephan, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 11486−11494.

[68] Wei, P.; Stephan, D. W. *Organometallics* **2003**, *22*, 1992−1994.

[69] Scollard, J. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1997**, *16*, 1810−1812.

Scheme 14. Synthesis and Reactivity of "Cage-Phosphinimide" Complexes



However, electron-donating ligands and sterically demanding substituents preclude this deactivation pathway.[70]

In an attempt to improve catalyst activity by phosphinimide ligand modification, we noted that in the early screening the data are consistent with improved activity with increased steric demand of the ancillary ligands. To this end, we noted the work of Pringle et al.,[71] who reported bulky bidentate phosphine ligands in which the phosphorus atoms are incorporated in a sterically demanding adamantane-like cage. In the derived Pd complexes, these ligands displayed very large ligand cone angles. Molecular modeling was employed to discern that phosphaadamantyl-phosphinimides exhibit ligand cone angles significantly larger than that of tris-*tert*-butylphosphinimide. The precursor "cage phosphines" $PR(C_6H_4O_3Me_4)$ are readily prepared by the reaction of the respective RPH_2 compound with 2,4-pentanedione in water (Scheme 14). In a straightforward manner, these phosphines were oxidized with Me_3SiN_3 to the corresponding phosphinimines, and subsequent reaction with titanium chlorides followed the established procedures.[72] Initial screening of the complexes $CpTi(NPR(C_6H_4O_3Me_4))Cl_2$ and $CpTi(NPR(C_6H_4O_3Me_4))Me_2$ (R = Ph, Cy) containing these bulky phosphinimide ligands for catalytic activity in ethylene polymerization showed surprisingly low activities (<10 g of PE $mmol^{-1}$ h^{-1} atm^{-1}) upon activation by MAO or $[Ph_3C][B(C_6F_5)_4]$.[72] This stands in marked contrast to the bulky alkyl phosphinimide systems described above.

The poor performance of these titanium "cage phosphinimide" derivatives as polymerization catalysts was probed by studying the interaction with $AlMe_3$. A complex mixture of products, consistent with Lewis acid attack at the titanium−nitrogen fragment, was observed. This view was substantiated by the isolation of one of the minor products, $CpTiMe_2(NPCy(C_6H_4O_3Me_5)(\mu\text{-}AlMe_2)(AlMe_3))$ (Scheme 14), in which Lewis acid induced ligand rupture is confirmed.[72] The resulting product presumably is inactive in catalysis. A similar mixture of products was found in the reaction of $CpTiMe_2(NPR(C_6H_4O_3Me_3))$ with $B(C_6F_5)_3$. This presumably accounts for the similarly low activity when $[Ph_3C][B(C_6F_5)_4]$ was used as an activator. These observations confirm that sterically bulky ancillary ligands alone are not the key to useful olefin polymerization catalysts.

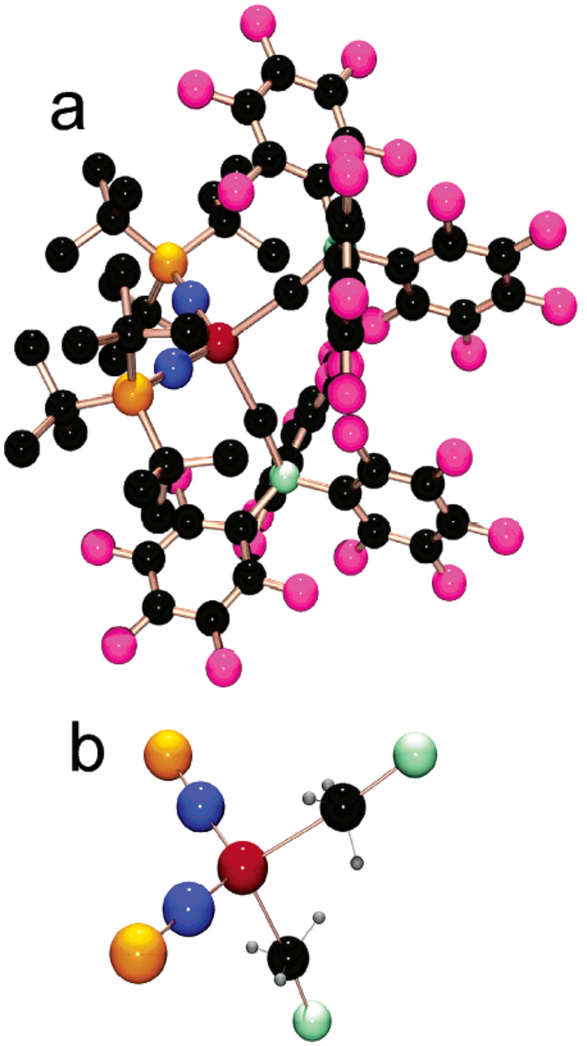


Figure 16. POV-ray depiction of $(t\text{-}Bu_3PN)_2Ti(\mu\text{-}MeB(C_6F_5)_3)_2$: Ti, scarlet; B, light green; F, pink; N, blue; P, orange; C, black.

$B(C_6F_5)_3$ as Catalyst Poison. The product obtained in the stoichiometric reaction of $(t\text{-}Bu_3PN)_2TiMe_2$ with $B(C_6F_5)_3$ depended on the way the reactants were mixed. Addition of $(t\text{-}Bu_3PN)_2TiMe_2$ to a solution of the $B(C_6F_5)_3$ led to the generation of a catalyst with poor activity (<50 g of PE $mmol^{-1}$ h^{-1} atm^{-1}), whereas addition of the $B(C_6F_5)_3$ to a solution of $(t\text{-}Bu_3PN)_2TiMe_2$ gave a product with significantly increased catalyst activity (265 g of PE $mmol^{-1}$ h^{-1} atm^{-1}). These observations are consistent with the formation of the 1:1 zwitterion $(t\text{-}Bu_3PN)_2TiMe(\mu\text{-}Me)B(C_6F_5)_3$ in the absence of an excess of the borane and the formation of $(t\text{-}Bu_3PN)_2Ti(\mu\text{-}MeB(C_6F_5)_3)_2$ in the presence of an excess of the borane.[73] The formation of the latter compound was confirmed by X-ray crystallography (Figure 16). This complex showed negligible polymerization activity and is surprisingly stable with respect to conproportionation with $(t\text{-}Bu_3PN)_2TiMe_2$. Thus, while $B(C_6F_5)_3$ is an activator, it can also act as catalyst poison.

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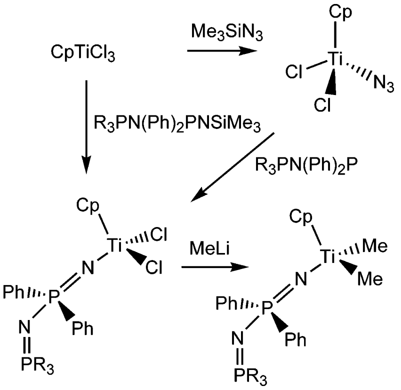
(70) Wondimagegn, T.; Xu, Z.; Vanka, K.; Ziegler, T. *Organometallics* **2004**, *23*, 3847−3852.

(71) Gee, V.; Orpen, A. G.; Phetmung, H.; Pringle, P. G.; Pugh, R. I. *Chem. Commun.* **1999**, 901−902.

(72) Carraz, C.-A.; Stephan, D. W. *Organometallics* **2000**, *19*, 3791−3796.

(73) Guerin, F.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1298−1300.

Scheme 15. Synthesis of Phosphinimido-Phosphinimide Complexes



Strategies to Second-Generation Olefin Polymerization Catalysts

As the above efforts were focused on the expeditious demonstration of high activity by titanium phosphinimide catalysts under industrially relevant conditions, the question of the catalyst structure/activity relationship optimization remained open. To this end, our interests were in developing new avenues to ligand design and synthesis.

Phosphinimido-Phosphinimide Ligands. An approach to an alternative bulky ancillary phosphinimide ligand involves the use of phosphinimide substituents on a phosphinimide ligand. The phosphines $PPh_2(NPR_3)$ (R = *i*-Pr, *t*-Bu) were prepared in high yield.[74] They were readily converted to the corresponding phosphinimines $Me_3SiNPPh_2(NPR_3)$. In the standard manner, compounds of the type $CpTi(NPPh_2(NPR_3))Cl_2$ were prepared and subsequently alkylated with MeMgBr (Scheme 15). These catalysts, evaluated using preliminary screening methods, demonstrated intermediate levels of activity.[74] For example, $CpTi(NPPh_2(NP\text{-}i\text{-}Pr_3)Cl_2$ upon activation with MAO yielded polyethylene with an activity of 299 g of PE $mmol^{-1}$ h^{-1} atm^{-1} at 25 °C. This suggests that the steric bulk of these ligands precludes complex degradation by the Al-based activators, as has been seen in related systems.[74] In marked contrast, the methyl derivatives $CpTi(NPPh_2(NPR_3))Me_2$ upon reaction with $[Ph_3C][B(C_6F_5)_4]$ showed minimal polymerization activity. Independent reactions of $CpTi(NPPh_2(NPR_3))Me_2$ with $B(C_6F_5)_3$ were consistent with the expected methyl abstraction, although the resulting zwitterion apparently is highly reactive, affording a complex mixture of products derived from borate-substituent redistribution as well as reaction with the solvent.[74] This suggests that phosphinimido substituents on phosphinimide ligands result in highly Lewis acidic, and consequently reactive, Ti centers making them prone to deactivation.

Chelating Phosphinimides. We have previously commented on the activity of the Ti bis-phosphinimide complexes. This prompted efforts to extend this chemistry to analogous chelating bis-phosphinimide ligands.[75] The diphosphines $m\text{-}C_6H_4(CH_2PR_2)_2$ (R = *t*-Bu, Cy) were prepared and converted to phosphinimines and the latter used to prepare Ti and Zr amido, halo, and alkyl derivatives such as $m\text{-}C_6H_4(CH_2R_2PN)_2Ti(NMe_2)_2$, $m\text{-}C_6H_4(CH_2R_2PN)_2MX_2$ (M = Ti, Zr), and $m\text{-}C_6H_4\text{-}(CH_2(t\text{-}Bu)_2PN)_2TiR_2$ (R = Me, CH_2Ph) (Scheme 16) as well as $(m\text{-}C_6H_4(CH_2(t\text{-}Bu)_2PN)_2)_2Zr$.[75] In general, evaluation of these compounds as ethylene polymerization catalysts showed poor activity, regardless of the activation procedure employed. It was speculated that this was attributable to the acidity of the protons of the xylyl linkage. Similar inferences have been made for related titanium complexes.[76]

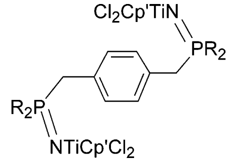
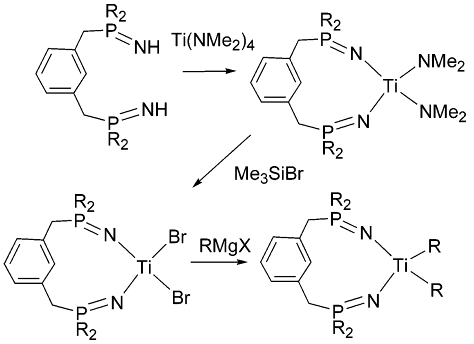


Figure 17. Bimetallic phosphinimide derivatives.

Scheme 16. Synthesis of Chelating Bis-Phosphinimide Complexes



Bimetallic Phosphinimide Derivatives. Much effort has been devoted in attempts to alter the polydispersities of the polyethylenes obtained when single-site polymerization catalysts were used. One such approach involves linking catalyst sites together. To that end, a series of bimetallic phosphinimide-based titanium catalysts were prepared. The complexes $p\text{-}C_6H_4(CH_2PR_2NTiCp'Cl_2)_2$ (R = *t*-Bu, Cy; Cp′ = Cp, Cp*) (Figure 17) and the methylated analogues were prepared using the usual synthetic methods. The halide derivatives upon activation with MAO or $[Ph_3C][B(C_6F_5)_4]$ catalyzed the polymerization of ethylene, although with activities somewhat lower than those obtained using the monometallic analogues. Such differences were attributed to solubility issues. The resulting polyethylenes had relatively high molecular weights, up to 1 416 000, but showed broad bimodal molecular weight distributions. While this was initially attributed to the presence of two possible catalytic sites, related monometallic catalysts also showed broadened molecular weight distributions. These observations suggest that the catalyst undergoes some sort of transformation during polymerization. It has been suggested that the benzylic protons could be the site of such reactivity, and this is supported by the metalation of the methylene protons of $(CH_2PPh_2NTiCp^*Cl_2)_2$, noted by Bochmann and coworkers.[76]

Tris-Amido-Phosphinimide Ligands. A contrived approach for catalyst design was based on the judicious choice of catalyst modification based on an examination

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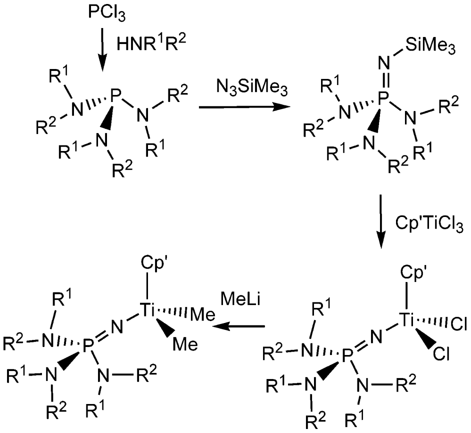
(74) Yue, N. L. S.; Stephan, D. W. *Organometallics* **2001**, *20*, 2303–2308.

(75) Hollink, E.; Stewart, J. C.; Wei, P.; Stephan, D. W. *Dalton* **2003**, 3968–3974.

(76) Said, M.; Hughes, D. L.; Bochmann, M. *Dalton* **2004**, 359–360.

Scheme 17. Synthesis of Tris-Amido-Phosphinimide Complexes



of the mechanism from a computational perspective.[77] While Ziegler and co-workers have previously described the mechanism of the first two insertions of ethylene using the model precursor $CpTi(NPH_3)Me_2$ and the model activator BCl_3, we examined similar computations for the series $CpTi(NPR_3)Me_2$ (R = Me, NH_2, Cl, F). These computational results were consistent with previous results that indicated the dominance of the energy profile by the ion pair separation energies for the methyl and propyl cations, $[CpTi(NPR_3)Me]^+$.[77] Moreover, they indicate that use of electron-donating substituents results in a significantly smaller ion pair separation energy, thus enhancing catalyst activity. In particular, alkyl and amido substituents show similar ion pair separation energies. From a synthetic perspective, amido-phosphinimides offer several synthetic advantages over bulky alkylphosphines. They are much easier to prepare and are readily varied, and some are commercially available.

On the basis of this strategy, the series of titanium complexes $Cp'Ti(NP(NR_2)_3)Cl_2$ (Cp′ = Cp, R = Me, Et, *i*-Pr, *t*-Bu, R_2 = *i*-PrMe, EtPh; Cp′ = Cp*, R = Me, Et, *i*-Pr, *t*-Bu, R_2 = *i*-PrMe, EtPh) (Scheme 17) as well as the corresponding Ti dimethyl derivatives were prepared.[77] These complexes upon activation by MAO showed generally low activity, although the more sterically demanding phosphinimide ligand complexes afforded significantly higher activities. Activation of the analogous dimethyl derivatives with $B(C_6F_5)_3$ resulted in much higher ethylene polymerization activity (1200−2600 g of PE $mmol^{-1}$ h^{-1} atm^{-1}). At lower concentrations (4 μmol/L) a dramatic increase in the polymerization activities to the range 2200−10 000 g of PE $mmol^{-1}$ h^{-1} atm^{-1} was observed. These increases in activity parallel the steric demands of the amido substituents.

Future Directions

The present work firmly established the potential of phosphinimide complexes in early-transition-metal olefin polymerization catalysis. Moreover, these systems have been shown to be highly effective under the rigors of commercially relevant polymerization conditions. The rich chemistry offered by transition-metal phosphinimide complexes foreshadows the potential for applications of these systems as well as of related ligands in other stoichiometric and catalytic transformations. It is these aspects that are now the focus of our current research efforts.

Acknowledgment. I wish to acknowledge the enthusiastic and very bright scientists I have had the pleasure of working with during the course of the studies described herein. These include Jeff Stewart, Fred Guerin, Jim Kickham, Charles Carraz, Chris Ong, Chad Beddie, Emily Hollink, Sarah Hawkeswood, Steve Clemens, Lourisa Cabrera, Silke Courtenay, Todd Graham, Chris Frazer, and Pingrong Wei. I am also grateful to researchers at NOVA Chemicals Corp. for their contributions and continuing financial support. I particularly want to thank Paul Clark, Daryll Harrison, Steve Brown, John Swabey, Rupert Spence, Linda Koch, Xaoliang Gao, Qinyan Wang, Wei Xu, and Peter Zoricak. The NSERC of Canada is also thanked for financial support.

OM050096B

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[77] Beddie, C.; Hollink, E.; Wei, P.; Gauld, J.; Stephan, D. W. *Organometallics* **2004**, *23*, 5240−5251.