Bis(imidodithiodiphosphinato) Titanium and Zirconium Complexes: Synthesis, Characterization, and Their Catalytic Activity in the Polymerization of α-Olefins

Fapu Chen,[†] Moshe Kapon,[†] J. Derek Woollins,[‡] and Moris S. Eisen^{*,†}

Schulich Faculty 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, St Andrews, Fife KY16 9ST, Scotland, U.K.

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The synthesis, characterization, and low-temperature crystal structures of a family of group 4 complexes containing different numbers of imidodithiodiphosphinate ligands and different metal oxidation states is presented. Their catalytic activity in the polymerization of ethylene and propylene was studied. For ethylene, when these complexes are activated with methylalumoxane (MAO), they are active catalysts in the polymerization producing extremely high molecular weight, high-density polyethylene with very narrow polydispersities. However, for propylene, the activity of these complexes is low, producing only atactic polypropylene. The bis(imidodithiodiphosphinate)titanium(bis(amido)) complex **6e** has a singular reactivity, which upon heating forms the corresponding imido complex with the concomitant elimination of Et_3N and the formation of the homoleptic complex tris(imidodithiodiphosphinate)titanium(III) (**6h**).

Introduction

The polymerization of olefins by single-site catalysts has experienced a phenomenal growth in the last two decades, from academic to industrial research groups engaging in the design of new coordinative unsaturated complexes 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 complex² are able to induce specific changes in the skeleton of the obtained polymers, providing access to unusual materials, such as hemi-isotactic polypropylene and stereoblock (isotacticatactic) materials, some of them with elastic properties.¹⁻³ It is remarkable that the chemical nature of the active organometallic complexes can produce distinctive polymeric materials, exhibiting sometimes spectacular insights.²⁻⁴

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During the last decade, we have been interested in the synthesis of group 4 complexes containing the heteroallylic N-C-N moieties, as part of the ancillary ligation motif, such as in benzamidinate $(1a, 1b)^5$ and amidopyridines (2).⁶



When activated with the cocatalyst, methylalumoxane (MAO), the corresponding complexes containing these ancillary ligands were found to be active catalytic precursors for the polymerization of α -olefins. ⁷ Recently, also we have shown that titanium and zirconium heteroallylic complexes containing the P–N–X (X = Ph (**3a**), PPh₂ (**3b**)) ligand functionalities⁸ or the expanded heteroallylic acetylacetonate moiety **4a**–**4e**⁹ are also active catalysts for the polymerization of propylene, forming a unique

^{*} Corresponding author. E-mail: chmoris@tx.technion.ac.il.

[†] Technion-Israel Institute of Technology.

^{*} University of St Andrews.

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type of elastomeric materials; for the latter complexes, remarkable activity in the polymerization of cyclic esters was observed.



Interestingly, Novak et al.,^{10a} and later Kim et al.,^{10b} have found that the β -diketiminate complexes of zirconium (**5a**) are highly active catalysts in the polymerization of ethylene. In parallel, we have shown that the corresponding bis(β -diketiminate) titanium dichloride complexes (**5b**) are also very active complexes in the polymerization of α -olefins.¹¹ An intriguing conceptual question that we wished to consider regards the synthetic approach toward the general family of complexes containing the imidodithiodiphosphinate ancillary ligand as in complex **A**.



The rationale behind the synthetic approach of these inorganic ligands regards their isolobal identity to the ligand motif presented in complexes 4 and 5. It was interesting to compare their chemical reactivity with group 4 metal salts and the molecular structure of the new inorganic compounds (σ vs π ; planar vs chair-like). In addition, it was important to evaluate the activity of the latter complexes in the polymerization of α -olefins. In this article, we report the synthesis, characterization, and low-temperature crystal structures of a family of group 4 complexes containing different numbers of the imidodithiodiphosphinate ligands and different metal oxidation states. Furthermore, we present their catalytic activities in the polymerization of ethylene and propylene. We show that when these complexes are activated with methylalumoxane (MAO), they are active for the polymerization of ethylene, producing extremely high molecular weight, high-density polyethylene with very narrow polydispersities. However, for propylene, unexpectedly, the activity of these complexes is low, nonetheless producing a medium molecular weight atactic polypropylene.

Results and Discussion

Syntheses and Characterization of Bis(imidodithiodiphosphinate) Complexes. The synthesis of titanium and zirconium imidodithiodiphosphinate complexes was performed following two different synthetic pathways. The first route uses the metal chloride salts (MCl₄, M = Ti, Zr) with the corresponding lithium salt of the imidodithiodiphosphinate ancillary ligand, whereas the second route utilizes the homoleptic diethylamido complexes (MNEt₂)₄ (M = Ti, Zr) with the corresponding neutral aminodithiodiphosphinate ligand. The deprotonation of the neutral ligand (Ph₂PS)₂NH (**6a**) in THF with a slight excess of *n*-BuLi

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Scheme 1. Synthetic Approach for the Synthesis of Complexes 6b-6h



gives quantitatively the corresponding lithium salt of the imidodithiodiphosphinate ligand solvated with two THF molecules, producing (Ph₂PS)₂NLi • 2THF (6b) (isolated yield 94%) (Scheme 1). Similar literature reactions, which have been utilized to prepare the same complex 6b, using lithium metal as the deprotonation reagent proceed in lower yields (78%).¹² Slow recrystallization of complex **6b** in THF at -35 °C for 24 h yields single crystals, suitable for X-ray diffraction studies. The crystal structure of complex 6b is presented in Figure 1. The lowtemperature X-ray analysis of complex 6b shows the lithium metal as a part of a six-membered ring in an almost $C_{2\nu}$ symmetry about the N-Li vector. The deprotonation of 6a surprisingly induces a small expansion of the PNP angle $(133.9(2)^{\circ})$ as compared to either the free ligand $(132.6(1)^{\circ})^{13}$ or the analogous potassium salt, K[SPPh₂NPPh₂S] (128.6(2)°).¹⁴ In addition, there is an expected shortening of the P-N bonds (1.578(3) and 1.591(3) Å) as compared to **6a** (1.671(2) and 1.684(2) Å) and identical bond lengths to those exhibited by the corresponding potassium salt (1.592(2) Å). Furthermore, also an increase in the length of the P=S bonds (1.9839(14) and 1.9851(14) Å) in complex **6b** is observed as compared to those of **6a** (1.950(1) and 1.936(1) Å) and almost identical to those of the potassium salt (1.978(1) Å). The increase of the N–P–S bond angles in complex **6b** (119.61(13)° and 120.22(12)°) and in the corresponding potassium salt $(120.7(1)^{\circ})$ as compared to the free ligand $(114.7(1)^{\circ} \text{ and } 115.3(1)^{\circ})$ indicates the increased delocalization of the charge in the metal complexes within the

S-P-N-P-S core unit. The metal exhibits a tetrahedral geometry environment coordinating to two sulfur atoms and two oxygen atoms of the THF solvent molecules with bond lengths falling within the normal range (Li-O = 1.894(8) and 1.917(8) Å; Li-S = 2.473(8) and 2.474(8) Å). Interestingly, when comparing the lithium and the potassium complexes, in the



Figure 1. ORTEP plot of the molecular structure of the lithium complex **6**. All hydrogens were removed for clarity and thermal ellipsoids are given at 50% probability. Selected bond lengths (Å) and angles (deg): Li-S(1) = 2.474(8), Li-S(2) = 2.473(8), P(1)-N(1) = 1.591(3), P(2)-N(1) = 1.578(3), O(1)-Li-O(2) = 109.3(4), O(2)-Li-S(2) = 112.5(4), O(1)-Li-N(1) = 89.59(8), S(2)-Li-S(1) = 109.5(3).

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Figure 2. Possible dynamic processes in complexes 6c and 6d.

former the S–Li–S bond angle $(109.5(3)^\circ)$ is much larger than in the latter complex $(S-K-S = 80.5(1)^\circ)$.¹⁴ Presumably, this contracted angle is an outcome of the K–S ladder-like polymeric structure of the latter as compared to a solvated lithium complex. In solution, however, the ³¹P NMR spectrum of the lithium complex exhibits only one singlet, suggesting that the two phosphine atoms are magnetically equivalent in solution at room temperature.

The reaction of lithium salt (**6b**) with 0.5 equiv of either the titanium or the zirconium tetrachloride salt afforded the corresponding disubstituted titanium or zirconium dichlorides complexes, **6c** and **6d**, in high yields, respectively (isolated yields: Ti = 91%; Zr = 89%) (Scheme 1). Complexes **6c** and **6d** were characterized spectroscopically and by elemental analysis. These two complexes were found to be insoluble in nonpolar solvents, neither in CH₂Cl₂ or in diethyl ether, and showed only ~10% solubility in THF solutions at either room or reflux temperatures. Our attempts to obtain single crystals suitable for X-ray diffraction studies were unsuccessful due to the constant presence of microcrystalline material.

The THF- d_8 solutions of complexes **6c** and **6d** showed narrow singlet signals in the ³¹P NMR, at 41.5 and 43.9 ppm, respectively, indicating the magnetic equivalence of the four phosphorus atoms in each complex at room temperature. The dynamic behavior of the complexes may be due to one of the following possibilities: (i) a Bailar twist¹⁵ that proceeds via a nondissociative mechanism resulting in the opposite enantiomer (Figure 2a) or (ii) a disconnection and recoordination of the chelating ligands through the weaker Ti–S bond, resulting in the formation of different stereoisomers/oligomers in solution (Figure 2b).

In order to establish which dynamic process takes place, lowtemperature ¹H and ³¹P NMR experiments were performed in an attempt to calculate ΔS^{\ddagger} for the processes. The rapid precipitation of the complexes prevented us from obtaining good line broadening data; however the formation of precipitate oligomeric structures implies a dissociative mechanism and excludes the possibility of a Bailar twist as the main operative pathway for the dynamic process.¹⁶

Taking into consideration the low solubility of complexes **6c** and **6d**, we decided to follow a different synthetic methodology for the preparation of similar soluble complexes. Hence, the reaction of the neutral ligand **6a** with a half equivalent of the homoleptic complexes $M(NEt_2)_4$ (M = Ti, Zr) allowed the

formation of the corresponding $[(Ph_2PS)_2N]_2Ti[N(CH_2CH_3)_2]_2$ (6e) and $[(Ph_2PS)_2N]_2Zr[N(CH_2CH_3)_2]_2$ (6f) in 73% and 89% isolated yields, respectively. Both diethylamido complexes were characterized spectroscopically and by elemental analysis, and for the latter zirconium complex, 6f, single-crystal X-ray diffraction studies were also performed. Both diethylamido complexes were found to be soluble in toluene or more polar solvents, in contrast to their related chloride complexes. In addition, the melting points of the diethylamido complexes were found to be much lower than those of the corresponding chloride complexes (**6e** = 79 °C; **6f** = 91–93 °C; **6c** = 173–175 °C; 6d = 229 °C (dec)). The high melting temperatures of the chloride complexes may be indicative, again, of the large chlorine-metal intermolecular interactions, inducing their low solubility. In solution, the ³¹P NMR of **6e** and **6f** also exhibits only one narrow singlet line for each complex at 39.9 and 41.8 ppm, respectively, indicating also a rapid equilibrium among the disposition of the ligands around the metal center, inducing the magnetic equivalence of the phosphorus atoms. Interestingly, the diethylamido groups of both complexes are also magnetically equivalent, as revealed by NMR showing only one triplet and one quartet for all four methylene and methyl groups, respectively, in the ¹H NMR, and one singlet line for all four methylenes and one singlet line for the methyl groups in the ¹³C NMR.¹⁷ The dynamic behavior of these complexes was studied by ¹H and ³¹P NMR low-temperature experiments, indicating a $\Delta S^{\dagger} > 0$, implying that a rapid disconnection and recoordination of the chelating ligands through the weaker Ti-S bond is the main operative mechanism, resulting in the rapid formation of the different stereoisomers in solution

We have found that complex **6f** is thermally stable even when refluxing for long periods of time in toluene. Complex **6f** was recrystallized from a solution of toluene/hexane at room temperature for 24 h, yielding yellow crystals suitable for X-ray diffraction studies. The crystal structure of complex **6f** is presented in Figure 3. The X-ray analysis of complex **6f** shows that the zirconium atom is arranged in a slightly distorted octahedral environment with two diethylamido ligands disposed in the *cis* stereochemistry. The equatorial plane is formed by the N(58)–N(63)–S(1)–S(68) atoms with a sum of angles of 360.2°, and the apical positions are occupied by the S(29) and S(30) atoms, forming an angle of 174.13°. The metal nitrogen bond lengths are alike and are within the normal range for other zirconium amido bond lengths.¹⁸

Different metal—sulfur bond lengths are exhibited in complex **6f**: two short distances between Zr-S(2) (2.6487(14) Å) and Zr-S(3) (2.6658(14) Å) and two longer distances in Zr-S(1) (2.7666(14) Å) and Zr-S(4) (2.7723(14) Å). The longer distances are the result of the larger *trans* effect between the sulfur and the nitrogen atom of the amido groups. Regarding the imidodithiodiphosphinate moiety, the bond lengths within the ligand (besides the metal—sulfur distance and the *trans* effect) are very alike (S(2)-P(2) = 2.0150(18) Å, S(1)-P(1) = 2.0026(18) Å, P(2)-N(1) = 1.591(4) Å, P(1)-N(1) = 1.586(4) Å). This disposition of atoms indicates a high delocalization effect of the electronic charge, although the geometry of the ligand is *not planar*. Therefore, the delocalization must be operative through the d-orbitals of the phosphorus and sulfur atoms.

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Figure 3. ORTEP plot of the molecular structure of the zirconium complex **6f**. All hydrogens were removed for clarity, and thermal ellipsoids are given at 50% probability. Selected bond lengths (Å) and angles (deg): S(1)-P(1) = 2.0026(18), S(4)-P(4) = 2.0067(18), N(1)-P(2) = 1.591(4), N(2)-P(3) = 1.589(4), N(1)-P(1) = 1.586(4), Zr-S(1) = 2.7666(14), Zr-S(2) = 2.6487(14), Zr-S(3) = 2.6658(14), Zr-S(4) = 2.7723(14), N(4)-Zr-N(3) = 102.34(16), N(4)-Zr-S(2) = 97.73(12), N(3)-Zr-S(2) = 83.60(16), N(4)-Zr-S(3) = 84.56(12), S(2)-Zr-S(3) = 174.13(15), S(2)-Zr-S(4) = 86.86(4), S(3)-Zr-S(4) = 89.48(4), S(2)-Zr-S(1) = 89.04(4), S(3)-Zr-S(1) = 85.53(4), S(4)-Zr-S(1) = 73.80(4), N(3)-Zr-S(1) = 165.97(12).



Figure 4. ORTEP plot of the molecular structure of the zirconium complex **6g**. All hydrogens were removed for clarity, and thermal ellipsoids are given at 50% probability. Selected bond lengths (Å) and angles (deg): Ti-N(3) = 1.667(7), Ti-S(4) = 2.514(2), Ti-S(2) = 2.522(3), Ti-S(3) = 2.573(2), Ti-S(1) = 2.525(3), N(3)-C(49) = 1.450(10), N(3)-Ti-S(4) = 98.0(2), N(3)-Ti-S(2) = 101.9(2), N(3)-Ti-S(1) = 104.9(2), N(3)-Ti-S(3) = 101.0(2), S(4)-Ti-S(1) = 86.97(8), S(4)-Ti-S(2) = 160.05(10), S(2)-Ti-S(1) = 89.20(8), S(4)-Ti-S(3) = 90.14(8), S(1)-Ti-S(3) = 154.17(10), S(2)-Ti-S(3) = 84.82(8).

When the reaction of the neutral ligand **6a** with 0.5 equiv of Ti[(NEt₂)₄] was performed in toluene at 110 °C, two unexpected products were produced: the bis(imidodithiodiphosphinate)titanium(IV) ethylimido complex (**6g**) as the major product (isolated in 70% yield) and the tris(imidothiophosphonate)titanium(III) (isolated in 5% yield) (**6h**) complex (Scheme 1). These compounds are easily separated by fractional precipitation from toluene/hexane (**6g**) and then from hexane only (**6h**) solutions at low temperatures. Single crystals for both complexes were obtained by their recrystallization at -45 °C for 72 h. Spectroscopically, complex **6g** shows only one singlet in the

³¹P NMR at 39.8 ppm, similar to those found for complexes **6c** and **6e**, indicating again the magnetic equivalence of the ligands.

The crystal structure of complex **6g** is presented in Figure 4. The X-ray analysis of complex **6g** shows the presence of a distorted square-planar pyramid of a five-coordinated imidotitanium complex, in which the central titanium is connected to one nitrogen atom (N3) at the apical position. The Ti=N bond length (1.667(7) Å) is close to the typical range found for other crystallographically characterized imidotitanium complexes (1.672(7)–1.723(4) Å), ¹⁹ as well as the angle of the imido moiety with the metal, C(49)–N(3)–Ti = 172.8(6)°. The



Figure 5. ORTEP plot of the molecular structure of the zirconium complex **6h**. All hydrogen atoms were removed for clarity, and thermal ellipsoids are given at 50% probability. Selected bond lengths (Å) and angles (deg): Ti-S(4) = 2.486(2), Ti-S(5) = 2.487(2), Ti-S(3) = 2.497(2), Ti-S(6) = 2.501(2), Ti-S(2) = 2.553(2), Ti-S(1) = 2.573(2), S(4)-Ti-S(5) = 97.89(8), S(4)-Ti-S(3) = 96.28(8), S(5)-Ti-S(3) = 87.96(8), S(4)-Ti-S(6) = 85.89(8), S(5)-Ti-S(6) = 95.00(8), S(3)-Ti-S(6) = 176.07(9), S(4)-Ti-S(2) = 87.85(8), S(5)-Ti-S(2) = 171.94(9), S(4)-Ti-S(1) = 177.15(9).

Scheme 2. Proposed Mechanism for the Formation of Complex 6g



imidodithiodiphosphinate ligands in **6g** have essentially the same geometry as each other and those in **6f** (*vide infra*). Remarkable is again the delocalization of the charge through the ligand. Both ligands are η^2 and *nonplanar* in the solid state: one ligand has a chair conformation, whereas the second ligand maintains a boat conformation.²⁰ Hence if delocalization is operative, it is plausibly being performed through the d-orbitals of the P and S atoms of the ligands in the solid state, and in solution, by their rapid rotation.

Normally the formation of monomeric imido complexes proceeds either via the corresponding bisamido complex, in which the amido groups contain at least one hydrogen atom (descendent from a primary amine), or by heating an alkyl amido complex (also containing a hydrogen attached to the nitrogen), eliminating an alkane moiety. ²¹ The formation of complex **6g** is presumably via the metathesis elimination of an ethyl moiety of the corresponding bisamido complex, eliminating Et₃N (Scheme 2). To corroborate the proposed mechanism, we have to investigate the thermal stability of complex **6e**. Hence, by refluxing complex **6e** in a toluene solution for 1 h, Et₃N and complex **6g** were formed. This result supports the remarkable ability of this titanium complex to induce the ethyl migration toward the formation of the imido complex. Interestingly, heating of the zirconium complex **6f** for long periods of time did not induce any amine elimination, indicating the higher thermal stability of the complex as compared to that of the isolobal titanium complex.

The formation of the small amounts of complex **6h** is very surprising and totally unexpected. The complex is paramagnetic and is NMR silent. The crystal structure of complex **6h** is presented in Figure 5. The X-ray analysis of the complex shows a slightly distorted octahedral environment around the metal

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⁽²⁰⁾ For late transition complexes, the boat/chair conformation has been observed; see: (a) Phillips, J. R.; Slawin, A. M. Z.; White, A. J. P.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2467. (b) Bhattacharyya, P.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2001**, *20*, 1831.

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center. We have chosen the apical atoms to be S(2) and S(5) due to the better angles of the formed square-planar geometry around the metal utilizing the other four sulfur atoms (sum of angles = 360.0°).

Two of the three η^2 -chelating ligands are in a chair conformation, whereas the remaining ligand is in a distorted boat conformation with normal distances and geometrical dispositions similar to those found for the other titanium and zirconium imidodithiodiphosphinate complexes presented above. As regards the metal-ligand environment bond length distances, two ligands exhibit similar Ti-S distances and one ligand presents a slightly longer Ti-S bond distance. When comparing the Ti(IV)-S and Ti(III)-S bond length distances, it has been recognized that Ti(IV)-S bond lengths (2.378-2.397 Å)²² are somewhat shorter than Ti(III)-S (2.487-2.584 Å)²³ bond lengths by ca. 0.14 Å, which may be compared with the difference of the ionic radii for $Ti(III)^+$ (0.81 Å) and $Ti(IV)^+$ (0.75 Å).²⁴ However, in complexes **6g** (Ti(IV)–S: 2.514–2.573 Å) and **6h** (Ti(III)-S: 2.486-2.573 Å) similar bond distances (Ti-S) are appreciably in contrast to the expectations, probably due to the steric repulsions among the congener phenyl groups of the ligands.

Recently, we and others have reported the formation and solid state characterization of some Ti(III) complexes, when TiCl₄ was reacted with either an allylic or a heteroallylic ligand in which a carbon–carbon bond was formed as the corresponding oxidation step.^{10,25} Hence, the formation of complex **6h** presumably proceeds in two steps. In the first step a redistribution of ancillary ligands must be operational at high temperature, whereas in the second step, the metal may undergo a reduction to form complex **6h** and probably the oxidation of the amine (Scheme 3). We were able to trap only trace amounts (GC-MS) of the tetraethylhydrazine (Et₂NNEt₂) presumably since it is mainly bound to the coordinatively unsaturated monoimi-

dodithiodiphosphinate complex as found for amines with isolobal metal complexes.²⁶ Our attempts to fully characterize this latter complex were unproductive, most likely due to the formation of oligomeric structures. The synthesis of complex **6h** was performed following an independent route in good yield (69%) from the reaction of Ti(III)Cl₃(THF)₃ with 3 equiv of the ligand **6b** in THF at reflux temperatures. The complex is highly oxygen sensitive and decomposes rapidly in air at room temperature. Crystalline and analytically pure material can be obtained from its recrystallization in hexane at low temperatures (-45 °C) for 72 h, and the collection of the crystals was via a swivel frit under argon.

Catalytic Polymerizations. The catalytic polymerization of ethylene and propylene was studied with the catalytic precursors **6c**, **6d**, **6e**, **6f**, **6g**, and **6h**. Cationic catalysts were generated in solution by the reaction of the corresponding precursor with an excess of MAO. To shed some light on the structure of the active cationic complexes, we have followed the reactions of complexes **6c** and **6d** with an excess of MAO by ¹³C NMR in BrC₆D₅. Hence, for complex **6c**, a Ti-CH₃⁺ cationic signal was observed at 102 ppm, whereas for the isolobal complex **6d**, the Zr-CH₃⁺ is obtained at 60.3 ppm. It is important to point out that for octahedral benzamidinate complexes, similar M-CH₃⁺ chemical shifts have been observed for the corresponding cationic complexes.²⁷

The polymerizations were carried out under strictly anaerobic/ anhydrous conditions. The reactions were quenched after measured time intervals with methanol/HCl solution prior to polymer collection, washing, and drying. In the case of ethylene, high-density polyethylene (mp 133-136 °C) was always obtained. However, at 1 atm of ethylene, all complexes showed low catalytic activities (ca. ~3000 g PE/mol·cat·h atm) with almost no differences for the various complexes. Under pressure (30 atm), the activities of the complexes were much higher and the results are summarized in Table 1.

The polymerization of ethylene with complex **6c** was the most active, and the produced polymer was obtained with a very high

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Table 1. Activity, Molecular Weight, and Melting Point Data for the Polymerization of Ethylene^a

entry	complex	time (h)	activityA $\times 10^{-4b}$	$M_{ m w}$ $ imes$ 10^{-3}	$M_{\rm n} imes 10^{-3}$	MWD^d	mp (°C)
1	6c	3	10.0	$HMWPE^{c}$	HMWPE	HMWPE	136.6
2	6d	3	4.0	2567	1955	1.31	136.3
3	6e	3	4.1	1973	1676	1.18	132.5
4	6f	3	3.0	2166	1540	1.40	135.9
5	6g	3	3.2	2060	1588	1.29	133.2
6	6h	3	4.3	1576	1395	1.13	134.4
7	6h	6	4.9	2005	1604	1.25	135.1
8	6h	20	5.5	2195	1845	1.19	135.3

^{*a*} Al:complex ratio = 1600; the methylaluminoxane solvent was removed from a 20% solution in toluene at 25 °C/10⁻⁶ Torr, toluene, RT, 5 mmol of catalyst, 30 atm of olefin (kept constant via a solenoid). ^{*b*} Activity in g PE/mol cat \cdot h \cdot atm. ^{*c*} Molecular weight too high to be measured by regular GPC (out of the measurement limit) and low solubility at 165 °C in 1,2,4-trichlorobenzene. ^{*d*} M_w/M_n .

Table 2. Activity, Molecular Weight, and Melting Point Data for the Polymerization of Propylene^a

		• ·		•	•		
entry	complex	MAO:M	solvent	A \times 10 ⁻³	$M_{ m w}$	$M_{ m n}$	MWD^{c}
1	6c	400	toluene	2.4	513 000	315 000	1.6
2	6c	1600	toluene	3.3	91 200	21 700	4.2
3	6h	400	toluene	42.5	424 000	286 000	1.5
4	6h	1600	toluene	86.4	324 000	79 600	4.1

^{*a*} The methylaluminoxane solvent was removed from a 20% solution in toluene at 25 °C/10⁻⁶ Torr, toluene, RT, 4 h, 5 mmol of catalyst, 10 atm of olefin (kept constant having liquid propylene in excess). ^{*b*} Activity in g PP/mol cat \cdot h \cdot atm. ^{*c*} M_w/M_n .

 $M_{\rm w}$, beyond our measurements limits, >7 \times 10⁶ g/mol. All the other complexes were active in a similar way, producing in all cases high M_w polymers (>10⁶ g/mol) with unexpectedly very narrow polydispersities (MWD = 1.18-1.31). Although we have shown that bisamido group IV complexes can be used instead of similar dichloride complexes as the precursor for the catalytic polymerization of olefins,²⁸ in these systems the dichloride complexes are more active than the corresponding bisamido complexes. Moreover, the titanium complexes show better catalytic activities than the corresponding zirconium complexes regardless of the ligands. A very interesting result regards the polymerization with complex 6h. In the absence of MAO, no catalytic activity was observed. When reacted with MAO and a small amount of ethylene, the ESR signal for the Ti(III) disappears and polymer is obtained. We have recently disclosed that for some octahedral heteroallylic complexes in the presence of two cocatalysts in the polymerization of α -olefins, the first activation step is the reduction of the metal to the oxidation state M(III) by MAO (M = Ti, Zr). The addition of the olefin induced the oxidation of the metal and the formation of the active hydride species (for ethylene) after β -H elimination.²⁹ Hence, it is not strange that the activation of complex 6h will be somewhat lower than that of complex 6c; however the polymer formation will be expected to be comparable. Monitoring the polymerization over time for complex **6h** (entries 6, 7, and 8, Table 1) reveals a linear increase of M_n with increasing polymerization time. In a polymerization that proceeds in a living manner an increase of both the polymer weight and M_n is observed, whereas in a nonliving polymerization only an increase of the polymer weight is expected. Therefore, an increase of $M_{\rm n}$ over time in this case suggests that a certain percentage of the polymerization proceeds in a living manner. The percentage of living polymerization was calculated according to the formula presented in eq 1 $(n_1$ is the moles of living species and n_{cat} is the moles of catalyst).

% of living polymerization =
$$(n_1 100)/n_{cat}$$
 (1)

Number of moles of living species, n_i , was isolated from eq 2 (where *t* is the polymerization time, R_i is the rate of monomer

insertion, and M_n is the number-average molecular weight; t = 20 h was taken for $t \rightarrow \infty$). These calculations showed that at 25 °C about 70% of the polymerization is living.³⁰

$$M_{\rm n} = {\rm MW}_{\rm monomer} t R_{\rm i} / (n_1 + ({\rm MW}_{\rm monomer} t R_{\rm i}) / M_{n(t \to \infty)})$$
(2)

When the complexes were used for the polymerization of propylene, an elastomeric polypropylene was obtained (Table 2). Complexes **6d**, **6e**, and **6f** produced only trace amounts of the polymer, low activities were obtained by complex **6c**, and the best catalytic activities were observed for complex **6h**.

¹³C NMR spectra of polypropylene prepared with complex **6c** or **6h** were determined in 1,2,4-trichlorobenzene/DMSO- d_6 at 135 °C, exhibiting signals at 15.0, 17.1, 30.8, and 35.1 ppm, characteristic of isolated 2,1 mis-insertion units. Since no vinylidene or vinyl chain end groups were observed in the ¹H or ¹³C NMR, presumably due to the higher molecular weight, we decided to study the effect of MAO.³¹ Hence, for both complexes 6c and 6h, when the polymerization was carried with a larger amount of MAO (MAO:complex = 1600, instead of 400), a faster reaction was achieved and the polymers obtained were characterized to have a lower molecular weight and a much higher polydispersity. For the polymer obtained with complexes 6c and 6h (entries 2 and 4, Table 2), no chain end besides an isobutyl group was observed in the NMR, indicating that with this catalyst chain transfer to MAO seems to be the main operative termination mechanism, and the presence of larger amounts of MAO not only reduces the polymer molecular weights but induces the formation of various types of active sites, resulting in large molecular weight distributions.

Conclusions

Nowadays there is a major effort in the search for nonmetallocene complexes that can be active for the polymerization

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of olefins. The synthetic approach to the general family of complexes containing the imidodithiodiphosphinate ancillary ligands was introduced. These complexes are isolobal with the β -diketiminate or the acetylacetonate complexes and hence expected to show remarkable properties as to their reactivities. We have shown that the imidodithiodiphosphinate ligand can be incorporated with group 4 metal complexes. The chloride complexes were difficult to work with since low solubility/ oligomeric species are formed. However the corresponding bis(amido) complexes were monomeric in solution. Moreover, the reactivity of the titanium complex 6e is unique since upon heating it forms the corresponding imido complex. The use of such complexes for the hydroamination of secondary amines is under investigation. The formation of the homoleptic complex Ti(III) (6h) via the disproportionation of complex 6e is fascinating, describing the high reactivity of these complexes due to the induced coordinative unsaturation acquired by opening the Ti-S bonds. The catalytic ability of these complexes, upon their activation with MAO, in the polymerization of ethylene and propylene is described. For ethylene, high molecular weight and monodisperse polymers were attained, whereas for propylene, the larger the amount of MAO used, the larger the polydispersity and the lower the molecular weight of the polymers obtained. In addition, the X-ray solid state diffraction study of four different complexes was presented.

Experimental Section

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenktype glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10⁻⁵ Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1-5)ppm O₂). Argon, ethylene, propylene, and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4 Å activated molecular sieve column. Ether solvents were distilled over argon from sodium benzophenone ketyl. Hydrocarbon solvents (toluene, C₆D₆, hexane, THF-d₈) were distilled over Na/K alloy. All solvents for vacuum line manipulation were stored under vacuum over Na/K alloy in resealable bulbs. NMR spectra were recorded on Bruker AM 200 and AM 400 spectrometers. Chemical shifts for ¹H, ¹³C, and ³¹P NMR were referenced to internal solvent resonances and are reported relative to TMS and 85% H₃PO₄. NMR experiments were conducted on Teflon valve-sealed tubes (J-Young) after vacuum transfer of the solvent in a high-vacuum line. The polypropylene NMR experiments were conducted in 1,2,4-trichlorobenzene at 135 °C with DMSO-d₆ as external standard and when possible in CDCl₃ at room temperature. ESR spectra were recorded on a Bruker EMX-10/12 X-band ($\nu = 9.4$ GHz) digital ESR spectrometer equipped with Bruker N2-temperature controller. All spectra were recorded at microwave power 10-1 mW, with 100 kHz magnetic field modulation of 1.0-0.5 G amplitude. Digital field resolution was 2048 points per spectrum, allowing all hyperfine splitting to be measured directly with accuracy better than 0.2 G. EI mass spectra were recorded on a Finnigan TSQ-70B mass spectrometer using fresh distilled dry THF as solvent. Melting points of complexes were measured in nitrogen-sealed capillaries and are uncorrected. Melting points of the polymers were measured by DSC (Polymer Laboratories, UK) from the second heating thermogram (heating rate = 5 $^{\circ}$ C/min). Molecular weights of polymers were determined by the GPC method on the Waters-Alliance 2000 instrument using 1,2,4-trichlorobenzene as a mobile phase at 160 °C. Polystyrene standards were used for the standard calibration curve of the GPC. Elemental analysis was performed by the microanalytical laboratory at the Hebrew University of Jerusalem. ZrCl₄ (Aldrich) was sublimed twice (150 °C, 10^{-5} Torr) before use. All other reagents were purchased from Aldrich and Fluka and used without further purification unless otherwise stated. $(Ph_2PS)_2NH$,³² Ti[N(CH₂CH₃)₂]₄,³³ and Zr[N(CH₂CH₃)₂]₄³⁴ were prepared by literature procedures.

(**Ph₂PS**)₂**NLi** • **2THF** (**6b**). *n*-BuLi (1.6 M) in hexane (9.5 mL, 15.2 mmol) was added dropwise via a gastight syringe during 5 min to a stirred solution of $(Ph_2PS)_2NH$ (6.25 g, 13.9 mmol) in THF (50 mL) under an argon flow at 0 °C. The mixture was allowed to warm slowly to room temperature and stirred overnight under inert conditions. The solvent was then removed under vacuum, and the obtained solid was washed three times with hexane, affording a white powder. Yield: 7.85 g (94%). Mp: 158 °C (dec, 167 °C).³⁵ ¹H NMR was identical to that reported in the literature.³¹ Recrystallization of **6b** from THF (-35 °C) gave crystals suitable for X-ray.

 $[(Ph_2PS)_2N]_2TiCl_2$ (6c). TiCl₄ (102 μ L, 0.93 mmol) was added via a gastight syringe to a 15 mL toluene suspension of 6b (1.11 g, 1.85 mmol) under argon at -50 °C. After the addition, the color of the reaction mixture changed to brown-red and all ligand 6b dissolved immediately. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight under argon. The volume of the mixture was reduced to half via a vacuum pump, inducing the precipitation of a brown-red material. Filtering the solids via a swivel frit followed by washing with 3×20 mL of toluene afforded 0.93 g (91%) of complex 6c. Mp: 173-175 °C. Anal. Calc for $C_{48}H_{40}N_2Cl_2P_4S_4Ti \cdot 2LiCl: C, 52.69; H, 3.96; N,$ 2.54; Cl, 12.89. Found: C, 52.93; H, 4.38; N, 2.35; Cl, 12.59. ¹H NMR (THF-*d*₈, 25 °C, 400 MHz) δ: 7.3 (m, 24H, *o*-, *p*-*H*), 8.0 (m, 16H, *m*-H). ³¹P{H} NMR (THF-*d*₈, 25 °C, 160 MHz) δ: 41.5. EI-MS (THF): 965, 964, 963, 961 (M⁺ -2Cl + OH), 955, 954, 912, 898, 851, 819, 695, 681, 680, 663, 649, 648, 512, 511, 510, 449 (free ligand, $(Ph_2PS)_2NH$, base peak), 416 ($(Ph_2PS)_2NH - HS$).

[(Ph₂PS)₂N]₂ZrCl₂ (6d). 6b (1.19 g, 2.0 mmol) was added via a solid addition tube to a stirred solution of 0.224 g (1.0 mmol) of ZrCl₄ in 15 mL of THF under argon at room temperature. Stirring was continued for 24 h. THF was removed under vacuum. Washing the residue three times with hexane afforded a white powder, mp 229 °C (dec). Yield: 1.15 g (89%). Anal. Calc for C₆₄H₇₂N₂Cl₂-O₄P₄S₄Zr • 2LiCl • 4THF: C, 53.67; H, 5.07; N, 1.95; Cl, 9.90. Found: C, 53.63; H, 5.48; N, 2.09; Cl, 9.76. ¹H NMR (C₆D₆, 25 °C, 400 MHz) δ: 6.9 (m, 24H, *o*-, *p*-H), 8.4 (m, 16H, *m*-H); THF signals 3.54 (t, 16H), 1.31 (t, 16H). ³¹P{H} NMR (THF-*d*₈, 25 °C, 160 MHz) δ: 43.9.

[(Ph₂PS)₂N]₂Ti[N(CH₂CH₃)₂]₂ (6e). Ti[N(CH₂CH₃)₂]₄ (0.88 g, 2.62 mmol) was added via a gastight syringe to 20 mL of a toluene suspension containing 2.35 g (5.23 mmol) of 6a under argon at 0 °C (water/ice bath). The color of the reaction mixture changed to brown immediately, and 6a was dissolved. The mixture was allowed to warm to room temperature and stirring was continued overnight. The toluene was removed under vacuum, and the solids were washed 3×30 mL with hexane, affording a brown-red powder, mp 79 °C (dec). Yield: 2.08 g (73%). Anal. Calc for C₅₆H₆₀N₄-P₄S₄Ti: C, 61.76; H, 5.55; N, 5.14. Found: C, 61.39; H, 5.60; N, 4.94. ¹H NMR (THF-*d*₈, 25 °C, 400 MHz) δ: 0.79 (t, 12H, CH₃, J = 6.8 Hz), 3.83 (q, 8H, CH₂, J = 6.8 Hz), 7.2 (m, 24H, o-, p-H), 7.8 (m, 16H, *m*-H). ¹³C{H} NMR (THF-*d*₈, 25 °C, 100.576 MHz) δ: 142.36, 140.18, 133.87, 133.14, 131.80, 131.55, 129.25, 129.13 (aromatic C), 13.86 (CH₃), 49.55 (CH₂). ³¹P{H} NMR (THF-d₈, 25 °C, 160 MHz) δ: 39.9. EI-MS: 962, 960, 955, 954, 912, 898, 851, 819, 695, 681, 680, 663, 649, 648, 512, 511, 510, 449 (free ligand, $(Ph_2PS)_2NH$, base peak), 416 ($(Ph_2PS)_2NH - HS$).

 $[(Ph_2PS)_2N]_2Zr[N(CH_2CH_3)_2]_2 (6f). Zr[N(CH_2CH_3)_2]_4 (1.1 g, 2.9 mmol) was added via a gastight syringe to 12 mL of a toluene$

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suspension of 6a (2.37 g, 5.3 mmol) under argon at room temperature (water bath). The color of the reaction mixture changed to orange immediately and 6a was fully dissolved. The reaction mixture was heated to reflux and stirred for 12 h. After cooling the reaction mixture to room temperature, 10 mL of hexane was added. Yellowish crystals suitable for X-ray were obtained after a day when the solution stood at room temperature. The solvents were filtered and the resulting crystals were washed three times \times 20 mL of hexane. The crystalline material was dried under vacuum to afford 2.65 g (89%) of yellow plate crystals. Mp: 91-93 °C. Anal. Calc for C₅₆H₆₀N₄P₄S₄Zr: C, 59.39; H, 5.34; N, 4.95. Found: C, 59.18; H, 5.64; N, 4.55. ¹H NMR (THF-d₈, 25 °C, 400 MHz) δ: 0.79 (t, 12H, CH_3 , J = 6.9 Hz), 3.38 (q, 8H, CH_2 , J = 6.9 Hz), 7.2 (m, 24H, o-, p-H), 7.8 (m, 16H, m-H). ¹³C{H} NMR (THF-d₈, 25 °C, 100.576 MHz) &: 13.93 (CH₃), 44.39 (CH₂), 129.19, 129.46, 131.77, 132.97, 133.19, 139.71, 141.90 (aromatic C). ³¹P{H} NMR (THFd₈, 25 °C, 160 MHz) δ: 41.8. EI-MS (toluene): 982, 981 ([(Ph₂PS)₂N]₂ZrN(CH₂CH₃)₂ -Ph), 953, 952 ([(Ph₂PS)₂N]₂ZrNCH₂-CH₃ -Ph), 449 (free ligand, (Ph₂PS)₂NH, base peak). 416 $((Ph_2PS)_2NH - HS).$

 $[(Ph_2PS)_2N]_2Ti=N(CH_2CH_3)_2$ (6g) and $[(Ph_2PS)_2N]_3Ti$ (6h). Ti[N(CH₂CH₃)₂]₄ (0.88 g, 2.62 mmol) was added via a gastight syringe to 20 mL of a toluene suspension containing 2.35 g (5.23 mmol) of the ligand 6a, under argon at room temperature. The mixture was heated to reflux under argon and stirred for 19 h. Toluene was removed under vacuum, and the solids were washed three times with 20 mL of hexane in a swivel frit to afford 1.8 g (70%) of brown powder of 6g. Mp: 127 °C (dec). Anal. Calc for C₅₀H₄₅N₃P₄S₄Ti: C, 60.79; H, 4.59; N, 4.25. Found: C, 60.45; H, 5.35; N, 4.00. ¹H NMR (THF-*d*₈, 25 °C, 400 MHz) δ: 0.81 (t, 3H, CH_3 , J = 6.9 Hz), 3.85 (q, 2H, CH_2 , J = 6.9 Hz), 7.25 (m, 24H, o-, p-H), 7.84 (m, 16H, m-H). ¹³C{H} NMR (THF-d₈, 25 °C, 100.576 MHz) δ: 16.11 (CH₃), 57.60 (CH₂), 142.15, 140.01, 133.84, 133.20, 131.78, 131.67, 129.22, 129.10 (aromatic C). ³¹P{H} NMR (THF- d_8 , 25 °C, 160 MHz) δ : 39.8. EI-MS (toluene): 1296 (M⁺-3S), 963, 962, 961 (M^+ – CH₂CH₃), 955, 954, 912, 898, 897, 851, 819, 695, 681, 680, 663, 649, 648, 512, 511, 510, 449 (free ligand, (Ph₂PS)₂NH, base peak), 416 ((Ph₂PS)₂NH - HS). Recrystallization of the powder from 20 mL of a 1:1 toluene/hexane mixture (-38 °C) gave fine red needle crystals of 6g suitable for X-ray studies.

After the crystallization of complex **6g** was completed, the crystallization of the remaining solid with hexane at -45 °C yielded dark green crystals in small amounts, 0.03 g, of complex **6h**.

 $[(Ph_2PS)_2N]_3Ti$ (6h). Ti(Cl₃)(THF)₃ (0.6 g, 1.61 mmol) in 20 mL of THF was added via a gastight syringe to 20 mL of a THF solution containing 3.40 g (5.56 mmol) of the ligand 6b, under argon at -45 °C. The reaction was heated to reflux for 72 h and the solvent evacuated through a high-vacuum line. The reaction mixture was dissolved in toluene, filtered, and dried to separate the insoluble LiCl. Crystallization of complex 6h in hexane at -45 °C yielded dark green crystals, 1.6 g (67%).

Mp: 154 °C (dec). Anal. Calc for $C_{72}H_{60}N_3P_6S_6Ti$: C, 62.06; H, 4.34; N, 3.02. Found: C, 61.75; H, 3.99; N, 3.32. EI-MS (toluene): 1392 (M⁺), 976, 559, 449 (free ligand, (Ph₂PS)₂NH, base peak), 416 ((Ph₂PS)₂NH - HS). ESR measurements show a single line centered at g = 1.976 at 298 K.

Ethylene Polymerization. Ethylene polymerization was carried out in a 35 mL stainless steel autoclave equipped inside with a 26 mL glass container and a magnetic stirring bar. In the glovebox, the reactor was charged with a catalyst (typically, 5 mg) and a specific amount of MAO. The reactor was connected to a Schlenk line, and 8 mL of dry toluene was quickly added via syringe in an argon flow. After stirring for 1 h at room temperature (preactivation), a certain amount of ethylene was inserted into the reactor,

resulting in an appropriate pressure of the mixture. During the polymerization the decreased pressure showed in a manometer and a solenoid valve inserts ethylene to maintain the starting pressure ($\Delta P = 2$ atm). After a measured amount of time the reaction reactor is released of the excess of ethylene in a well-ventilated hood, and the reaction mixture is quenched adding a methanol/HCl mixture (9:1). The polymer product was collected by filtration and washed with methanol, water, and acetone. The polymer was dried under vacuum (10⁻⁵ Torr) at 65 °C for 24 h or until constant weight was obtained.

Propylene Polymerization. A 100 mL heavy wall glass reactor with a magnetic stirring bar was charged with 5 mg of the corresponding catalyst and a specific amount of MAO in the glovebox. The reactor was connected to a Schlenk line, and 5 mL of dry solvent was quickly added via a gastight syringe in an argon flow. After stirring the mixture for 1 h at room temperature, it was inserted into a liquid nitrogen bath and propylene was condensed into the reactor after been condensed in a measured container kept at liquid nitrogen temperature. The temperature of the reactor was rapidly raised and equilibrated through a thermostatted bath. The reaction was stirred vigorously, and after a measured amount of time the reactor was opened in a well-ventilated hood to exhaust any excess of propylene gas followed by the addition of a methanol/ HCl mixture. The polymer was then washed with methanol, water, and acetone. The resulting polymer was dried under vacuum (10^{-5}) Torr) at 65 °C for 24 h or until constant weight.

Characterization of the Polymers. NMR spectra of the polymers were conducted in deuterated tetrachlorethane at 85 °C and recorded on a Bruker Avance 500 MHz spectrometer. Chemical shifts for ¹H and ¹³C NMR were referenced to internal solvent resonances and reported relative to SiMe₄.

X-ray Crystallographic Measurements. The single-crystalline material was immersed in Paratone-N oil and was quickly fished with a capillary tube and mounted on the Kappa CCD diffractometer under a cold stream of nitrogen at 200 K. Data collection was performed using monochromatized Mo K α radiation using omega and phi scans to cover the Ewald sphere.³⁶ Accurate cell parameters were obtained with the number of indicated reflections.^{30,37} The structure was solved by SHELXS97 direct methods³⁸ and refined by the SHELXL97 program package.³⁹ The atoms were refined anisotropically. Hydrogens were included using the riding mode. Software used for molecular graphics: ORTEP, TEXRAY Structure Analysis package.⁴⁰

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Supporting Information Available: Derivation of eq 2. Crystallographic data and structure refinement details for complexes **6b**, **6f**, **6g**, and **6h**. Cif files for the characterization of compounds **6b**, **6f**, **6g**, and **6h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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