Macromol. Symp. ***173,*** *105–115 (2001)*

Olefin Polymerization and Deactivation Pathways of Titanium-Phosphinimide Catalysts

Douglas W. Stephan

School of Physical Sciences, Chemistry and Biochemistry, University of Windsor,
Windsor, ON Canada N9B 3P4
Fax 519-973-7098, Email: stephan@uwindsor.ca

SUMMARY: This paper reviews our recent progress in the development of new olefin polymerization catalysts based on titanium-phosphinimide catalysts. Initial studies of steric effects are considered as well as the chemical pathways of activation and deactivation.

Introduction

The next generation of commercial homogeneous early transition metal olefin polymerization catalysts has been the subject of research for a number of groups around the world for some time. A variety of strategies have been employed to this end. Many include modification of the ancillary ligands about titanium or zirconium, however of the non-metallocene catalysts made to date only those in the family known as "constrained geometry catalysts (CGC)"1), has been put into commercial practice. The high activity of this system is attributed to the exposure of the metal center precipitated by the strain inherent in the chelating cyclopentadienyl-amide ligand. In developing our approach to catalyst design, we noted the work of Wolczanski et al2) who described the steric analogy between the tri-*t*butylmethoxide and cyclopentadienyl ligands. Applying a related steric analogy, we focused attention on the potential of titanium complexes of bulky phosphinimide ligands. This approach offers several potential advantages. Firstly, the conical nature of phosphinimides approximates the cone occupied by cyclopentadienyl ligands. However, the bulk is more removed from the metal center offering potentially enhanced reactivity. Secondly, the ease of synthesis of phosphinimide ligands from the readily available phosphine precursors provides the flexibility to tune the steric and electronic properties of the ligands. Finally, the inclusion of phosphorus based ligands permits use of ^{31}P NMR spectroscopy as a convenient spectroscopic handle for monitoring reaction progress.

CCC 1022-1360/00/$ 17.50+.50/0

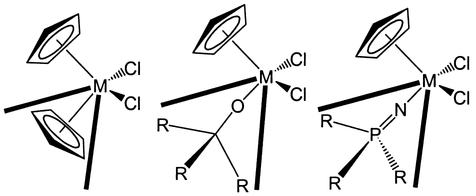


Fig.1: Steric analogy of Cp_2MCl_2, $CpM(OCR_3)Cl_2$ and $CpM(NPR_3)Cl_2$

Synthesis of Catalyst Precursors

The syntheses of phosphinimide ligands of the form $R_3PNSiMe_3$ are readily prepared via the Staudinger reaction of phosphine with N_3SiMe_3.[3] Subsequent formation of the complexes $CpTiCl_2(NPR_3)$ follows in the facile reaction of $CpTiCl_3$ with the appropriate trimethylsilyl-phosphinimine.[4] This synthetic route provides considerable flexibility tolerating a range of substituents on either the phosphinimide or the cyclopentadienyl rings. In a similar fashion, cyclopentadienyl-free titanium complexes are readily obtained in stoichiometric reactions of the lithium phosphinimide ($t$$Bu_3PNLi$) and $TiCl_4$. In this manner the species ($t$$Bu_3PN)TiCl_3$, ($t$$Bu_3PN)_2TiCl_2$ and ($t$$Bu_3PN)_3TiCl$ were prepared.[5,6] Subsequent alkylation of both the cyclopentadienyl-titanium halides as well as the cyclopentadienyl-free complexes is achieved in a straightforward manner employing alkyl-lithium or Grignard reagents.

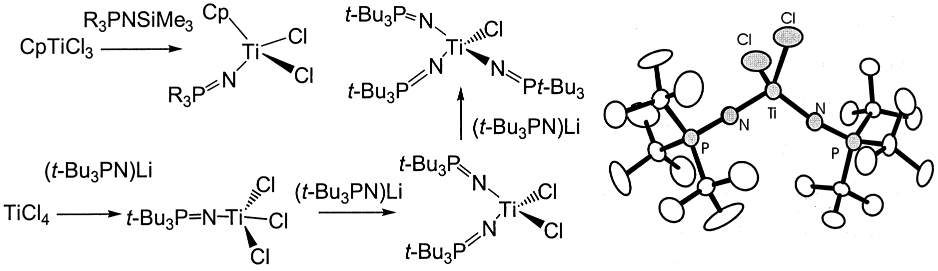


Fig.2: Synthetic pathways to titanium-phosphinimide complexes; X-ray structure of (t-$Bu_3PN)_2TiCl_2$

The zwitterionic complexes $CpTiMe(NPR_3)(\mu\text{-}MeB(C_6F_5)_3)$[4)] and $(t\text{Bu}_3PN)_2TiMe(\mu\text{-}MeB(C_6F_5)_3)$[5)] were obtained upon reaction of the $CpTiMe_2(NPR_3)$ or $(t\text{Bu}_3PN)_2TiMe_2$ with $B(C_6F_5)_3$. These species are analogous to those previously reported from metallocenes.

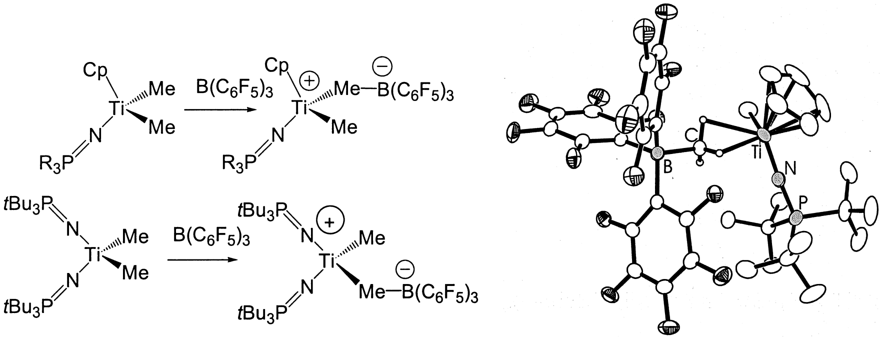


Fig. 3: Synthetic pathways to zwitterionic titanium-phosphinimide complexes; X-ray structure of $CpTiMe(NPt\text{Bu}_3)(\mu\text{-}MeB(C_6F_5)_3)$

Ethylene Polymerization

The cyclopentadienyl-titanium-phosphinimide compounds in the presence of 500 equivalents of methyl alumoxane (MAO) effect the catalytic polymerization of ethylene at 1 atmosphere and 25°C (Table 1). The level of activity appears to be dependent on the substituents on the phosphorus center. For example, while the catalysts derived from $CpTiCl_2(NPCy_3)$ and $CpTiCl_2(NPi\text{Pr}_3)$ and MAO exhibit relatively low activity (Table 1), the complex $CpTiCl_2(NPt\text{Bu}_3)$ gives rise to a catalyst with an activity of 652 g PE/mmol/h, approaching that observed from Cp_2ZrCl_2 under the same conditions (895 g PE/mmol/h). It is also noteworthy that the latter phosphinimide catalyst gives polyethylene of 89,000 molecular weight with a polydispersity of 1.6 consistent with single-site catalysis.[4,5)]

The encouraging result above prompted the study of related catalysts generated by activation with $[Ph_3C][B(C_6F_5)_4]$. This strategy results in higher activity, single-site catalysts that generate polyethylene of higher molecular weight (135-321,000 g/mol). It is noteworthy that the catalysts derived from $CpTiMe_2(NPCy_3)$ and $CpTiMe_2(NPi\text{Pr}_3)$ show a substantial increase in activity giving 231 and 225 g PE/mmol/h respectively. Perhaps more importantly, systems with additional steric crowding such as $t\text{BuCpTiMe}_2(NPR_3)$ ($R = Cy$, $i\text{Pr}_3$, $t\text{Bu}_3$) show a marked increase in activity giving 1807, 1193 and 1293 g PE/mmol/h respectively. In these cases, the high activity together with the observation of polydispersities in the range of 7-12 suggest that these screening polymerizations rapidly become diffusion-controlled reactions.

The active species in the above polymerizations is believed to be cationic titanium species generated by methyl abstraction. These species are related to the zwitterionic species isolated above (Fig. 3). That related stoichiometric reactions of $CpTiMe_2(NPR_3)$ species with $Ph_3C[B(C_6F_5)_4]$ in the presence of the donor PMe_3 gives Ti(IV) cations of the form $[CpTiMe(NPR_3)(PMe_3)][B(C_6F_5)_4]$ further supports this proposition.[4)]

Table 1: Catalysis of Ethylene Polymerization

Catalyst Precursor	Co-Catalyst[a)]	Productivity (g PE/mmol/h)	M_w	Polydispersity
$CpTiCl_2(NPCy_3)$	MAO	42	3,590	1.8[b)]
			336,000	2.2[b)]
$CpTiCl_2(NP\mathit{i}Pr_3)$	MAO	49	18,700	2.8[b)]
			578,000	2.4[b)]
$CpTiCl_2(NP\mathit{t}Bu_3)$	MAO	652	89,000	1.6
$CpTiMe_2(NPCy_3)$	TB	231	134,600	2.8
$CpTiMe_2(NP\mathit{i}Pr_3)$	TB	225	163,800	3.9
$CpTiMe_2(NP\mathit{t}Bu_3)$	TB	401	165,800	3.4
t-$BuCpTiMe_2(NPCy_3)$	TB	1807	310,200	7.5
t-$BuCpTiMe_2(NP\mathit{i}Pr_3)$	TB	1193	259,200	9.9
t-$BuCpTiMe_2(NP\mathit{t}Bu_3)$	TB	1293	321,300	12.3
Cp_2ZrCl_2	MAO	895	116,300	2.8

a) 25°C, toluene, MAO = methylalumoxane; TB = trityl tetrakis(pentafluorophenyl)borate;
b) bimodal

More demanding conditions of higher temperatures and pressures of ethylene often lead to the degradation of many catalysts that are active under the mild conditions of initial laboratory screenings.

The viability of the *bis*-phosphinimide-based catalyst was demonstrated when tested under conditions relevant to the commercial solution production of high and low-density polyethylene (160°C). The flow of reagents and the activator were optimized for catalyst activity (Table 2). The species Cp_2ZrMe_2 and $(C_5Me_4SiMe_2N\mathit{t}Bu)TiMe_2$, were also tested under these conditions for comparison. The results demonstrate that the catalyst derived from $(\mathit{t}Bu_3PN)_2TiMe_2$ continues to act as a single-site ethylene polymerization catalysts under these stringent conditions as evidenced by the relatively low polydispersity of 1.9. While the molecular weight of the polymer is lower than that produced by the constrained geometry catalyst, the titanium-phosphinimide catalyst provides remarkably high activity, producing almost four-times as much polyethylene under similar conditions.[5)]

Table 2: Catalysis of Ethylene Polymerization Under Industrial Conditions

Catalyst Precursor	Co-Catalyst[a)]	Productivity (g PE/mmol/h)	M_w	Polydispersity
Cp_2ZrMe_2	TB	8,850	12,300	3.8
$(C_5Me_4SiMe_2N\textit{t}Bu)TiMe_2$	TB	16,130	134,500	2.5
$(\textit{t}Bu_3PN)_2TiMe_2$	TB	62,310	77,500	1.9

[a)] TB = trityl tetrakis(pentafluorophenyl)borate; 160°C, flow conditions, hexane

Several of the above phosphinimide systems were also screened for activity in catalysis of higher olefin polymerization. The results for the polymerization of 1-hexene are summarized in Table 3. In general, the activities for polyhexene formation are lower than for polyethylene, consistent with the greater steric demands associated with the monomer and the growing polymer chain. Nonetheless, these systems do act as single site catalysts providing polyhexene with molecular weights of 3,600-12,100 g/mol. The application of these systems to other polyolefins continues to be an area of study.

Table 3: Catalysis of Hexene Polymerization

Catalyst Precursor	Co-Catalyst[a)]	Productivity (g PH/mmol/h)	Mw	Polydispersity
$CpTiCl_2(NP\textit{t}Bu_3)$	BCF	233	3,590	1.8
$Cp^*TiMe_2(NP\textit{i}Pr_3)$	TB	102	8,100	1.9
$(t\text{-}Bu_3PN)_2TiMe_2$	TB	293	12,100	3.8

[a)]BCF = tris(pentafluorophenyl)borane; TB = trityl tetrakis(pentafluorophenyl)borate; hexane, 25°C,

Catalyst Deactivation Pathways

The promising results for the *bis*-phosphinimide-based catalyst described above clearly warrant further study. From an academic perspective we would like to understand the unique characteristics of this new class of early metal catalysts. While the studies above provide some insight into the nature of the catalyst activation process, we were interested in the ways in which these systems become deactivated as well. Clearly such information will add both in the understanding of these systems as well as the design of new ones.

$B(C_6F_5)_3$ as a Catalyst Poison

The zwitterionic species ($t$$Bu_3PN)_2TiMe(\mu\text{-}MeB(C_6F_5)_3)$ (Fig. 2) is an active catalyst for ethylene polymerization. However, we noted in preliminary screening studies that the order of addition of the reagents had a dramatic effect on the activity (Table 4). Addition of ($t$$Bu_3PN)_2TiMe_2$ to a solution of the $B(C_6F_5)_3$ at 25°C under an ethylene atmosphere gave poor activity and only a small amount of polyethylene. In contrast, addition of $B(C_6F_5)_3$ to a solution of ($t$$Bu_3PN)_2TiMe_2$ gave significantly increased activity. In probing these observations, we found that reaction of ($t$$Bu_3PN)_2TiMe_2$ with excess $B(C_6F_5)_3$ under N_2 leads to the formation of the zwitterionic species ($t$$Bu_3PN)_2Ti(\mu\text{-}MeB(C_6F_5)_3)_2$ (Fig. 4). This species exhibits negligible polymerization activity. This observation demonstrates that while $B(C_6F_5)_3$ activates ($t$$Bu_3PN)_2TiMe_2$ to generate an active catalyst, excess $B(C_6F_5)_3$ poisons the active species by di-zwitterion formation. This reactivity for $B(C_6F_5)_3$ demonstrates an unprecedented mode of catalyst deactivation. It is presumably the remote nature of the steric bulk of the phosphinimide ligands that allows access to the metal center by two equivalents of the borane.[7)]

Table 4: Catalysis of Ethylene Polymerization

Catalyst Precursor	Co-Catalyst[a)]	Productivity (g PE/mmol/h)	Order of Addition
$(t\text{-}Bu_3PN)_2TiMe_2$	BCF	<50	Precursor to BCF
$(t\text{-}Bu_3PN)_2TiMe_2$	BCF	265	BCF to Precursor

[a)] BCF = trispentafluorophenylborane

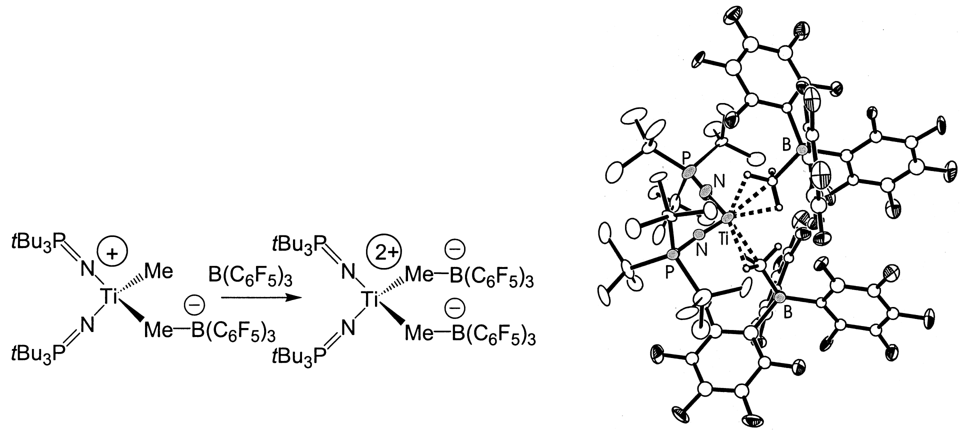


Fig. 4: Formation and crystal structure of $(t\mathrm{Bu}_3\mathrm{PN})_2\mathrm{Ti}(\mu\text{-}\mathrm{MeB}(\mathrm{C}_6\mathrm{F}_5)_3)_2$

Catalyst Deactivation via C-H Bond Activation

Although the titanium-phosphinimide polymerization catalysts above are generally active, they do generally show lower activity when activated by MAO. This observation was particularly true for complexes containing sterically less demanding phosphinimide ligands. To probe the lower activity in these cases, reactions of the titanium-phosphinimide complexes with excess AlMe_3 were undertaken. For example, reaction of $\mathrm{CpTi(NPR_3)Me_2}$ with AlMe_3

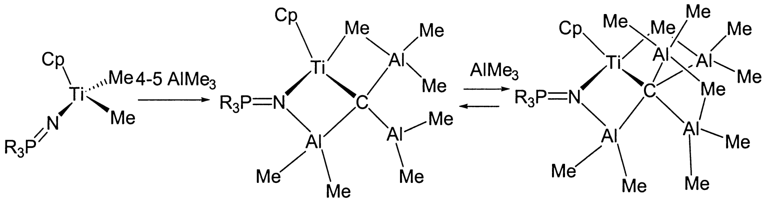


Fig. 5: Synthesis of $[\mathrm{CpTi}(\mu^2\text{-Me})(\mu^2\text{-NPR}_3)(\mu^4\text{-C})(\mathrm{AlMe}_2)_3]$ and $[\mathrm{CpTi}(\mu^2\text{–Me})(\mu^2\text{-NPR}_3)(\mu^5\text{-C})(\mathrm{AlMe}_2)_3\bullet(\mathrm{AlMe}_3)]$

leads to triple C-H bond activation and the quantitative formation of the unique Ti-Al-carbide cluster [CpTi(μ^2-Me)(μ^2-NPR$_3$)(μ^4-C)(AlMe$_2$)$_3$] (Fig. 5, 6). This complex remains Lewis acidic at the central aluminum center, reacting with donors to form alane-donor adducts. In addition, this cluster is Lewis basic at the central carbide carbon. This is evidenced by reaction with additional AlMe$_3$ that yield a five-coordinate carbide [CpTi(μ^2–Me)(μ^2-NPR$_3$)(μ^5-C)(AlMe$_2$)$_3$•(AlMe$_3$)] characterized in solution and the solid state. (Fig. 6)$^{8)}$

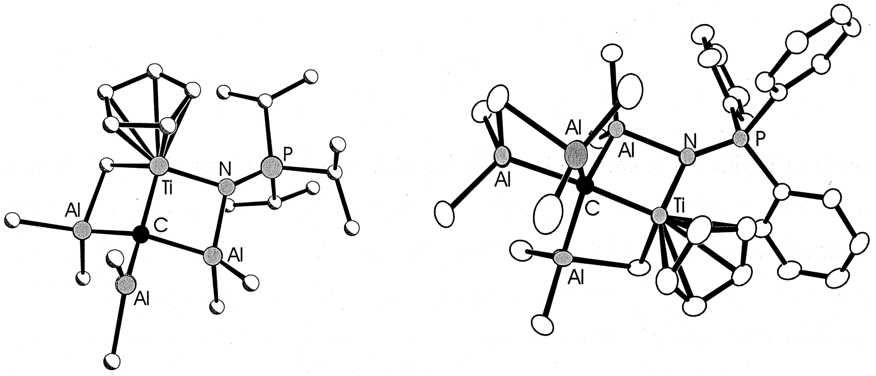
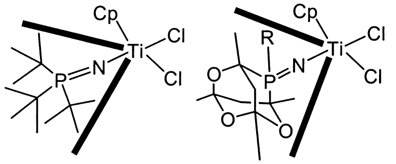


Fig. 6: X-ray structures of [CpTi(μ^2-Me)(μ^2-NP*i*Pr$_3$)(μ^4-C)(AlMe$_2$)$_3$] and [CpTi(μ^2–Me)(μ^2-NPPh$_3$)(μ^5-C)(AlMe$_2$)$_3$•(AlMe$_3$)]

While the isolation of these C-H bond activation products and the inter-conversion of four and five coordinate carbon is interesting from an academic perspective, the isolation of these species has some implications for the catalyst activity. Certainly, the expectation that AlMe$_3$ will react in a similar manner to MAO prompts the suggestion that catalytic activity may be suppressed by C-H bond activation processes. However, this may be overstated. It may be that interaction of the phosphinimide nitrogen atom in sterically accessible systems with an aluminum center of MAO is sufficient to diminish activity.

Ligand Degradation in "Cage-Phosphinimide" Complexes

The above observations prompted an investigation of related systems with highly sterically demanding ligands. In this regard we noted the work of Pringle et al.$^{9)}$ who have reported a new class of bulky bidentate phosphine ligands where the P atoms are incorporated in a sterically demanding adamantane-like cage. The resulting Pd derivatives of these ligands showed a very large ligand cone angle.



Cone angle: 85° Cone angle: 108°

Fig. 7: Cone-angles of *t*butylphosphinimide and the "cage-phosphinimide" ligands.

Molecular modelling suggests titanium complexes of phospha-adamantyl-phosphinimides exhibit a ligand cone angle significantly larger than that of *t*butylphosphinimide (Fig. 7), thus in principle offering greater steric protection of the metal center. The "cage-phosphines" $PR(C_6H_4O_3Me_4)$ were conveniently prepared from the reaction of RPH_2 with 2,4-pentanedione. Oxidation to the corresponding phosphinimine and subsequent complexation by titanium followed the methodologies established above (Fig. 8).[10)]

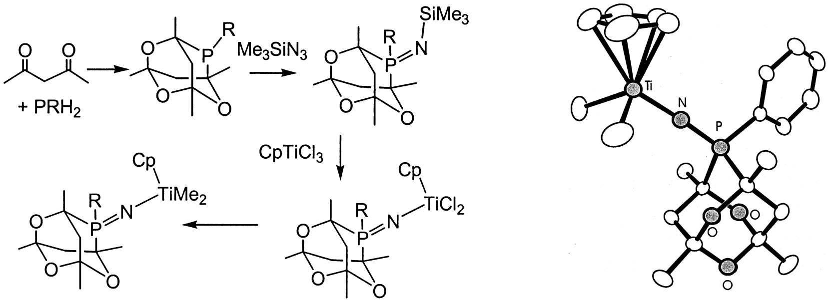


Fig. 8: Synthetic pathways to the titanium "cage-phosphinimide" complexes; X-ray structure of $CpTiMe_2(NPPh(C_6H_4O_3Me_3))$

Screening of these bulky phosphinimide ligand complexes for catalytic activity in ethylene polymerizations in the presence of 500 equivalents of methylalumoxane (MAO) or combined with $[Ph_3C][B(C_6F_5)_4]$ showed surprisingly low activities (<10g PE/mmol/h). This stands in marked contrast to systems described above. In an effort to understand the poor performance of these titanium complexes $CpTiMe_2(NPR(C_6H_4O_3Me_3))$ as catalysts, the interactions with aluminum reagents was investigated. Reaction with $AlMe_3$ revealed the generation of a number of products, suggesting the possibility that Lewis-acid activators attack the titanium complexes. This proposition was supported by the isolation of the one of the minor products, namely $CpTiMe_2(NPCy(C_6H_4O_3Me_5)(\mu\text{-}AlMe_2)(AlMe_3))$ (Fig 9).(10) The structure of this species affirmed that the aluminum reagent effected ligand cage rupture, leading to species which are inactive in catalysis. It is noteworthy that a similar mixture of products is derived from the reactions of $CpTiMe_2(NPR(C_6H_4O_3Me_3))$ and $B(C_6F_5)_3$, presumably accounting for the similarly low activity when $[Ph_3C][B(C_6F_5)_4]$ is used as an activator.

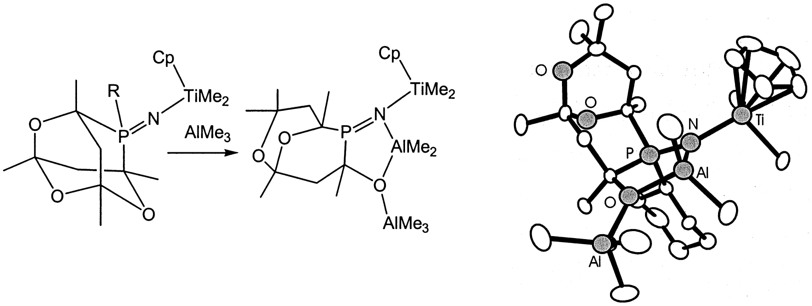


Fig. 9: The X-ray structure of $CpTiMe_2(NPCy(C_6H_4O_3Me_5)(\mu\text{-}AlMe_2)(AlMe_3))$

Summary

In summary, the *bis*-phosphinimide-based catalyst precursor $(tBu_3PN)_2TiMe_2$ provides an active ethylene polymerization catalyst that rivals and in some cases surpasses commercial catalysts in terms of activity. This discovery certainly suggests that the basic premise of the steric analogy between phosphinimide and cyclopentadienyl ligands is a useful strategy for catalyst design and prompts further study of compounds in the family $(R_3PN)_2MX_2$. While the more remote nature of the steric bulk in these ligands may account for the increase in activity, it also precipitates several unprecedented deactivation pathways. These include deactivation by double activation of Ti-C bonds by borane and C-H bond activation or ligand degradation by interaction with Al reagents. The utility and unique chemistry of phosphinimide complexes and catalysts continues to be the subject of interest and study. It is through a thorough understanding of the chemistry that new applications and catalysts will be uncovered.

Acknowledgements

The excellent young scientists in my group are gratefully acknowledged for their diligent efforts. In particular, Dr. Fred Guerin, Dr. Jim Kickham, Dr. C. Carraz, Dr. Jeff Stewart, Chris Ong, Edyta Urbanska and Chad Beddie for their contributions to the work described herein. NSERC of Canada is and NOVA Chemicals Corporation are thanks for financial support. Research staff at NOVA are also thanked for technical assistance and helpful discussion.

References

1. J. C. Stevens, *in* "Catalyst Design for Taylor-made Polyolefins, Studies in Surface Science and Catalysis" (K. Soga and M. Terano, eds.), Vol. 89, p. 277. Elsevier, Amsterdam, 1994.
2. T. V. Lubben, P. T. Wolczanski, and G. D. Van Duyne, *Organometallics* **3**, 977 (1984).
3. K. Dehnicke and F. Weller, *Coord. Chem. Rev.* **158**, 103 (1997).
4. D. W. Stephan, J. C. Stewart, F. Guerin, R. E. v. Spence, W. Xu, and D. G. Harrison, *Organometallics* **18**, 1116 (1999).
5. D. W. Stephan, F. Guerin, R. E. v. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak, and D. G. Harrison, *Organometallics* **17**, 2046 (1999).
6. F. Guérin, J. C. Stewart, C. Beddie, and D. W. Stephan, *Organometallics*, **19**, 2994(2000).
7. F. Guerin and D. W. Stephan, *Angew. Chem. Int. Ed. Engl.* **39**, 1298 (2000).
8. J. E. Kickham, F. Guerin, J. C. Stewart, and D. W. Stephan, *Angew. Chem. Int. Ed. Engl.* **39**, 3263 (2000).
9. V. Gee, A. G. Orpen, H. Phetmung, P. G. Pringle, and R. I. Pugh, *Chem. Commun.* 901 (1999).
10. C. Carraz and D. W. Stephan, *Organometallics* **19**, 3791 (2000).