Formation of Elastomeric Polypropylene Promoted by a Dynamic Octahedral Titanium Complex

Elena Smolensky,[†] Moshe Kapon,[†] J. Derek Woollins,[‡] and Moris S. Eisen[*,†]

Department of Chemistry and Institute of Catalysis Science and Technology, Technion—Israel Institute of Technology, Haifa, 32000, Israel, and Department of Chemistry, University of St. Andrews, Fife, U.K. KY16 9NB

Received January 9, 2005

The complex Ti(Ph_2PNpy)(NEt_2)$_2$ (**2**) was prepared by the reaction between 2 equiv of the neutral ligand Ph_2PNHpy (**1**) and 1 equiv of the homoleptic titanium tetrakis(diethylamine). Complex **2** exhibits two dynamic processes as a function of the temperature. An equilibrium among the diphenylphosphino moieties and a strong agostic interaction between the titanium atom and one of the hydrogens of each of the methylene groups of the diethylamido ligand. The strength of the chelating ligand was studied by its reaction with ethylamine, producing the imido complex **3**, showing that during the transformation **2** → **3** the pyridine rings of the ligand are able to dissociate and recoordinate with different stereochemistries. In the polymerization of propylene by complex **2** activated by MAO, elastomeric polymers are obtained. The elastomeric polymers are a result of monomer insertions into two enantiomerically close configuration complexes, as is encountered in cationic nonbridged metallocenes.

Introduction

The area of polymerization of propylene by a single-site catalyst has experienced a phenomenal growth in the last two decades, from academic to industrial research groups engaging in the design of new coordinatively unsaturated catalysts for the controlled polymerization.[1] Since the discovery of *ansa*-metallocene complexes as active precatalysts for the stereoregular polymerization of propylene (isotactic or syndiotactic), it has been established that clever designs of the organometallic complex are able to induce specific changes in the skeleton of the obtained polymers,[2] providing access to unusual materials, such as hemi-isotactic polypropylene and stereoblock (isotactic−atactic) materials with elastic properties.[3] Although the microstructure of the polypropylene obtained in the presence of well-defined single-site catalysts has been correlated with the symmetry of the active organometallic complex, some complexes were found not to follow such expectations and have produced distinctive polymeric materials, giving spectacular new insights into the mechanism for the polymerization of propylene.[2−4] One important challenge in the polymerization of olefins has been the rational design of elastic polyolefins, a material of potentially great interest for applications as a thermoplastic elastomer.[5] Regarding elastomeric polypropylene, it is important to acknowledge that Natta in 1957 was the first to isolate such a type of material from a mixture of polypropylenes.[6] Although Du Pont has produced mixtures of polypropylenes with elastic properties without the fractionation of the polymers,[7] the first homopolymer of polypropylene with elastic properties was obtained by Chien.[8] The stereoblock structure was a result of interconversion between specific and nonspecific sites of the catalyst during the polymerization. Recent strategies using *ansa*-metallocenes and/or nonbridged metallocene complexes have been followed for the production of different types of elastomeric polypropylene such as ethylene−α-olefin copolymers,[9] high-molecular-weight atactic polypropylene,[10] binary isotactic−atactic compatibilized polypro-

---

[†] Technion—Israel Institute of Technology.

[‡] University of St. Andrews.

(1) (a) Razavi, A. *Hydrocarbon Eng.* **2003**, *8*, 27. (b) Nayak, P. L. *Pop. Plast. Packag.* **2003**, *48*, 86.

(2) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Kaminsky, W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3911.

(3) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.

(4) (a) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253 and references therein. (b) Rodriguez-Delgado, A.; Hannant, M. D.; Lancaster, S. J.; Bochmann, M. *Macromol. Chem. Phys.* **2004**, *205*, 334 and references therein.

(5) Moore, E. P. J. *Polypropylene Handbook: Polymerization, Characterization, Properties, Applications*; Hanser: Munich, Germany, 1996.

(6) (a) Natta, G. *J. Polym. Sci.* **1959**, *34*, 531. (b) Natta, G.; Mazzanti, G.; Crespi, G.; Moraglio, G. *Chim. Ind. (Milan)* **1957**, *39*, 275.

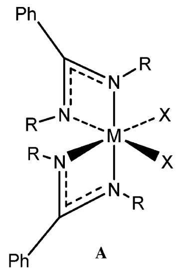
(7) (a) Collete, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrel, J. R.; Mülhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 3851. (b) Collete, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858.

(8) (a) Llinas, G. H.; Raush, M. D.; Lin, G. Y.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 8569. (b) Lin, Y. G.; Mallin, D. T.; Chien, J. C.; Winter, H. H. *Macromolecules* **1991**, *24*, 850. (c) Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242. (d) Babu, G. N.; Newmark, R. A.; Chen, H. N.; Llinas, G. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 6980. (e) Llinas, G. H.; Day, R. O.; Rausch, M. D.; Chien, J. C. W. *Organometallics* **1993**, *12*, 1283.

(9) (a) Banzi, V.; Angiolini, L.; Caretti, D.; Carlini, C. *Angew. Makromol. Chem.* **1995**, *229*, 113. (b) Uozumi, T.; Miyazawa, K.; Sano, T.; Soga, K. *Macromol. Rapid Commun.* **1997**, *18*, 883. (c) Uozumi, T.; Ahn, C. H.; Tomisaka, M.; Jin, J.; Tian, G.; Sano, T.; Soga, K. *Macromol. Chem. Phys.* **2000**, *201*, 1748. (d) Arndt, M.; Kaminsky, W.; Schauwienold, A. M.; Weingarten, U. *Macromol. Chem. Phys.* **1998**, *199*, 1135. (e) Fan, W.; Leclerc, M. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 9555. (f) Galimberti, M.; Piemontesi, F.; Fusco, O.; Camurati, I.; Destro, M. *Macromolecules* **1998**, *31*, 3409. (g) Reybuck, S. E. Waymouth, R. M. *Macromolecules* **2004**, *37*, 2342.

10.1021/om050015b CCC: $30.25

pylene,[11] intermediate isotactic–atactic microstructure polypropylenes,[12] isotactic polypropylene with controllable stereoerror sequences,[13] and stereoblock of isotactic-atactic microstructures.[14] It is clear that the elastomeric properties of the polypropylene rely either on the chain entanglements of the high-molecular-weight amorphous phase or on the cross-link crystallite lamellae phase produced by the isotactic domains.



A

(M = Ti, Zr, Hf; X = Cl, alkyl; R = Pr^i, Bu^t, SiMe$_3$)

Figure 1. Bis(benzamidinate) dichloride or dialkyl complexes of group 4 metals.

During the past decade, nonmetallocene complexes containing chelating ancillary ligands, such as dialkoxides,[15] amine-phenolate,[16] diamides,[17–19] and benzamidines,[20] have received attention as potential Ziegler–Natta catalysts. Our group and other scientists have already investigated the catalytic α-olefin polymerization with bis(benzamidinate) dichloride or dialkyl complexes of group 4 metals (Figure 1), which are obtained as a racemic mixture of cis octahedral complexes with C_2 symmetry.[20] When they were activated with methylalumoxane (MAO) or perfluoroborane compounds, these complexes were found to be active catalyst precursors for the polymerization of ethylene, propylene, 1-hexene, and 2,5-hexadiene.[20]

We have shown that highly isotactic polypropylene (% mmmm = 95%) was obtained by octahedral complexes with C_2 symmetry, whereas atactic polypropylene was obtained by tetrahedral C_{2v} symmetry complexes.[18h,20m] A basic conceptual question is whether simple octahedral or even tetrahedral complexes, which have a dynamic Lewis basic pendant group that can donate an electron lone pair to the highly electrophilic

---

(10) (a) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998. (b) Ewart, S. W.; Sarsfield, M. J.; Jeremic, D.; Tremblay, T. L.; Williams, E. F.; Baird, M. C. *Organometallics* **1998**, *17*, 1502. (c) Xie, B. H.; Wu, Q.; Lin, S. G. *Macromol. Rapid Commun.* **1999**, *20*, 167.

(11) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. *Macromolecules* **1997**, *30*, 3447.

(12) (a) Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000. (b) Gauthier, W. J.; Collins, S. *Maromol. Symp.* **1995**, *98*, 223. (c) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779. (d) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Atwood, J. L.; Bott, S. G. *J. Polym. Sci. A: Polym. Chem.* **1992**, *30*, 2601. (e) Llinas, G. H.; Dong, S. H.; Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242.

(13) (a) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelä, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348. (b) Dietrich, U.; Hackmann, M.; Rieger, B. *Rubber Chem. Technol.* **1998**.

(14) (a) Coates, G.; Waymouth, R. M. *Science* **1995**, *267*, 217. (b) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586. (c) Kravchenko, R.; Masood, A.; Waymouth, R. M. *Organometallics* **1997**, *16*, 3635. (d) Maciejewski-Petoff, J. L.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909. (e) Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174. (f) Kravchenko, R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 1. (g) Kravchenko, R.; Masood, A.; Waymouth, R. M.; Myers, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 2039. (h) Lin, S.; Hauptman, E.; Lal, T. K.; Waymouth, R. M.; Quan, R. W.; Ernst, A. B. *J. Mol. Catal. A* **1998**, 1. (i) Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908. (j) Carlson, E. D.; Krejchi, M. T.; Shah, C. D.; Terakawa, T.; Waymouth, R. M.; Fuller, G. G. *Macromolecules* **1998**, *31*, 5343.

(15) (a) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847. (b) Matsukawa, N.; Matsui, S.; Mitani, M.; Saito, J.; Tsuru, K.; Fujita, T. *J. Mol. Catal. A: Chem.* **2001**, *169*, 99. (c) Saito, J.; Mitani, M.; Mohri, J.; Yoshida, Y.; Matsui, S.; Ishii, S.; Kojoh, S.; Kashiwa, N. Fujita, T. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2918. (d) Sobota, P.; Przybylak, K.; Urko, J.; Jerzykiewicz. L. B.; Pombiero, A. J. L.; da Silva, M. F. C. G.; Szczegot K. *Chem. Eur. J.* **2001**, *7*, 951. (e) Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A.; Okuda, J. *Organometallics* **2000**, *19*, 2498. (f) Okuda, J.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P. *Eur. J. Inorg. Chem.* **2000**, 1321.

(16) (a) Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477 and references therein. (b) Mitani, M.; Saito, J.; Ishii, S.-I.; Nakayama, Y.; Makio, H.; Matsukawa, N.; Matsui, S.; Mohri, J.-I.; Furayama, R.; Terao, H.; Bando, H.; Tanka, H.; Fujita, T. *Chem. Rec.* **2004**, *4*, 137. (c) Groysman, S.; Goldberg, I.; Kol, M.; Genizi, E.; Goldschmidt, Z. *Inorg. Chim. Acta* **2003**, *345*, 137. (d) Tshuva, E. Y.; Groysman, S.; Goldberg, I.; Kol, M. *Organometallics* **2002**, *21*, 662. (e) Mason, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 16326. (f) Reinartz, S.; Mason, A. F.; Lobkovsky, E. B.; Coates, G. W. *Organometallics* **2003**, *22*, 2542. (g) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626.

(17) (a) Goodman, J. T.; Schrock, R. R. *Organometallics* **2001**, *20*, 5205. (b) Schrock, R. R.; Bonitatebus, P. J., Jr.; Schrodi, Y. *Organometallics* **2001**, *20*, 1056. (c) O'Connor, P. E.; Morrison, D. J.; Steeves, S.; Burrage, K.; Berg, D. J. *Organometallics* **2001**, *20*, 1153. (d) Yoshida, Y.; Matsui, S.; Takagi, Y.; Mitani, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Organometallics* **2001**, *20*, 4793. (e) Danièle, S.; Hitchcock, P. B.; Lappert, M. F.; Merle, P. G. *Dalton* **2001**, 13. (f) Mehrkhodavandi, P.; Bonitatebus, P. J., Jr.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841. (g) Skinner, M. E. G.; Cowhig, D. A.; Mountford, P. *Chem. Commun.* **2000**, 1167. (h) Nomura, K.; Oya, K.; Imanishi, Y. *Polymer* **2000**, *41*, 2755. (i) Lee, C. H.; La, Y.-H.; Park, J. W. *Organometallics* **2000**, *19*, 344 and references therein. (j) Kempe, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 468 and references therein. (k) Gade, L. H. *Chem. Commun.* **2000**, 173. (l) Shaviv, E.; Botoshansky, M.; Eisen,. M. S. *J. Organomet. Chem.* **2003**, *683*, 165.

(18) (a) Ziniuk. Z.; Goldberg, 1.; Kol, M. *Inorg. Chem. Commun.* **1999**, *2*, 549. (b) Liang, L.-C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797. (c) Graf, D. D.; Schrock, R. R.; Davis, W. M.; Stumpf, R. *Organometallics* **1999**, *18*, 843. (d) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649. (e) Guérin, F.; McConville, D. H.; Vittal, J. J. Yap, G. A. P. *Organometallics* **1998**, *17*, 5172. (f) Gibson, V. C.; Kimberley, V. S.; White, A. J. P.; Williams, D. J.; Howard, P. *Chem. Commun.* **1998**, 313. (g) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415. (h) Mack, H.; Eisen, M. S. *J. Organomet. Chem.* **1996**, *525*, 81. (i) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2001**, *20*, 3017. (j) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706.

(19) (a) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847. (b) Matsukawa, N.; Matsui, S.; Mitani, M.; Saito, J.; Tsuru, K.; Fujita, T. *J. Mol. Catal. A: Chem.* **2001**, *169*, 99. (c) Saito, J.; Mitani, M.; Mohri, J.; Yoshida, Y.; Matsui, S.; Ishii, S.; Kojoh, S.; Kashiwa, N. Fujita, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2918. (d) Sobota, P.; Przybylak, K.; Urko, J.; Jerzykiewicz, L. B.; Pombiero, A. J. L.; da Silva, M. F. C. G.; Szczegot, K. *Chem. Eur. J.* **2001**, *7*, 951. (e) Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A.; Okuda, J. *Organometallics* **2000**, *19*, 2498. (f) Okuda, J.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P. *Eur. J. Inorg. Chem.* **2000**, 1321.

(20) (a) Richter, J.; Edelmann, F. T.; Noltemeyer, M.; Schmidt, H.-G.; Shmulinson, M.; Eisen, M. S. *J. Mol. Catal.* **1998**, *130*, 149. (b) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640. (c) Walter, D.; Fischer, R.; Friedrich, F.; Gebhardt, P.; Görls, H. *Chem. Ber.* **1996**, *129*, 1389. (d) Walter, D.; Fischer, R.; Görls, H.; Koch, J.; Scheweder, B. J. *J. Organomet. Chem.* **1996**, *508*, 13. (e) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (f) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 939. (g) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 1827. (h) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 2106. (i) Herscovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307. (j) Gomez, R.; Duchateau, R.; Chernega, A. N.; Meetsma, A.; Edelmann, F. T.; Teuben, J. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 217. (k) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2607. (l) Volkis, V.; Shmulinson, M.; Averbuj, C.; Lisovskii, A.; Edelmann, F. T.; Eisen, M. S. *Organometallics* **1998**, *17*, 3155. (m) Volkis, V.; Nelkenbaum, E.; Lisovskii, A.; Hasson, G.; Semiat, R.; Kapon, M.; Botoshansky, M.; Eishen, Y.; Eisen, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 2179.

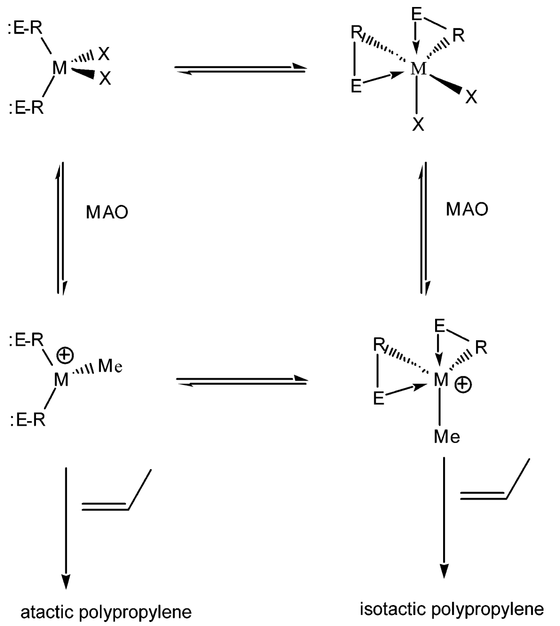


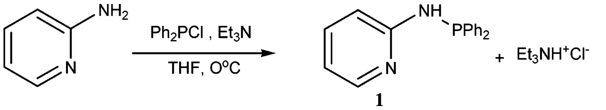
Figure 2. Dynamic equilibrium between the tetrahedal and octahedral configurations, resulting in an elastomeric polymer in the polymerization of propylene.

metal center, are suitable for the preparation of a unique type of polymer.[21] Thus, as shown in Figure 2, a dynamic equilibrium between the tetrahedal and octahedral configurations can induce the polymerization of an α-olefin, such as propylene in an elastomer manner (X = halide or amido, E = a donor group with a electron lone pair, R = C, N, P, or other anionic bridging group).

Here we present the synthesis, characterization, and solid-state X-ray diffraction studies of the dynamic complex Ti(Ph_2PNpy)(NEt_2)$_2$ (py = pyridine). In addition, we describe here the catalytic activity of the complex in the polymerization of propylene and the different effects of cocatalyst amounts and the polymerization time taken in the formation of the elastomeric polymer.

Results and Discussion

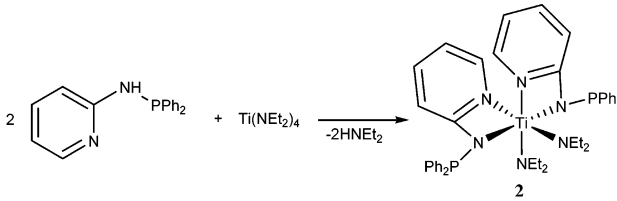
Synthesis of the Complex Ti(Ph_2PNpy)(NEt_2)$_2$ (2). The ligand 2-((diphenylphosphino)amido)pyridine (**1**) was synthesized by following the literature procedure of Woollings,[22] via the reaction between 2-aminopyridine and diphenylphosphino chloride in the presence of triethylamine (eq 1).



(1)

The ligand Ph_2PNHpy (**1**) was recrystallized from a saturated solution of toluene at −20 °C. X-ray diffraction shows that **1** is a dimeric structure, as a result of N−H- - -N interactions. We have recently published the crystal structure of **1** in an early paper,[23] and it is shown here (Figure 3) only for comparison purposes.

The complex Ti(Ph_2PNpy)(NEt_2)$_2$ (**2**) was prepared by the reaction between 2 equiv of the neutral ligand Ph_2PNHpy (**1**) and 1 equiv of the homoleptic titanium tetrakis(diethylamine) (eq 2). In the catalytic polymerization of α-olefins by early-transition-metal complexes, either the dichloro or the dialkyl complexes are normally used as the precatalysts. Those complexes are used, since they react with the different cocatalysts forming, as the active catalyst, the cationic methyl complex. We have found that bis(amido) complexes can also be used as precatalysts, since the amido ligands are transformed to the corresponding alkyl complexes when MAO is used as the cocatalyst. Therefore, the use of the titanium tetrakis(diethylamine) complex was planned to be used with the neutral ligand as a one-pot reaction. The side product of the reaction, diethylamine, is easily removed from the reaction flask by vacuum distillation. Recrystallization of the complex at −40 °C from a saturated solution of toluene affords the production of large single crystals suitable for diffraction studies.

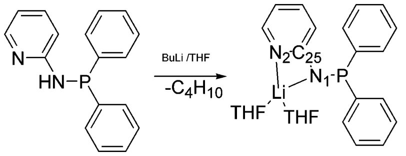


(2)

X-ray Structure Characterization of the Complex Ti(Ph_2PNpy)(NEt_2)$_2$ (2). The molecular structure of the complex Ti(Ph_2PNpy)(NEt_2)$_2$ (**2**) have been confirmed by X-ray single-crystal diffraction studies. The ORTEP plot of the complex is shown in Figure 4, and crystallographic data with structure refinement details are listed in Tables 1 and 2, respectively.

The single-crystal X-ray diffraction studies of the complex shows that the metal is disposed in a slightly distorted octahedral environment and exhibits a close C_2 symmetry. The most important feature of the complex is the mode of ligation of the titanium metal. For various late transition metals it is known that the neutral ligand **1** is coordinated to the metal via both the hard pyridine nitrogen atom and the soft phosphorus atom, forming a five-membered ring.[22] Until now, no characterization has been described for early transition metals in which both hard nitrogen atoms are attached to the metal, forming a four-membered ring.

Formation of the four-membered ring in the titanium complex is in agreement with Chatt theory,[24] claiming that hard metals such as Ti(IV) will prefer binding to hard ligands by N,N chelation rather than by soft N,P chelation. Recently, we have also synthesized the corresponding lithium salt of the neutral ligand, showing a structural configuration similar to that shown in eq 3.[23]



(3)

---

[21] Kühl, O.; Koch, T.; Somoza, F. B., Jr.; Junk, P. C.; Hey-Hawkins, E.; Plat, D.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *604*, 116.

[22] Aucott, S. M.; Slaein, A. M. Z.; Woollins, J. D. *Dalton* **2000**, 2559.

[23] Xavier, K. O.; Smolensky, E.; Kapon, M.; Aucott, S. M.; Woollings, J. D.; Eisen, M. S. *Eur. J. Inorg. Chem.* **2004**, 4795.

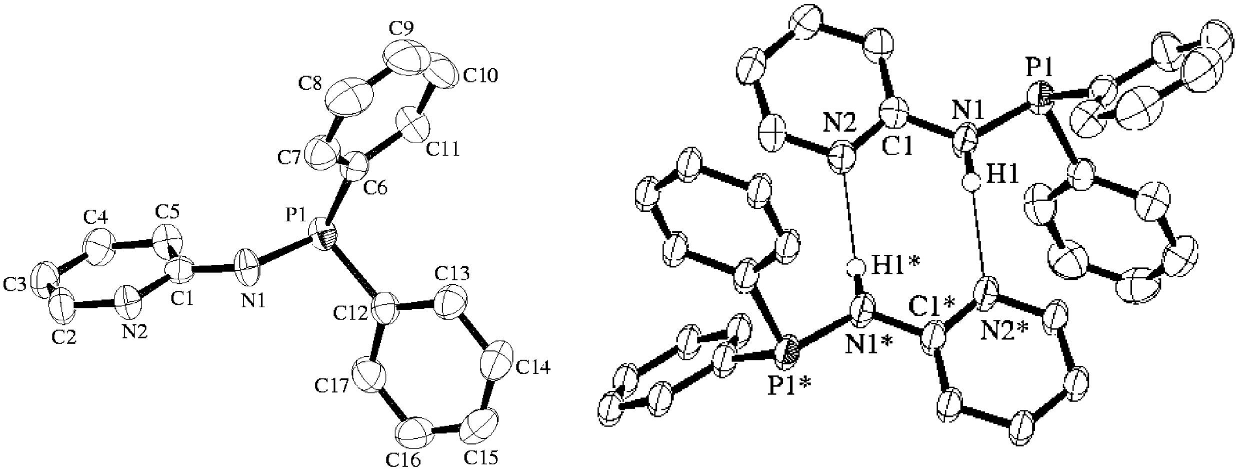
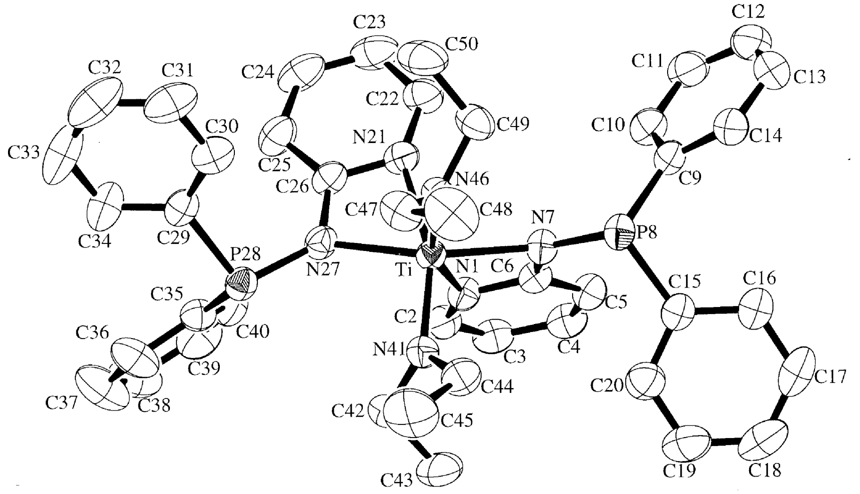


Figure 3. ORTEP plot of the molecular structure of the ligand Ph_2PNHpy (**1**) and its dimer in the crystal state (N1−N2* = 3.050 Å and H1−N2* = 2.18 Å), drawn at the 50% probability level. All hydrogens were removed for clarity. Selected bond distances (Å) and angles (deg): P(1)−N(1) = 1.695(3), P(1)−C(6) = 1.824(4), P(1)−C(12) = 1.831(3), N(1)−C(1) = 1.391(4); N(1)−P(1)−C(6) = 104.09(16), N(1)−P(1)−C(12) = 100.01(14), C(6)−P(1)−C(12) = 101.76(15), C(1)−N(1)−P(1) = 124.7(2).



2

Figure 4. ORTEP plot of the molecular structure of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**), drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

In the titanium complex **2**, six nitrogen atoms are bonded to the metal center. The two diethylamido nitrogens are disposed in a cis fashion (N(41)−Ti−N(46) = 105.14(8)°) and exhibit the shorter M−N bond lengths (Ti−N(41) = 1.9026(18), Ti−N(46) = 1.9053(17) Å). The two phosphinoamine nitrogen atoms are positioned transoid to each other (N(7)−Ti−N(27) = 145.77(7)°) and display longer M−N bond lengths (Ti−N(7) = 2.0985(17), Ti−N(27) = 2.1070(17) Å), whereas the two pyridine nitrogen atoms that are located trans to the diethylamido ligand (N(46)−Ti−N(1) = 154.88(7), N(41)−Ti−N(21) = 156.00(7)°) showed larger bond lengths due to the corresponding trans effect (Ti−N(1) = 2.2499(17), Ti−N(21) = 2.2553(18) Å).

It is interesting to compare the C−N bond length changes at the bridging carbon among the amido and pyridine nitrogen in the free ligand (**1**), the lithium salt, and the titanium complex (**2**) (Table 3). These changes can be related to the different strengths in bonding of the chelate ligand to each metal and the amount of charge distribution. For the hard lithium salt as compared to the free ligand, it can be seen that a strong resonance between the two nitrogen atoms is highly effective, equalizing both C−N bond lengths. The same trend is observed at the titanium complex **2** at each one of the ligand moieties, although a slight difference is observed between these two ligands. These results lead to the conclusion that in the solid state the ancillary ligands are bonded to the metal, forming a symmetrical η^2-N−C−N motif.

A very peculiar pattern results in the structure of complex **2** with regard to the distance between the ortho hydrogens of the diphenyl moieties with the meta hydrogen of the pyridine ring upon rotation. If the diphenylphosphine were to be in rapid free rotation, the distances among the mentioned hydrogens would pass within a close distance (maximum energy) situated at ~0.40 Å. This distance is extremely short, indicating

---

(24) Ahrland, S.; Chatt, J.; Davies, N. R. *Chem. Soc. Rev.* **1958**, *12*, 265.

Table 1. Crystal Data and Data Collection Details for Complexes 2 and 3

	complex **2**	complex **3**
empirical formula	$C_{42}H_{48}N_6P_2Ti$	$C_{72}H_{66}N_{10}P_4Ti_2$
formula wt	746.7	1291.03
temp (K)	230.0(1)	230.0(1)
wavelength (Å)	0.710 70	0.710 73
cryst syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
unit cell dimens		
a (Å)	10.06400(10)	9.4860(3)
b (Å)	18.3130(3)	13.7580(5)
c (Å)	22.0500(4)	14.1520(6)
α (deg)	90	62.8430(15)
β (deg)	95.6660(6)	80.1160(17)
γ (deg)	90	89.9030(16)
V (Å^3)	4044.00(11)	1612.75(10)
Z	4	1
D_{calcd} (g/cm^3)	1.226	1.329
μ (mm^{-1})	0.327	0.398
F(000)	1576	672
cryst size (mm^3)	0.25 × 0.30 × 0.40	0.36 × 0.12 × 0.03
θ range for data collecn (deg)	1.45−27.00	1.67−25.05
limiting indices	$0 \le h \le 12$ $0 \le k \le 23$ $-28 \le l \le 28$	$-11 \le h \le 11$ $-15 \le k \le 16$ $-16 \le l \le 16$
no. of collected/unique rflns	8803/8803 (R(int) = 0.0000)	9663/5696 (R(int) = 0.0517)
completeness to θ = 25.05° (%)	99.7	99.9
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	8803/0/652	5696/0/454
goodness of fit on F^2	1.032	0.879
final R indices ($I > 2\sigma(I)$)	R1 = 0.0435, wR2 = 0.1132	R1 = 0.0421, wR2 = 0.0824
R indices (all data)	R1 = 0.0751, wR2 = 0.1267	R1 = 0.1013, wR2 = 0.0921
largest diff peak and hole (e/Å^3)	0.290 and −0.422	0.237 and −0.326

Table 2. Comparison of the Bond Lengths (Å) and Angles (deg) for Complexes 2 and 3

complex **2**		complex **3**	
Ti−N(21)	2.2553(18)	Ti(1)−N(2)	2.216(2)
Ti−N(1)	2.2499(17)	Ti(1)−N(4)	2.281(3)
Ti−N(27)	2.1070(17)	Ti(1)−N(1)	2.131(2)
Ti−N(7)	2.0985(17)	Ti(1)−N(3)	2.059(2)
Ti−N(41)	1.9026(18)	Ti(1)−N(5)	1.966(2)
Ti−N(46)	1.9053(17)	Ti(1)−N(5)#1	1.851(2
C(6)−Ti−C(26)	103.51(6)	C(30)−Ti(1)−C(13)	100.26(8)
N(27)−Ti−N(21)	61.20(7)	N(1)−Ti(1)−N(2)	61.32(8)
N(7)−Ti−N(1)	61.25(6)	N(3)−Ti(1)−N(4)	61.44(9)
N(7)−Ti−N(21)	91.48(7)	N(4)−Ti(1)−N(1)	86.82(8)
N(27)−Ti−N(1)	91.35(6)	N(3)−Ti(1)−N(2)	139.75(9)
N(7)−Ti−N(27)	145.77(7)	N(1)−Ti(1)−N(3)	98.59(9)

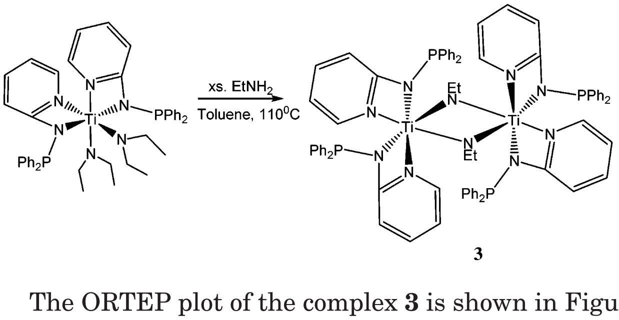
that in solution the aromatic rings are not equivalent. A second distinctive characteristic of $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) is an agostic interaction between the titanium atom and one of the hydrogens of each of the methylene groups of the diethylamido ligand (Ti−H = 2.9 Å). These two dynamic effects were also observed and studied in solution.

Dynamic Behavior of the Complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (2). As expected from the solid state, NMR investigation gives us a look at the dynamic behavior of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) in solution and as a function of temperature. The assignment of the signals in the ^{1}H NMR spectrum on the basis of 2D-NMR experiments is presented in Figure 5.

The ^{1}H NMR of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) in toluene shows a combination of broad and narrow signals. The narrow signals correspond to the hydrogens of the pyridine rings and the methyl groups, whereas the broad signals correspond to the aromatic phenyl rings and the methylenic hydrogens of the diethylamido moiety. The existence of two fully separated signals that belong to the same methylene groups (both hydrogens are connected to the same carbon, and they are coupled, as observed by 2D-COSY NMR) indicates that an agostic interaction between the titanium atom and one hydrogen of each of the methylene groups of the diethylamine ligand is very strong, even in solution at room temperature. Moreover, the separated broad signal for the ortho H1 and H3 hydrogens of the two phenyl rings corroborate the nonequivalence, as expected from the solid-state analysis.

Due to the nonequivalence of the different moieties in the solution, the dynamic behavior of the complex was followed by variable-temperature ^{1}H NMR analysis. This analysis revealed two dynamic consecutive processes (Figure 6). The first dynamic process, with a coalescence temperature at 310 K, is connected with the equivalence of the phenyl rings due to the rotation around the N−P bond. The second dynamic process, with coalescence at 340 K, is related to the equivalence of the methylenic hydrogens of the diethylamine moiety, equilibrating the agostic interactions within both hydrogens. For both processes, the exchange rate constants were calculated by line shape analysis (Table 4). It is important to point out that the hydrogen atoms of the methylene groups of the amido moiety are not equivalent. The agostic interaction between one of the hydrogens and the metal center is corroborated by the $^1J_{CH}$ coupling of the methylene moiety (NCH_2), showing a second-order splitting ($Vo\delta \ll J$; Vo = spectrometer operating frequency, and δ = chemical shift) with two different J values, 135.6 ± 0.5 and 132.7 ± 0.5 Hz, as compared to the $^1J_{C-H}$ coupling of the CH_3 (125.6 ± 0.5 Hz).[25]

The strengths of the different ancillary ligations to the metal in complex **2** were studied by reaction with an excess of $EtNH_2$. The reaction produces the imido dimeric compound $Ti_2(PPh_2Npy)_4(\mu\text{-}NEt)_2$ (**3**), in which the more labile diethylamido moieties were exchanged by the ethylamido motif (eq 4).



(4)

3

The ORTEP plot of the complex **3** is shown in Figure 7, and the crystallographic data with structure refinement details and selected bond lengths and angles are given in Tables 1 and 2, respectively. The X-ray structure of the complex $Ti_2(Ph_2PNpy)_4(\mu\text{-}NEt)_2$ (**3**) sheds

---

[25] The coalescence of the diastereotopic methylenes is not consistent with a Δ−Λ isomerization among enantiomers. See: Milano, G.; Cavallo, L.; Guerra, G. *J. Am. Chem. Soc.* **2002**, *124*, 13368.

Table 3. Comparison of Equivalent C−N Bond Lengths in the Free Ligation, and the Corresponding Lithium and Titanium Complexes

	bond length (Å)					
bond[a]	Ti complex **2**		Li salt		free ligand	
C−N(py)	C(6)−N(1)	1.348(3)	C(25)−N(1)	1.364(4)	C(1)−N(2)	1.341(4)
	C(26)−N(21)	1.354(3)				
C−$NPPh_2$	C(6)−N(7)	1.375(3)	C(25)−N(2)	1.355(4)	C(1)−N(1)	1.391(4)
	C(26)−N(27)	1.379(3)				

[a] The numbering of the atoms corresponds to the same numbering as presented in the ORTEP plots of the corresponding molecules or that in eq 3.

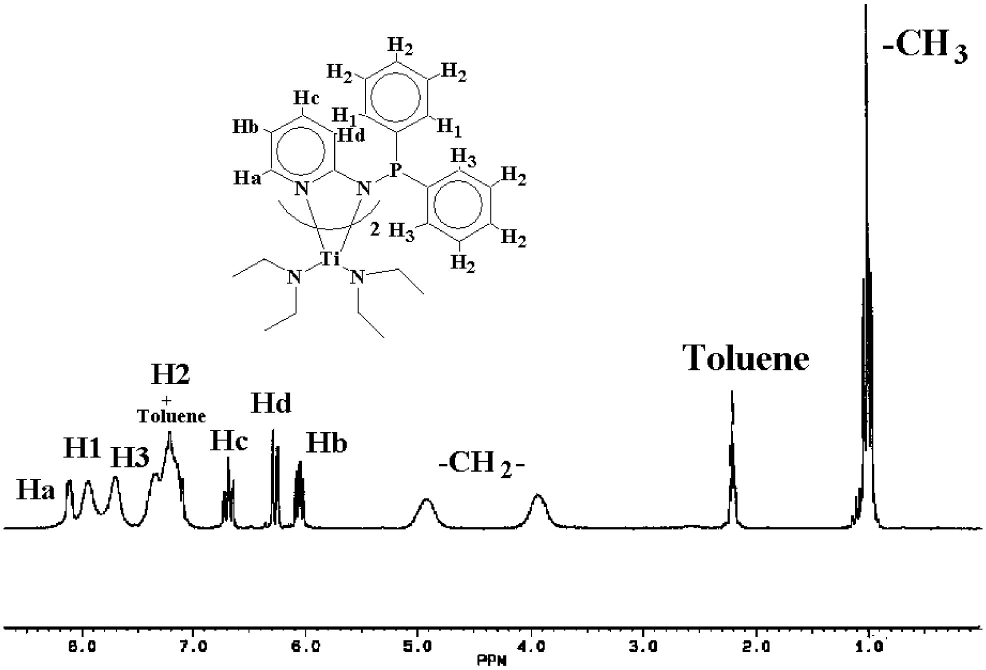


Figure 5. ^1H NMR of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) in toluene-d_8 at room temperature.

light on the strength and the dynamic behavior of the 2-((diphenylphosphanyl)amino)pyridine ligand (**1**). In complexes **2** and **3**, the three titanium centers preserve a similar octahedral environment. However, while in the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) both pyridine rings are located trans to the diethyl amido groups, in the complex $Ti_2(Ph_2PNpy)_4(\mu\text{-}NEt)_2$ (**3**) two of the four pyridine rings are located cis and the other two are located trans to the bridging ethylamine groups. It is important to point out that a Berry pseudorotation via a pentacoordinate imido complex, as a plausible mechanism for the transformation of **2** into **3**, will yield a dimeric complex with the ligands disposed as in complex **2** (due to the microscopic reversibility principle). For early transition metals, it is known that the imido complexes are obtained through a four-center transition state, hence keeping the stereochemistry of the ligands around the metal without change.[26] Interestingly, even for titanium metallocenes such as Cp_2TiMe_2, the lability of one the Cp rings has been observed by its replacement with a primary amine.[27] This result indicates that in the formation of complex **3** the pyridine rings are labile enough to be capable of disconnecting and recoordinating, although in a different stereo fashion, to the metal. This dynamic behavior would most probably result in the formation of different stereoisomers in solution, which would promote a unique environment when complex **2** is used for the polymerization of olefins.

Table 4. Rate Constants for the Dynamic Processes Observed in Complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (2) as a Function of Temperature

	process[a]	T (K)	K (s^{-1})
before coalescence temp	I	240	49 ± 1
	II	300	16 ± 1
at the coalescence temp	I	310	109 ± 10
	II	320	336 ± 10
after the coalescence temp	I	370	3200 ± 100
	II	370	1500 ± 100

[a] Legend: (I) equivalence of the phenyl rings due to the rotation around the N−P bond; (II) equivalence of the methylenic hydrogens of the diethylamine moiety toward the agostic interaction with the titanium metal.

Comparison between the bond lengths and angles in complexes **2** and **3** (Table 2) reveals that while in complex **2** both Ti−N(py) bonds have similar lengths (Ti−N(21) = 2.26 and Ti−N(1) = 2.25 Å), in complex **3** one of the Ti−N(py) bonds is longer and the other is shorter (Ti−N(2) = 2.22 and Ti−N(4) = 2.28 Å, respectively). The same tendency was observed for the Ti−$NPPh_2$ bonds: while in complex **2** both Ti−$NPPh_2$ bonds exhibit similar bond lengths (Ti−N(27) = 2.11 and Ti−

---

[26] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 4. (b) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017.

[27] Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935.

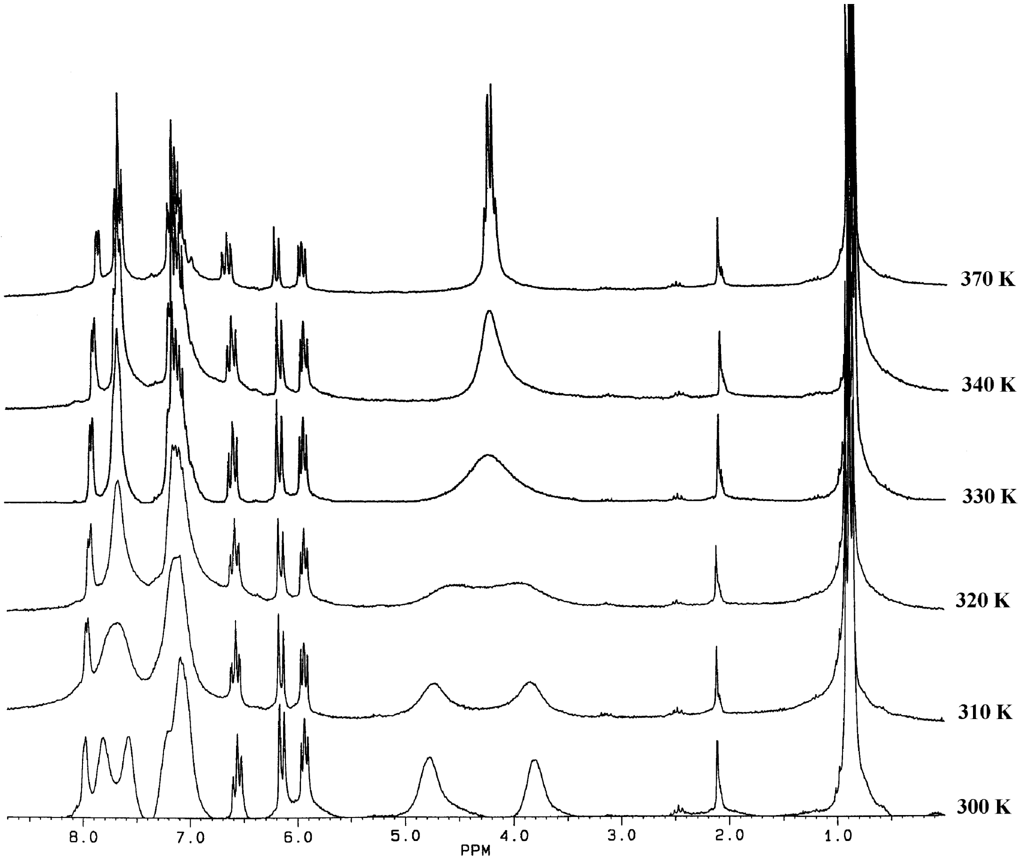


Figure 6. ^{1}H NMR spectra of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) at a temperature range from 300 to 370 K in toluene-d_8.

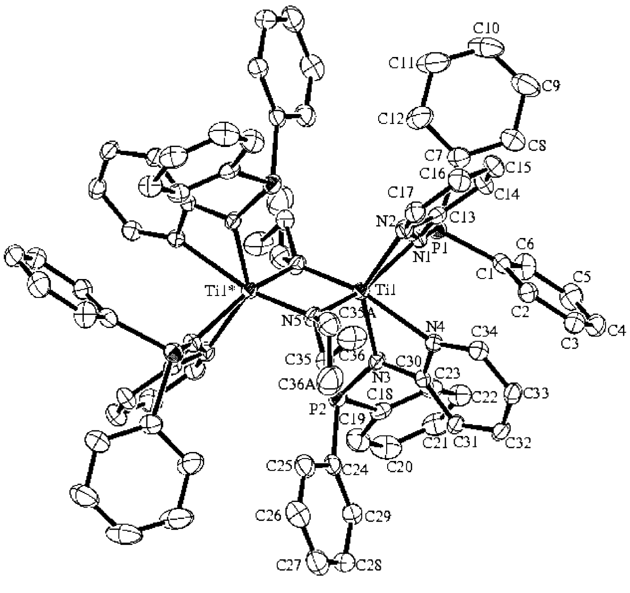


Figure 7. ORTEP plot of the molecular structure of the complex $Ti_2(Ph_2PNpy)_4(\mu\text{-}NEt)_2$ (**3**).

Table 5. Data for the Polymerization of Propylene Catalyzed by Complex 2 with MAO[a]

entry	MAO/cat	time (h)	yield (g)	A[b]	M_n	M_w	M_w/M_n
1	300	2	0.16	0.61	17 150	38 300	2.23
2	600	2	0.27	1.00	17 150	38 350	2.24
3	1000	2	0.17	0.62	15 550	32 150	2.07
4	2000	2	0.15	0.55	10 200	20 200	1.97
5	600	4	0.34	0.63	26 050	78 350	3.01
6	600	6	0.75	0.93	43 300	111 100	2.57
7	600	8	1.26	1.18	37 000	94 500	2.55
8	600	10	1.75	1.31	31 500	113 350	3.60
9	600	20	3.17	1.18	62 400	294 800	4.72

[a] All experiments were performed at 25 °C, in toluene. [b] *A* = activity, in units of (g of PP)/((mol of cat) h atm) × 10^4.

N(7) = 2.10 Å), in complex **3** both Ti−NPPh$_2$ bonds are different (Ti(1)−N(1) = 2.13 and Ti(1)−N(3) = 2.06 Å); these effects are a consequence of the different trans effects. Interestingly, the C−N bond lengths and N−C−N angles at the N−C−N chelate moiety of the ligands for both complexes are almost identical.

Propylene Polymerization. The catalytic activity in the polymerization of propylene was studied using as the precursor the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**), and the activation of the complex was accomplished using MAO as the cocatalyst. One of the most interesting conceptual questions regarding complex **2** was its ability to retain a specific symmetry upon its reaction with MAO. To gain some knowledge, we have followed the reaction of complex **2** with various amounts of MAO.

Upon the addition of small amounts of MAO in THF-d_8 (up to the ratio MAO:**2** = 50:1) no major differences were observed for the native complex **2**, besides the additional signals of the MAO. When additional amounts of MAO were introduced (MAO:**2** = 85:1), ^{1}H and ^{13}C NMR analysis revealed that the signals of the diethylamido groups disappeared from 3.80 and 4.75 ppm and from 13.2 and 45.6 ppm in the proton and carbon NMR, respectively. In addition, two new broad signals of a Et_2NAl moiety were observed at 2.84 and 1.19 ppm and at 43.0 and 13.6 ppm for the CH_2 and CH_3 groups in the

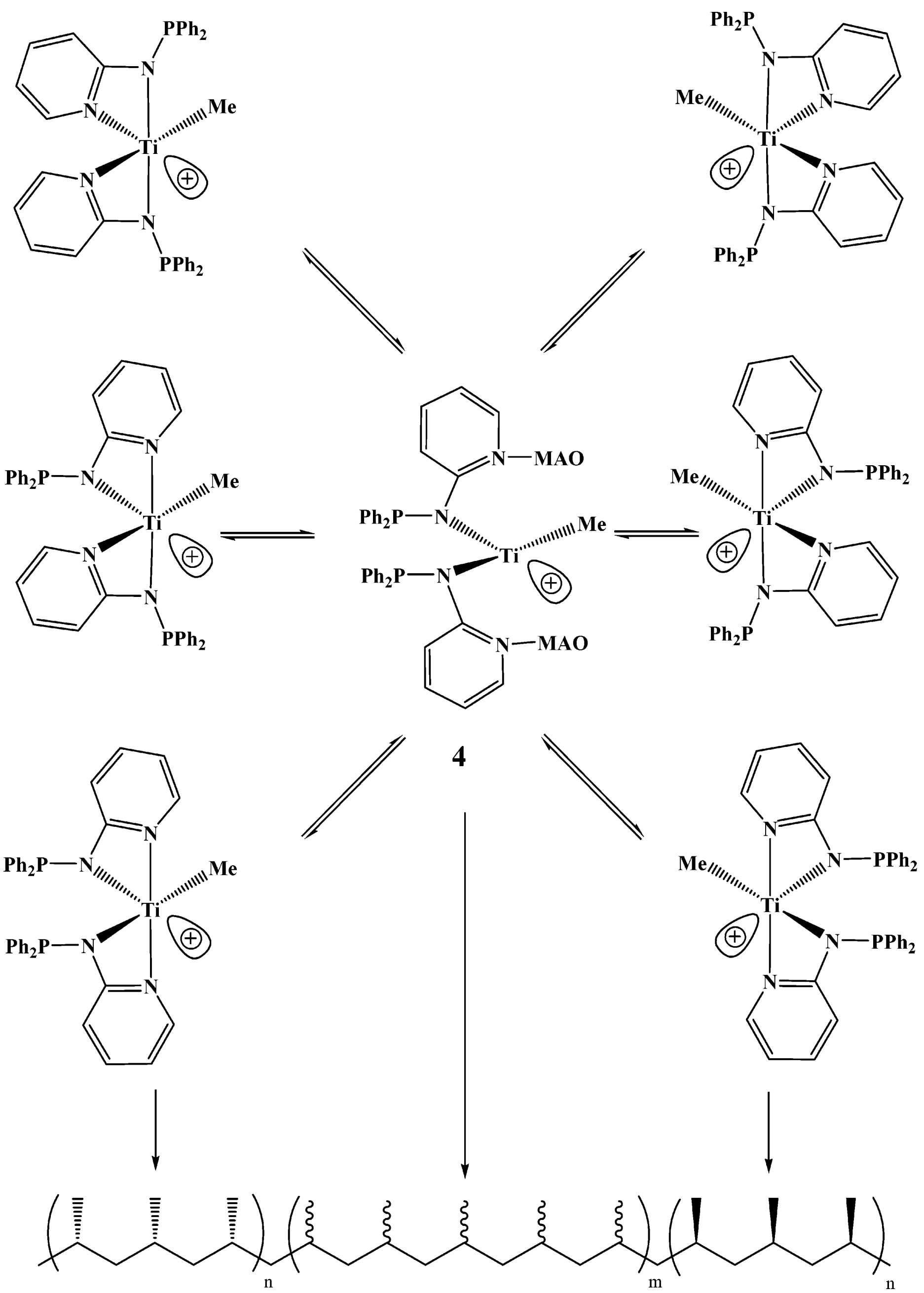


Figure 8. The six possible cis-octahedral enantiomeric structures that can be obtained in the reaction of **2** with MAO.

^{1}H and ^{13}C NMR, correspondingly. In addition, in the ^{1}H NMR, the signals of both pyridine rings broadened and almost disappeared completely and a new singlet signal of only one methyl group (integration for 3H) appeared at 2.29 ppm, which also correlates to a singlet line at 29.4 ppm in the ^{13}C NMR, corroborating the formation of a monomethyl cationic complex. Furthermore, this result confirms the lability of the pyridine rings, allowing their coordination to MAO to form the open, coordinatively unsaturated cationic complex **4** (the broadening of the signals in the ^{1}H NMR is due to the quadrupolar interactions of the aluminum center with the pyridine rings). The chemical shift of the methyl signal appears to high field as compared to other cationic methyl complexes of metallocenes or even amidinate complexes, indicating the electronic stabilization of the metal center by the nitrogen lone pair electrons.[20m,28]

To characterize the catalytic activity of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) and the different effects of MAO concentration and polymerization time, a series of polymerizations at different conditions were studied. The polymerization results are summarized in Table 5.

Among the many parameters that the catalyst was tested for, the most important was found to be the stability of the complex. Normally, benzamidinate catalysts are active in the polymerization of α-olefins, but they will start to decompose as a function of time.[29] Complex **2** was found to maintain its catalytic activity for more than 20 h, resulting in a linear growth in the polymerization yield as a function of time (Figure 9).

---

(28) (a) Yang, X. M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (b) Yang, X. M.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375.

(29) (a) Volkis, V. Ph.D. Thesis, Technion—Israel Institute of Technology, Haifa, Israel, 2000. (b) Valder, E. Ph.D. Thesis, Technion—Israel Institute of Technology, Haifa, Israel, 2004.

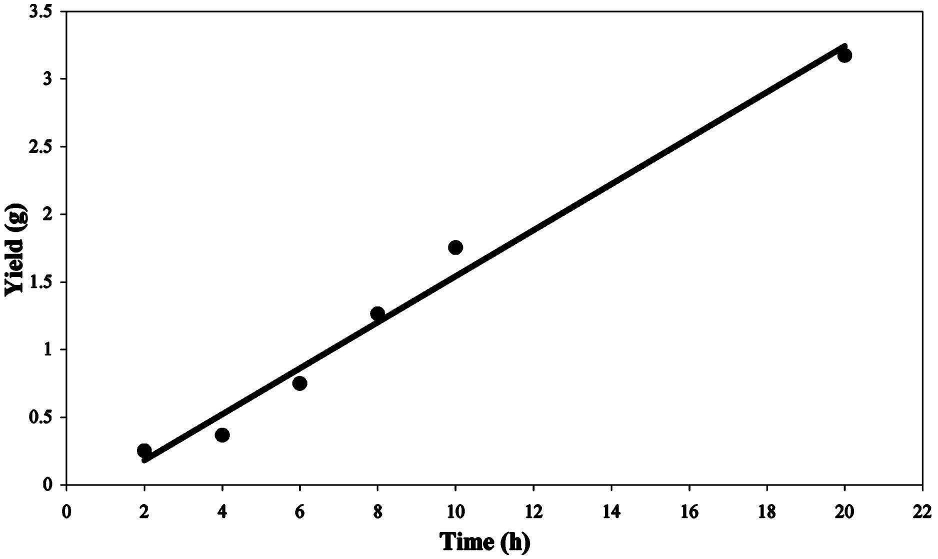


Figure 9. Yield in the polymerization of propylene catalyzed by complex **2** activated by MAO as a function of time (MAO/**2** = 600).

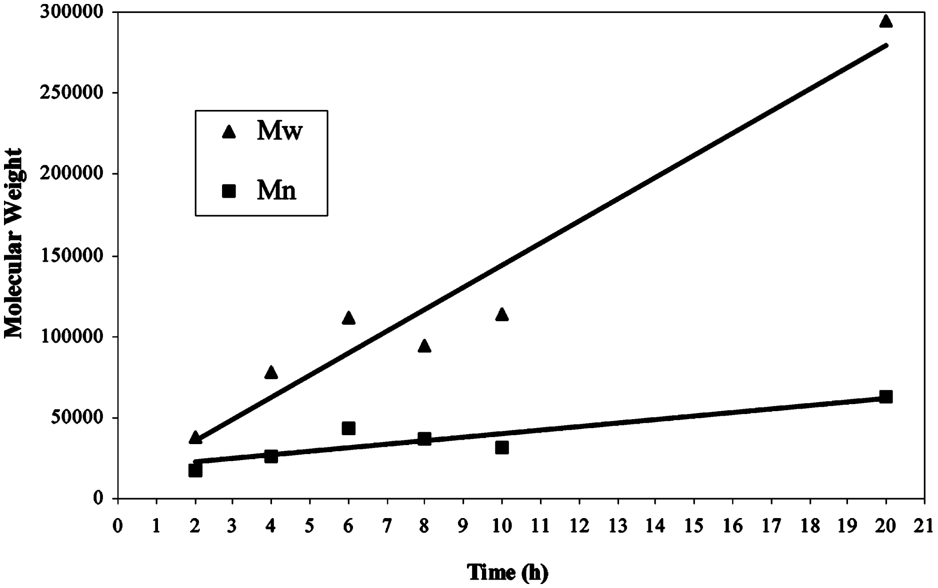


Figure 10. Molecular weight (M_w and M_n) of the polymers obtained in the polymerization of propylene by complex **2** activated by MAO as a function of time (MAO/**2** = 600).

In addition, a linear increase of M_w as a function of time was also observed, although, contrary to expectations, M_n was slightly changed (Figure 10). Concomitantly, it is important to point out that the molecular weight distributions (MWDs) of the polymers were increased as a function of time from ~2.0 up to 4.7 (entries 2 and 5−9 in Table 5). These results indicate the increase in viscosity of the solution, which reduces the monomer takeup and the stirring rate, as observed for the living complex Cp*TiMe$_3$.[30,31]

The influence of the ratio between the complex and the cocatalyst MAO on the polymerization activity was found to follow two different regimes. Up to a ratio of 1:600 a maximum activity was obtained, whereas larger MAO concentrations induced a reduction in the complex activity, achieving a plateau at a ratio of ~1:1000. Similar behavior has also been observed in various early-transition-metal benzamidinate complexes (Figure 11).[20a,b,i] Interestingly, an increase in the MAO ratios induces a slight lowering of the molecular weights of polymers (Figure 12). This result argues that the higher the MAO concentration, the larger the termination process that is operative through an aluminum transfer mechanism. Moreover, there is a small change in the MWDs or isotacticities of the polymers as a function of the MAO:**2** ratio (compare entries 1−4 in Table 5).

It is important to point out that in the experiments presented in Table 5 all the polypropylenes were obtained as nonsticky elastomeric polymers, regardless of the isotacticities. Fractionalization of the obtained polymers shows only one fraction. The ^{13}C NMR of the polymer shows a “quasi-atactic” structure that is almost identical with that obtained with the complex [(2-phenylindenyl)$_2$ZrCH$_3$]$^+$ at 20 °C with the cocatalysts

---

[30] Sassmannshausen, J.; Bochmann, M.; Rösch, J.; Lilge, D. *J. Organomet. Chem.* **1997**, *548*, 23.

[31] Billmeyer, F. W. *Textbook of Polymer Science*, 3rd ed.; Wiley: New York, 1984.

Table 6. Pentad Distributions (in %) for Polymers Obtained in Propylene Polymerization Catalyzed by Complex 1

entry	[*mmmm*]	[*mmmr*]	[*rmmr*]	[*mmrr*]	[*mmrm*] + [*rrmr*]	[*mrmr*]	[*rrrr*]	[*rrrm*]	[*mrrm*]
1	11.9	9.8	7.0	6.2	21.9	14.1	6.3	15	7.8
2	11.1	11.4	4.7	12.2	19.6	10.6	8.0	12.8	9.5
3	10.3	9.5	5.4	9.8	21.9	11.0	10.3	13.6	8.2
4	10.7	8.9	5.7	14.0	19.2	10.0	7.4	14.8	9.3
5	10.6	9.7	5.4	10.1	19.3	13.9	5.6	17.6	7.8
6	8.0	9.8	5.1	9.9	19.8	15.3	5.3	16.7	10.1
7	9.5	9.8	5.6	12.0	18.2	14.4	8.7	14.0	7.8
8	8.8	9.3	7.0	10.3	17.2	16.3	5.7	11.8	13.6
9	9.6	9.6	5.0	11.4	20.3	13.3	8.0	13.2	9.6
10[a]	9.0	13.9	7.1	12.7	24.3	12.0	4.3	10.0	6.7

[a] "Quasi-atactic" polypropylene obtained in the polymerization of propylene catalyzed by the complex $[(2\text{-phenylindenyl})_2ZrCH_3]^+$ at 20 °C with the cocatalysts borate/TIBA ($[HMe_2NC_6H_5][B(C_6F_5)_4]/Al(isobutyl)_3$) in bromobenzene, as reported by Busico.[32]

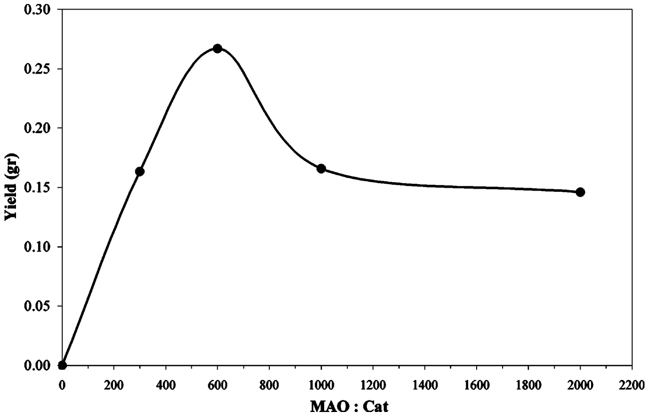


Figure 11. Yield obtained in the polymerization of propylene by complex **2** activated by MAO as a function of the ratio of MAO to complex.

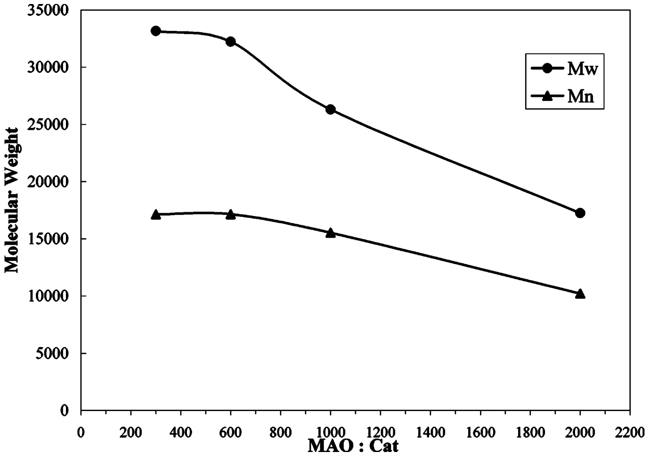


Figure 12. Plot of the molecular weight obtained after 2 h as a function of MAO/complex **2** in the polymerization of propylene.

borate/TIBA ($[HMe_2NC_6H_5][B(C_6F_5)_4]/Al(isobutyl)_3$) in bromobenzene (Table 6, comparison of entries 1−9 with entry 10).[32] The stress strain curve of the polymer obtained in entry 2 was measured, showing a maximum stress at 860% with a break at a yield of 1.25 MPa. The starting active species is plausible as a single-site complex; on the basis of the MWD (see Table 5), it seems conceivable that the formation of such a type of polymer can be explained by the rapid interconversion of mainly two enantiomeric structures, from a total of six, as presented in Figure 8.[33] This assumption is reasonable, as the open intermediate complex (**4**) will be expected to produce an atactic complex.[18h,j] While we are discussing a polymer that we have named "quasi-atactic", we must take into account two facts that will shed light on the formation of the elastomeric material. The first fact is that the molecular weights of the obtained polymers are in the range of oils to sticky gums for real atactic polymers.[10,30] The second fact is that the polymers obtained do not dissolve in diethyl ether as real atactic polymers, but they do dissolve in hot hexane. Since the dynamic interconversion between the two enantiomers must take place through an open symmetry of at least one of the ancillary ligands, and the obtained polymers exhibit almost ^{13}C NMR spectra almost identical with those of the oscillating metallocenes,[32,34] we can conclude that the elastomeric formation of polypropylene is an outcome of the monomer insertions between two "oscillating" close configuration catalysts (Figure 8). The number of isotactic monomeric units in the elastomeric polymer was calculated to be 6, indicating a lack of melting as observed for other short isotactic fragments in elastomeric polypropylenes ($T_g = -10.5$ (polymer obtained in entry 2 of Table 6)).[35] For these complexes we cannot cancel any minor contribution that might be present due to the open configuration complex.

Conclusions. The synthesis of complex **2** is presented, showing two dynamic processes. The complex has an agostic interaction, which was characterized in solution by NMR and in the solid state by X-ray diffraction studies. Complex **2** was found to be an active catalyst for the formation of elastomeric polypropylene when activated by MAO. The formation of the polymer is attributed mainly to an equilibrium of the cationic complex, forming two isospecific polymerization sites. In addition to this equilibrium, some atactic domains can be produced when the same complex is in its open configuration. Complex **2** exhibits a long-term activity, in addition to the almost linear increase of the molecular

---

[32] Busico, V.; Van Axel Castelli, V.; Aprea, P.; Cipullo, R.; Segre, A.; Talarico, G.; Vacatello, M. *J. Am. Chem. Soc.* **2003**, *125*, 5451.

[33] From the six possible chelating stereoisomers it is not easy to rationalize why two enantiomers are more stable or are obtained more easily than the other four. However, if more enantiomers are indeed operative during the polymerization, they must have similar catalytic properties that make us unable to decide which are the complexes obtained.

[34] (a) Busico, V.; Cipullo, R.; Segre, A. L.; Talarico, G.; Vacatello, M. Van Axel Castelli, V. *Macromolecules* **2001**, *34*, 8412. (b) Busico, V.; Cipullo, R.; Kretschmer, W. P.; Talarico, G.; Vacatello, M.; Van Axel Castelli, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 505.

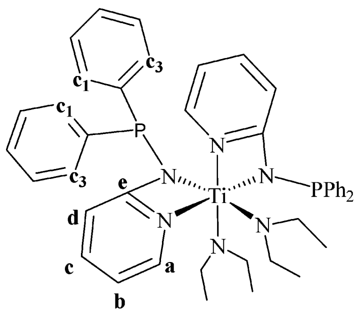
[35] (a) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779. (b) Mansel, S.; Pérez, E.; Benavente, R.; Pereña, J. M.; Bello, A.; Röll, W.; Kirsten, R.; Beck, S.; Brintzinger, H.-H. *Macromol. Chem. Phys.* **1999**, *200*, 1292.

weight of the polymers as a function of time (20 h). Additional complexes allowing the rational design of an elastomeric polymer via a dynamic process of coordination are under investigation.

Experimental Section

General Remarks. All manipulations of air-sensitive materials were carried out with the vigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum (10^{-6} Torr) line or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1−2 ppm of O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Hexane and toluene-d_8 solvents were freshly distilled under argon from Na−K alloy. Toluene was freshly distilled under argon from sodium. All solvents for vacuum line manipulations were stored under vacuum over Na−K alloy in resealable bulbs. The neutral ligand Ph_2PNpy (**1**; py = pyridine) was prepared according to the literature method.[22] $Ti(NEt_2)_4$ was prepared from $TiCl_4$ and $HNEt_2$ according to a known procedure.[36] Ethylamine (Aldrich) was degassed and freshly vacuum-distilled. NMR spectra were recorded on Bruker AM-200, Bruker AM-400, and Avance 500 spectrometers. Chemical shifts for ^1H NMR and ^{13}C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Chemical shifts for ^{31}P NMR are referenced to H_3PO_4. The NMR experiments were conducted with Schlenk vessel sealed tubes (J. Young stopcock) after vacuum transfer of the solvent by a high-vacuum line. Molecular weights of polypropylene were determined by GPC recorded on a Waters Alliance 2000 instrument at 135 °C in 1,2,4-trichlorobenzene.

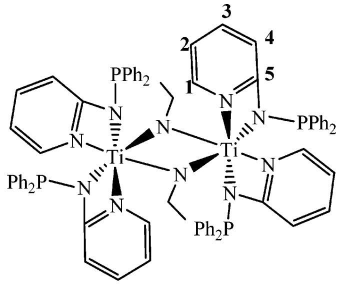
Synthesis of $Ti(Ph_2PNpy)_2(NEt_2)_2$ (2).



To a stirred solution of 0.34 g (1.22 mmol) of the ligand $Ph_2PNHPpy$ (**1**) in 10 mL of toluene was added 0.34 g (6.85 mmol) of $Ti(NEt_2)_4$ dropwise at 0 °C under a nitrogen atmosphere. The mixture was slowly warmed to room temperature and stirred for 24 h. The toluene and diethylamine were evacuated from the reaction flask overnight on a high-vacuum line. Traces of the ligand and $Ti(NEt_2)_4$ were removed from the complex by washing with hexane (3 × 50 mL). Orange crystals of the complex were obtained by recrystallization from toluene at −40 °C.

^1H NMR (200 MHz, toluene-d_8): δ 0.86 (t, 12H, $^3J_{HH} = 7$ Hz, $-CH_3$), 3.79 (br, 2H, $-CHH-CH_3$), 4.78 (br, 2H, $-CHH-CH_3$), 5.95 (dd, 2H, $^3J_{HH} = 4.0$ Hz, $^3J_{HH} = 6$ Hz, H(b)), 6.13 (dd, 2H, $^3J_{HH} = 8.5$ Hz, H(d)), 6.54 (dd, 2H,$^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 6$ Hz, H(c)), 7.22 (br, 6H, *m,p*-aromatic rings), 7.56 (br, 2H, *o*-aromatic ring), 7.81 (br, 2H, *o*-aromatic ring), 7.97 (d, 2H, $^3J_{HH} = 4$ Hz, H(a)). ^{13}C NMR (100 MHz, toluene-d_8): δ 13.0 ($-CH_2CH_3$), 45.7 ($-CH_2CH_3$), 111.9 (CH, *C*(b)), 112.2 (CH, *C*(d)), 128 (*C*H, *m,p*-aromatic rings), 131.8 (CH, C_1), 132.0 (CH, C_3), 137.5 (CH, *C*(c)), 143.4 (CH, *C*(a)), 168 (C, *C*(e)). ^{31}P NMR (81 MHz, toluene-d_8): δ 35.12 (s, PPh_2).

Synthesis of $Ti_2(Ph_2PNpy)_4(\mu\text{-}NEt)_2$ (3).



In a glovebox, 0.02 g (0.0268 mmol) of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ (**2**) was loaded into an NMR tube. A 0.5 mL portion of toluene-d_8 and an excess of $EtNH_2$ (6.0 μL, 0.095 mmol) were vacuum-transferred into the tube. The amount of $EtNH_2$ was measured in its liquid state and was confirmed by NMR. The tube was heated by means of a thermostatic oil bath to 110 ± 0.1 °C. After 4 days the tube was cooled to room temperature and the solvent, diethylamine, and excess $EtNH_2$ were removed from the tube by vacuum transfer to obtain an orange powder. Recrystallization of the orange powder from toluene yielded single crystals for X-ray diffraction.

^1H NMR (C_6D_6, 500 MHz, 295 K): δ 0.71 (t, 3H, $^3J_{HH} = 7$ Hz, $-CH_3$), 0.84 (t, 3H, $^3J_{HH} = 7$ Hz, $-CH_3'$), 2.89 (q, 2H, $^3J_{HH} = 7$ Hz, $-CH_2-$), 3.17 (q, 2H, $^3J_{HH} = 7$ Hz, $-CH_2'-$), 6.31 (t, 4H, H3), 7.00 (m, 28H, H2 + *m,p*-aromatic ring), 7.41 (m, 20H, H4 + *o*-aromatic ring), 7.90 (d, 4H, $^3J_{HH} = 5$ Hz, H1). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 14.0 ($-CH_3$), 16.1 ($-CH_3'$), 35.7 ($-CH_2'-$), 41.1 ($-CH_2-$), 108.8 (C2), 108.9 (C2′), 115.1 (C3), 115.2 (C3′), 128.7−129.1 (*p,m*-aromatic ring), 131.5 (*o*-aromatic ring), 131.7 (*o*-aromatic ring′), 137.5 (C4), 137.6 (C4′), 140.3 (C−P), 140.4 (C−P), 148.5 (C1), 148.6 (C1′), 159.5 (C5), 159.6 (C5′). ^{31}P NMR (81 MHz, C_6D_6, 295 K): δ 28.52 (s, PPh_2).

Propylene Polymerization. Polymerization reactions were conducted under dry anaerobic conditions on a Schlenk line. The general procedure was as follows: a 10 mg amount of catalyst and the desired amount of MAO were weighed into a heavy-walled glass reactor inside the glovebox. The reactor was connected to the Schlenk line, and 5 mL of the desired solvent was added via a syringe under an argon flow. The solution was degassed to enable the addition of the monomer. A 30 mL portion of propylene was vacuum-transferred into the reactor at low temperature. After monomer addition, the required temperature was maintained by means of a water bath and the reaction mixture was stirred for the duration of the reaction.

The reaction was quenched by venting the excess propylene in a hood, exposing to air, and washing with H_2O/acac (5/1) solution (acac = acetylacetonate). The polymer produced was then collected, washed with acetone, and dried under vacuum. For NMR and molecular weight analysis the polymers were dissolved in hot 1,2,4-trichlorobenzene.

Acknowledgment. This research was supported by the German Israel Foundation under Contract I-621-27.5/1999 and by the Fund for the Promotion of Research at the Technion. M.S.E. thanks the Fund for the Promotion of Research at the Technion.

Supporting Information Available: Figures giving COSY and $^{13}C-^1H$ correlation NMR spectra of complex **2** and a stress−strain curve for the polymer obtained in entry 2 of Table 5 and tables giving crystallographic data for complexes **2** and **3**; the crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050015B

---

(36) Bradelly, D. C.; Thomas, I. M. *J. Chem. Soc.* **1959**, 340.