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Titanium Complexes Bearing a Hemilabile Heteroscorpionate Ligand: Synthesis, Reactivity, and Olefin Polymerization Activity

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A series of titanium complexes (*bpzmp*)$TiR^1R^2R^3$ (*bpzmp* = (3,5-$^tBu_2$-2-phenoxo)bis(3,5-Me_2-pyrazol-1-yl)methane; $R^1 = R^2 = R^3 = Cl$ (**2**); $R^1 = R^2 = R^3 = NMe_2$ (**3**); $R^1 = Cl$; $R^2 = R^3 = NMe_2$ (**4**); $R^1 = R^2 = Cl$; $R^3 = NMe_2$ (**5**); $R^1 = R^2 = R^3 = Me$ (**6**)) has been synthesized and characterized by VT NMR spectroscopy and X-ray diffraction analysis (**2**, **3**, **5**). The complexes **2**−**6** adopt in the solid state an octahedral structure in which the *bpzmp* ligand is κ^3-coordinated to the metal via the phenoxy group and the imino nitrogens of the two pyrazolyl rings. The investigation of the solution structure of **3** by means of VT ^1H NMR spectroscopy revealed a fluxional behavior of the *bpzmp* ligand that produces an equilibrium between the octahedral and tetrahedral form of the titanium complex, the latter resulting from the η^1-coordination of the ligand through exclusively the phenolate group. The thermodynamic and kinetic parameters of this process were evaluated by VT NMR spectroscopy. The selective replacement of chloride for dimethylamide in **4** and **5** shifts the equilibrium toward the octahedral complex, which is the favorite configuration at room temperature. Site exchange of the nonequivalent methyl groups in **6** was observed at room temperature in the slow-regime ^1H NMR time scale: $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of 22.3 ± 1.1 $kcal{\cdot}mol^{-1}$ and -19.6 ± 3.7 cal mol^{-1} K^{-1} were respectively determined for the isomerization process occurring with a rate constant of 3 s^{-1} and $\Delta G^\ddagger$ of 28.1 ± 0.1 $kcal{\cdot}mol^{-1}$ at 293 K. Complexes **2** and **6** are active olefin polymerization catalysts after activation with MAO or $[Ph_3C][B(C_6F_5)_4]$. Linear polyethylene and atactic polypropylene were obtained in the polymerization experiments catalyzed by **6**-$[Ph_3C][B(C_6F_5)_4]$. Highest polymerization activities were found with the **2**-MAO catalyst, where leaching of the ligand due to MAO excess was suspected. Reaction of **6** with $[Ph_3C][B(C_6F_5)_4]$ in the presence of THF readily produces the ionic complex [(*bpzmp*)$TiMe_2$(THF)]$[B(C_6F_5)_4]$, proposed as a model of the active species in this class of olefin polymerization catalysts.

Introduction

Olefin polymerization catalysis has been widely dominated in the past decades by group 4 metallocenes, which allow the synthesis of stereoregular poly-1-olefins with properties rivalling those of the polymers by classical heterogeneous Ziegler−Natta catalysts.[1] Recently research efforts have been produced to enlarge the typology of the ligands used in the coordination chemistry of the group 4 metals, opening the so-called postmetallocene era.[2] In this framework considerable attention has been paid to mono- and polydentate ligands bearing oxygen and nitrogen donors. These ligands are synthesized in a simple manner and modified by well-established synthetic procedures, yielding group 4 metal complexes with tunable electronic properties, flexible coordination geometry, and coordination number higher than four, typically found in metallocenes. Examples of these ligands include bis-phenoxy-imine,[3] amidinate,[4] and pyrazolylborate.[5] Some recent reports highlighted the olefin polymerization performances of titanium complexes of the tris(pyrazolyl)-borate ligand carrying sterically demanding substitu-

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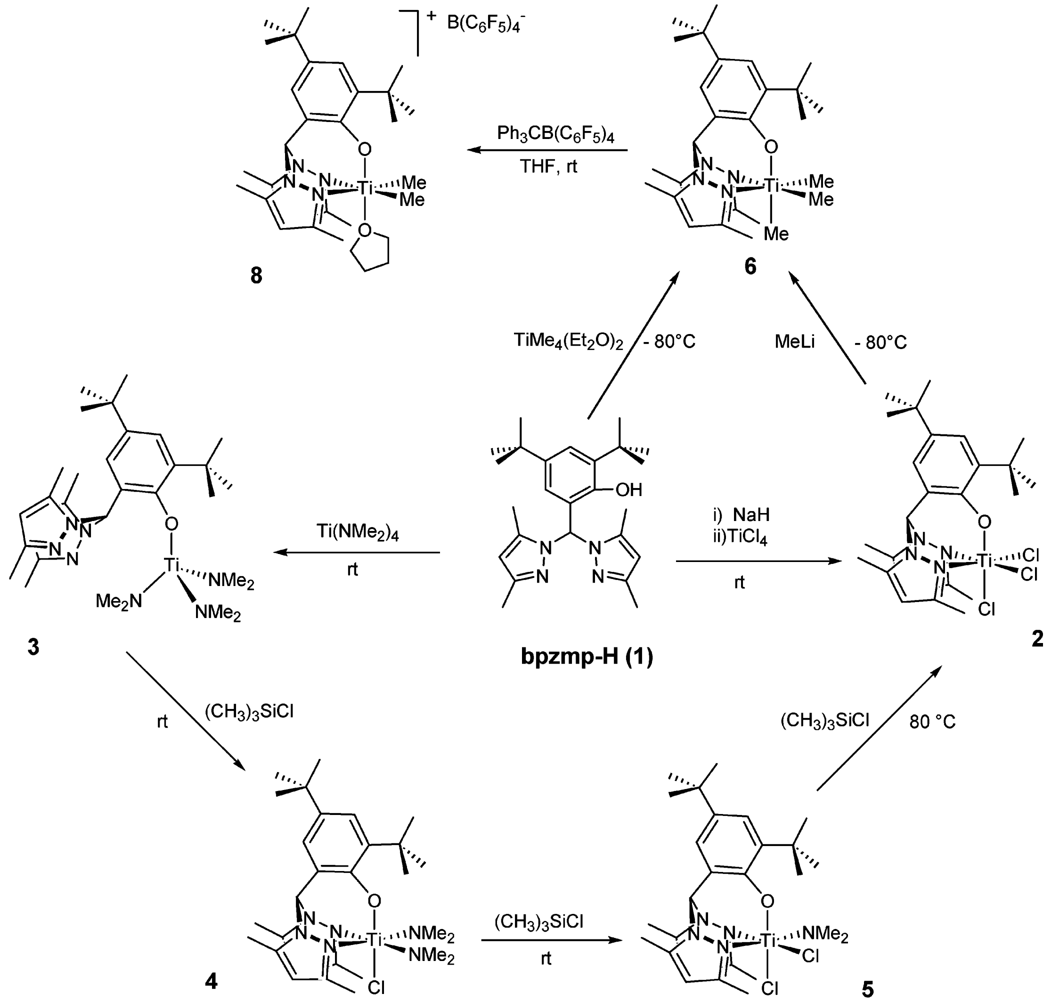
Scheme 1



ents in the 3,5-positions.[6] These ligands were expected to stabilize, better than cyclopentadienyl, the Ti(IV) metal center toward reduction to lower oxidation states after treatment with MAO excess.[6b]

When compared to titanocenes, the bis-phenoxy-imine titanium complexes exhibit a significant improvement: the corresponding MAO-activated polymerization catalysts show living properties in propene polymerization at room temperature, and olefin block copolymers with unprecedented architectures were successfully synthesized.[7] The syndiospecificity of the bis-phenoxy-imine titanium catalysts in propene polymerization was attributed to the chain end stereocontrol mediated by the fluxional behavior of the ligands, in turn controlled by the site chirality.[7a,b,8]

The use of polydentate ligands with fluxional coordination properties also permitted intriguing and novel reactivity patterns at the metal center.[9] The presence of a neutral pendant group, chemically linked to the cyclopentadienyl ligand, increased the thermal stability of the corresponding olefin polymerization catalysts.[9b] More remarkably, the coordination of a properly substituted aryl group switched the properties of (η^5-C_5H_4-CMe_2Ar)$TiCl_3$ (Ar = Ph, 3,5-$Me_2C_6H_3$) from an ethylene polymerization catalyst to a selective ethylene trimerization catalyst, and 1-hexene was thus selectively obtained under proper conditions.[10]

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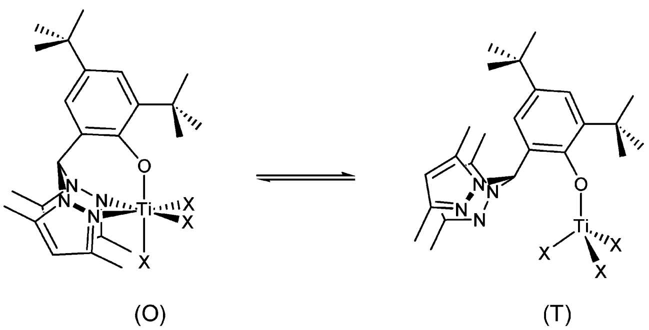
Scheme 2



The fluxionality of the ligand can also tune the electronic and steric properties of the metal center during the polymerization process and control the monomer incorporation in the growing polymer chain; thus interesting results could be expected in the field of olefin copolymerization with electron-rich monomers such as styrene and 1,3-conjugated dienes.

In this framework we explored the performances of the monoanionic tridentate heteroscorpionate ligand,[11] (3,5-^{t}Bu$_2$-2-phenoxo)bis(3,5-Me$_2$-pyrazol-1-yl)methane (*bpzmp*-H). A stable trialkyl zirconium derivative, (*bpzmp*)ZrBn$_3$, was synthesized and found active in ethylene polymerization after activation with $B(C_6F_5)_3$.[12] The polydispersity index of polyethylene samples was found to be temperature dependent with values approaching that of a single-site catalyst at −40 °C. Recently a titanium complex of the bis(3,5-dimethylpyrazol-1-yl)acetate (*bdmpza*) ligand was successfully synthesized by Otero et al. and found to be highly active in ethylene polymerization: unfortunately alkyl derivatives, modeling the active species, were not reported.[13]

Herein we describe the synthesis and solution properties of a series of heteroscorpionate titanium(IV) complexes of the *bpzmp* ligand as well as preliminary results on the performances of these catalysts in olefin polymerization.

Results and Discussion

1. Synthesis and Reactivity of the Complexes (*bpzmp*)TiR^{1}R^{2}R^3 (R^1 = R^2 = R^3 = Cl (2); R^1 = R^2 = R^3 = NMe$_2$ (3); R^1 = Cl; R^2 = R^3 = NMe$_2$ (4); R^1 = R^2 = Cl; R^3 = NMe$_2$ (5); R^1 = R^2 = R^3 = Me (6); R^1 = R^2 = Me; R^3 = THF (8)). The ligand *bpzmp*-H (**1**) was synthesized according to the literature[14] and the corresponding sodium salt prepared by reaction with NaH in toluene at room temperature. Treatment of a toluene solution of $TiCl_4$ with the sodium salt of **1** (Scheme 1) afforded (*bpzmp*)TiCl$_3$ (**2**) in good yield (61%). Crystallization of the crude product from dichloromethane/hexane gave **2** as a bright dark red microcrystalline solid, sparingly soluble in aromatic (toluene, benzene) and aliphatic (*n*-pentane, *n*-heptane) hydrocarbon solvents but soluble in polar solvents, such as dichloromethane and tetrahydrofuran. Complex **2** was thermally stable when exposed to the air in the solid state.

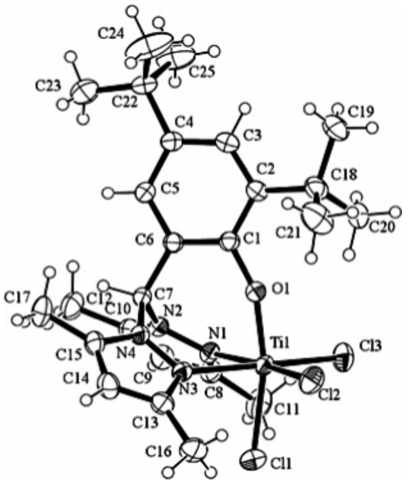


Figure 1. ORTEP diagram of the molecular structure of (*bpzmp*)TiCl$_3$ (**2**). Thermal ellipsoids are drawn at the 40% probability level.

The ^{1}H and ^{13}C NMR spectra of **2** are consistent with an octahedral C_s symmetric structure resulting from the κ^3-N,N,O coordination of the ligand to the metal center. Actually one set of ^{1}H NMR resonances, downfield shifted from those of the free ligand, was observed for the pyrazolyl protons. The ^{1}H−^{1}H NOESY experiments permitted the univocal attribution of the ^{1}H resonances, in particular those of the methyls of the pyrazolyl groups and of the *t*-Bu groups of the phenoxy ring. The chemical shift of the methine proton of the *bpzmp* bridge was a good probe for the assessment of the ligand coordination. When *bpzmp* is κ^3-coordinated to the metal, the methine ^{1}H signal is upfield shifted from 7.5 ppm, whereas it is found downfield shifted from this values for the ligand exhibiting η^1-coordination (vide infra). Upon warming of a 1,1,2,2-tetrachloroethane-d_2 solution of **2** up to 373 K, no broadening of the proton resonances was observed, in agreement with the high coordination energy of the ligand to the metal and the lack of any in−out fluxional equilibrium of the two *N,N* donors (Scheme 2).

Crystals of **2** were grown from a dichloromethane/hexane solution: the molecular structure, determined by X-ray diffraction, is in fine agreement with the solution structure observed in the NMR experiments. The ORTEP[15] view of complexes **2** is shown in Figure 1, and crystallographic data and selected interatomic distances and angles are given in Tables 1 and 2. The titanium geometry is distorted octahedral in which the heteroscorpionate ligand is coordinated via the two nitrogens of the pyrazole rings and the oxygen of the phenolate group, and three chlorine atoms occupy the other three sites of the octahedron. The Ti−Cl bond lengths in the *N,N* plane, namely, 2.278(1) and 2.290(1) Å, are shorter than Ti−Cl1 (2.332(1) Å); the former values are very similar to those observed in the pseudo-

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Table 1. Experimental Data for the Crystal Structure Determination of (*bpzmp*)TiCl$_3$ (2), (*bpzmp*)Ti(NMe$_2$)$_3$ (3), and (*bpzmp*)Ti(NMe$_2$)Cl$_2$ (5)

	2	**3**	**5**
formula	$C_{25}H_{35}Cl_3N_4OTi$	$C_{31}H_{53}N_7OTi\cdot 1/2(C_6H_{14})$	$C_{27}H_{41}Cl_2N_5OTi\cdot C_7H_8$
M	561.82	630.79	662.58
system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a/Å	11.6958(2)	10.7759(2)	12.8927(2)
b/Å	18.5980(3)	13.7408(3)	17.6351(3)
c/Å	13.0171(2)	14.4792(3)	16.4832(3)
α/deg	90	108.529(1)	90
β/deg	96.706(1)	107.328(1)	94.777(1)
γ/deg	90	103.069(1)	90
U/Å^3	2812.09(8)	1814.58(6)	3734.7(1)
Z	4	2	4
D_c/g cm^{-3}	1.327	1.154	1.178
μ/cm^{-1}	6.14	2.71	4.04
T/K	295	100	295
$\theta_{min}-\theta_{max}$/deg	3.7−30.0	2.1−30.0	3.0−28.0
unique reflns	8086	10 303	8961
R_{int}	0.037	0.054	0.044
obs. reflns [$I > 2\sigma(I)$]	5766	7818	6120
R (obsd reflns)	0.0468	0.0464	0.0545
wR_w (all reflns)	0.1258	0.1188	0.1629
S	1.03	1.03	1.04
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e Å^{-3}	0.65; −0.35	0.51; −0.45	0.48;−0.35

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 2, 3, and 5

	2	**3**	**5**
Ti1−Cl1	2.332(1)		2.376(1)
Ti1−Cl2	2.278(1)		2.337(1)
Ti1−Cl3	2.290(1)		
Ti1−O1	1.798(1)	1.986(1)	1.840(2)
Ti1−N1	2.248(2)	2.387(2)	2.211(2)
Ti1−N3	2.204(2)	2.398(1)	2.323(2)
Ti1−N5		1.965(2)	1.923(2)
Ti1−N6		1.954(2)	
Ti1−N7		1.944(1)	
Cl1−Ti1−Cl2	95.01(2)		91.76(3)
Cl1−Ti1−Cl3	93.19(2)		
Cl1−Ti1−O1	166.13(5)		166.01(5)
Cl1−Ti1−N1	83.74(4)		85.26(5)
Cl1−Ti1−N3	85.34(5)		83.80(5)
Cl1−Ti1−N5			95.18(7)
Cl2−Ti1−Cl3	95.06(2)		
Cl2−Ti1−O1	94.85(4)		95.53(5)
Cl2−Ti1−N1	173.99(5)		171.36(6)
Cl2−Ti1−N3	93.20(5)		92.65(5)
Cl2−Ti1−N5			95.72(7)
Cl3−Ti1−O1	95.63(5)		
Cl3−Ti1−N1	90.89(5)		
Cl3−Ti1−N3	171.71(5)		
O1−Ti1−N1	85.44(6)	74.86(5)	85.80(7)
O1−Ti1−N3	84.39(6)	85.51(5)	83.95(7)
N1−Ti1−N3	80.85(6)	77.54(5)	78.98(7)
O1−Ti1−N5		159.44(6)	95.95(8)
O1−Ti1−N6		91.95(6)	
O1−Ti1−N7		99.61(6)	
N1−Ti1−N5		86.39(6)	92.63(9)
N1−Ti1−N6		161.18(6)	
N1−Ti1−N7		101.17(6)	
N3−Ti1−N5		82.22(6)	171.60(8)
N3−Ti1−N6		88.26(5)	
N3−Ti1−N7		174.26(6)	
N5−Ti1−N6		104.05(7)	
N5−Ti1−N7		92.13(7)	
N6−Ti1−N7		94.14(6)	
Ti1−O1−C1	154.8(1)	149.0(1)	154.7(1)
Ti1−N1−N2	120.4(1)	123.1(1)	122.0(2)
Ti1−N1−C8	133.8(1)	132.0(1)	132.8(3)
Ti1−N3−N4	120.6(1)	122.8(1)	119.9(1)
Ti1−N3−C13	133.4(1)	128.8(1)	135.2(2)
N2−C7−N4	110.3(2)	110.2(1)	111.1(2)

octahedral structure of the hydrido-tris(pyrazol-1-yl)-borate titanium trichloride complex in which the chlorine atoms are *trans* to the pyrazolyl nitrogens.[16] The Ti1−Cl1 lengthening was ascribed to a *trans* effect[17] of the phenolate oxygen that is stronger than that produced by the neutral pyrazolyl nitrogens. The C-substituted pyrazolyl groups coordinated to the titanium atom form six-membered rings, N1−N2−C7−N4−N3−Ti1, in boat conformation.

We attempted the synthesis of the amido derivatives in order to get access to a wider family of heteroscorpionate titanium complexes. Treatment of a toluene solution of Ti(NMe$_2$)$_4$ with **1** affords the triamido derivative (*bpzmp*)Ti(NMe$_2$)$_3$ (**3**) (Scheme 1) in good yield (62%).[18] ^{1}H NMR monitoring of the reaction in a NMR tube showed that this is fast and quantitative in a few minutes. Complex **3** is very soluble in hexane, and crystals suitable for X-ray analysis were grown from this solvent at 253 K. The molecular structure of **3** (Figure 2) is very similar to that found for **2**; the only difference is the very strong *trans* effect exerted by the dimethylamido ligand, which produces bond lengths for Ti−N1 and Ti−N3 (2.39 Å on average) and for Ti−O(phenolate) [1.986(1) Å in **3** vs 1.798(1) Å in **2**] longer than in **2**. The relative orientation of the three amido groups, approximately orthogonal to each other, fits with the optimal disposition and better overlap of the nitrogen lone pairs with the d metal orbitals suitable for the one-to-one metal(d)−NMe$_2$(p) π-bonding interaction.[19] The O−Ti−N1 angle observed in **3** is smaller than in **2**, likely as a result of the steric congestion between the −NMe$_2$ groups and the ^{t}Bu substituent of the phenolate group. Weaker interaction of the ligand with the metal

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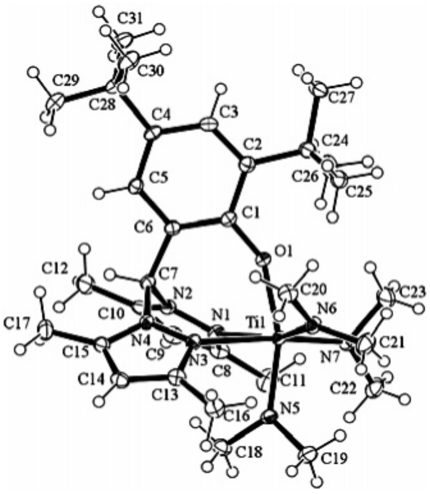

Figure 2. ORTEP diagram of the molecular structure of (*bpzmp*)Ti(NMe$_2$)$_3$ (**3**). Thermal ellipsoids are drawn at the 40% probability level.

center is thus expected, and an increased fluxional behavior of **3** in dichloromethane-d_2 solution was actually observed. In the room-temperature ^{1}H NMR spectrum, the pattern of the resonances is consistent with a C_s symmetric structure corresponding to the η^1 coordination of the ligand. Actually the methine ^{1}H signal is detected at 7.76 ppm as well as two singlets at 2.12 and 1.83 ppm for the four Me groups of the pyrazolyl rings and only one signal for the three NMe$_2$ groups at 3.06 ppm. Thus complex **3** adopts at room temperature a tetrahedral geometry with the heteroscorpionate ligand coordinated exclusively through the phenolate oxygen. The fast rotation of the amido groups about the Ti−N and Ti−O bonds produces the equivalence of the methyl groups of −NMe$_2$. The broadness of the ^{1}H singlets for the 5-pyrazolyl methyls, H^6 of the phenoxy ring, and the methine of the ligand bridge at 1.83, 6.54, and 7.76 ppm, respectively, suggests an equilibrium between the tetrahedral species (the most abundant) and a minor species in fast exchange regime in proton time scale at room temperature. Actually a new set of sharp resonances appeared in the ^{1}H NMR spectrum of **3** at 193 K, attributed to the octahedral form observed in the X-ray molecular structure. Indeed the methine resonance of the ligand bridge is now at 6.84 ppm (vs 7.62 ppm in the tetrahedral form at 193 K), the ^{t}Bu groups of the phenolate yield two singlets at 1.23 and 1.33 ppm, and the 3- and 5-pyrazolyl methyls are detected at 2.43 and 2.05 ppm, respectively. The octahedral and tetrahedral forms are in 7:3 molar ratio at 193 K. Noteworthy the NMe$_2$ protons still result as one singlet at 2.96 ppm, independently of their position in the octahedron. Although the kinetic constant $k_{\rm d}$ of the equilibrium reaction between the octahedral and tetrahedral forms at 193 K is small and yields sharp and well-resolved resonances for the two species, the kinetics of the intramolecular ligand exchange is so fast (on the NMR time scale) to produce a unique slightly broad ^{1}H resonance for the equatorial and axial amide groups.

Aiming to get a closer insight into the aforementioned fluxional behavior of the heteroscorpionate titanium complexes, particularly pronounced in the case of the triamide derivative, we attempted the synthesis of chloride-amide mixed coordination sphere compounds. Amide-halide exchange reaction is well documented in group 4 metal amide complexes: some representative examples are the reaction of CpTi(NMe$_2$)$_3$, Cp$_2$Zr(NMe$_2$)$_2$, or Cp$_2$Zr(NMe$_2$)$_2$ with MCl$_4$ (M = Si or Ge)[20] or Me$_3$SiCl[21] as a chlorinating reagent. Reaction of **3** with Me$_3$SiCl yielded the selective formation of the chloro derivatives **4** and **5** with varied reaction conditions. The addition of 1 equiv of Me$_3$SiCl to a benzene-d_6 solution of **3** turned the color from red-orange to dark red, and the selective and quantitative formation of (*bpzmp*)Ti(NMe$_2$)$_2$Cl (**4**) and Me$_3$SiNMe$_2$ (Scheme 1) was observed in 18 h. ^{1}H NMR analysis of the solution structure of **4** permitted the C_s symmetric structure to be identified in which the ligand is κ^3-*N,N,O*-coordinated to the titanium, the chloride atom is *trans* to the oxygen, and the four nitrogen atoms are in the equatorial plane. The methine of the ligand bridge was observed at 6.80 ppm, and the two pyrazolyl rings produce a unique symmetric ^{1}H pattern. The sharpness of the line width of the ^{1}H NMR signals suggests that the ligand dissociation does not occur in this case. When reaction of **3** with Me$_3$SiCl was monitored at room temperature by ^{1}H NMR spectroscopy, the 50% mol conversion of the reagents was observed in 10 min and two species, with C_s and C_1 symmetry, respectively, were detected in 3:2 molar ratio. The structural differences between the two isomers consist in the chloride placement that is *trans* to the nitrogen atom of the pyrazolyl ring in the C_1 isomer and *trans* to the oxygen atom of the phenoxy ring in the C_s form (see Scheme 3). The C_1 symmetric form exhibits two nonequivalent pyrazolyl rings: two ^{1}H signals were indeed observed for the H^4 of the pyrazolyl groups at 5.23 and 5.46 ppm, and the chemical shift for the methine of the ligand bridge at 6.75 ppm confirms the κ^3 coordination of the ligand to the metal. When the reaction mixture was left for 18 h at room temperature, the C_s isomer was detected pure and was the thermodynamically favored product of this reaction. Possibly the kinetic product displays the amide group *trans* to the oxygen atoms, but it is slowly converted to the more stable C_s symmetric isomer in which it is in the *N,N* plane. When **3** was treated at room temperature in benzene solution with a 3.5 equiv excess of Me$_3$SiCl, the selective and quantitative synthesis of the dichloride derivative (*bpzmp*)Ti(NMe$_2$)Cl$_2$ (**5**) (Scheme 1) was observed in 1 h. The excess of Me$_3$SiCl does not further react with **5**, even after 1 day at room temperature. The complex **5** is observed in the octahedral coordination environment, as indicated by the presence of one ^{1}H signal for the methine of the bridgehead at 6.77 ppm. Moreover the two pyrazolyl groups are not equivalent and produce two signals for the H^4 at 5.38 and 5.13 ppm, respectively. The C_1 stereoisomer did not convert to C_s in 24 h, suggesting that the former is the thermodynamically favored species. The molecular structure of **5** (Figure 3), determined by X-ray diffraction analysis, confirmed that both pyrazolyl ligands are coordinated to the metal in the solid state and the Ti−N3 bond length assumes an intermediate value between that observed in **2** and **3**. A consistent *trans* effect of the

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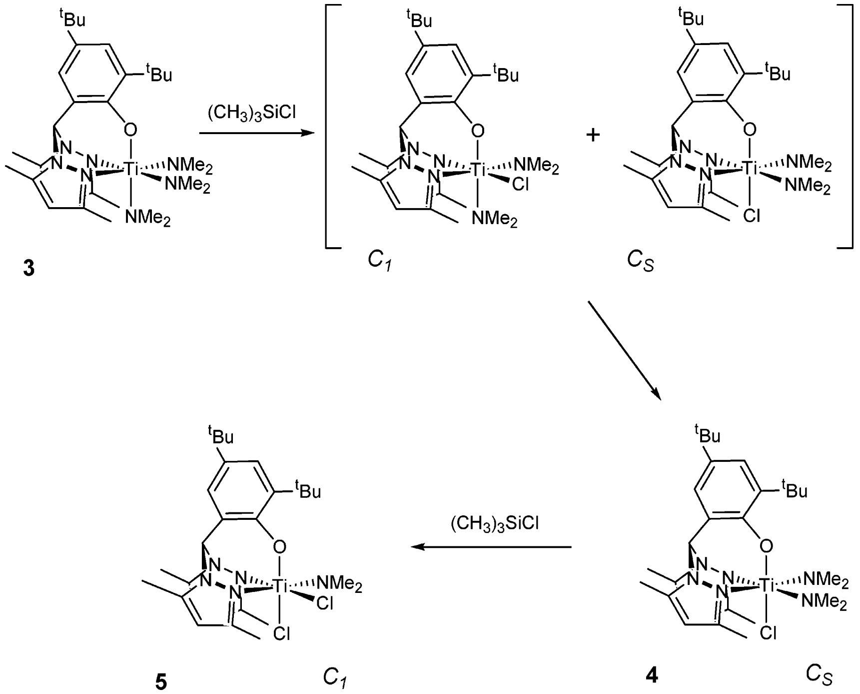
Scheme 3



amido ligand is well documented by the differences between the Ti−N1 (*trans* to chloride) and Ti−N3 (*trans* to the amido group) bond distances of 1.840(2) and 2.211(2) Å, respectively. Interestingly the Ti−N5 bond length is the shortest value observed for the amido groups in this class of heteroscopionate titanium complexes, suggesting a strong $d_\pi-p_\pi$ interaction of the lone pair of the amido group with the d orbitals of the metal. Finally, the chloro derivative **2** can be achieved by treatment of **3** with 3 equiv of Me_3SiCl at 353 K after 5 h in 1,1,2,2-tetrachloroethane-d_2.

Alkyl derivatives of hydrido-tris(pyrazol-1-yl)borate group 4 metal complexes are relatively rare,[22] and their presence in olefin polymerization processes is typically postulated in the reaction of the chloride, alkoxy, or amide derivatives with MAO. Aiming to explore the olefin polymerization catalysis promoted by the aforementioned titanium heteroscorpionates, we attempted the synthesis of alkyl derivatives. In situ alkylation of **3** with trialkylaluminum compounds as $AlMe_3$ or Al-^{i}Bu$_3$ were unsuccessful. The treatment of **2** with 3 equiv of methyllithium gave the expected methyl complex (*bpzmp*)$TiMe_3$ (**6**), as a crystalline yellow solid, in very low yield (10%). A black-green material was additionally obtained and attributed to side-products resulting from reduction of the Ti(IV) precursor to Ti species in lower oxidation state. Actually the ^{1}H NMR spectrum of the green mixture in benzene exhibited only very broad featureless resonances. On the contrary the one-pot synthesis of in situ preformed $TiMe_4(Et_2O)_2$ with **1** via alkane elimination was successful. The methyl complex was synthesized by metathesis of $TiCl_4$ with MeLi at 193 K in diethyl ether[23] and in situ treated with 1 equiv of **1** at this temperature. Under this condition the methyl complex **6** was isolated in higher yield (28%). Twinned crystals not suitable for a single-crystal X-ray diffraction analysis were grown from cold hexane. However the solution structure of **6** was definitively assessed by ^{1}H NMR, ^{13}C NMR, and gHMQC experiments and found corresponding to the C_s symmetric structure in which the heteroscorpionate ligand κ^3-*N,N,O*-coordinated to the metal. Actually one set of resonances are observed for the two pyrazolyl rings, and the methine signal of the ligand is observed at 7.04 ppm. The sharpness of the ^{1}H signals suggests an elevated coordination energy of the ligand to the metal center and the absence of any fluxional equilibrium of the two *N,N* donors at room temperature. A comparable thermal stability of the solution structure was previously observed for the heteroscorpionate trialkylzirconium complex (*bpzmp*)$Zr(CH_2Ph)_3$.[12] Noteworthy, the Ti-Me groups produce two broad singlets at 1.78 and 1.55 ppm in 1:2 molar ratio, respectively, attributed to the methyl group *trans* to the oxygen atom and to the nitrogen atoms, respectively. EXSY experiments revealed a site-exchange reaction between the nonequivalent methyl groups of the octahedral complex in the temperature range 303−333 K (see below for more details).

Heating a 1,1,2,2-tetrachloroethane-d_2 solution of **6** at 353 K produces in a few minutes the selective formation of **2**. The concomitant formation of methane detected by the presence of a ^{1}H resonance at 0.26 ppm suggests a radical mechanism as a possible pathway for this decomposition reaction.

Compound **6** was not reactive with **1** or sterically hindered phenols such as 2,6-di-^{t}Bu-4-Me-1-phenol (BHT). The ^{1}H NMR spectrum of a mixture of **6** with 1 equiv of BHT or **1** remained unchanged also after 24 h at room temperature. A similar behavior was previously observed for the tribenzyl heteroscorpionate zirconium complex and assumed as a result of the relative bulki-

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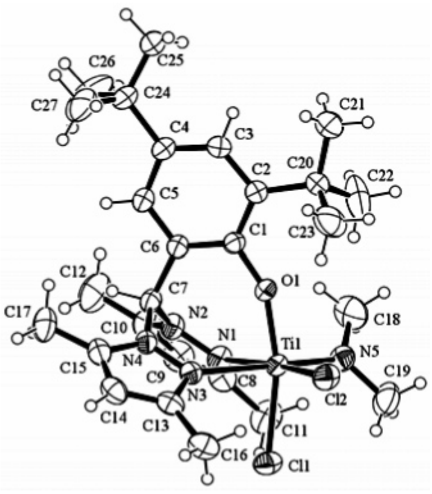

Figure 3. ORTEP diagram of the molecular structure of (*bpzmp*)Ti(NMe$_2$)Cl$_2$ (**5**). Thermal ellipsoids are drawn at the 40% probability level.

ness of the ligand and complex.[12] On the contrary, Tp*TiCl$_3$ was reactive with 1.5 equiv of 2-^{t}Bu-phenol at room temperature in dichloromethane in the presence of triethylamine, and the expected monophenoxo dichloro derivative was isolated from the reaction mixture.[6]

The generation of the cationic heteroscorpionate dimethyl titanium complex was attempted by reacting complex **6** with 1 equiv of $[PhC_3]^+[B(C_6F_5)_4]^-$ in benzene. The expected ionic species $[(bpzmp)TiMe_2]^+[B(C_6F_5)_4]^-$ (**7**) precipitated as a red oil in the NMR tube and was analyzed after dissolution in chlorobenzene-d_5. The ^{1}H NMR spectrum exhibits a ^{1}H signal at 2.14 ppm for the two equivalent Ti-Me groups, downfield shifted from the neutral complex **6** (1.78 and 1.55 ppm), and a ^{1}H signal at 7.00 ppm for the methine of the ligand bridge. Moreover, the presence of two equivalent pyrazolyl rings suggests a C_s symmetric octahedral structure in which the ligand is κ^3-coordinated to the metal. The ionic species is thermally unstable and decomposes in a few minutes at room temperature. When **6** was treated with 1 equiv of THF and then reacted with $[PhC_3]^+[B(C_6F_5)_4]^-$ (B/Ti = 1; C$_6$D$_6$; 25°C), the formation of the Lewis base adduct $[(bpzmp)TiMe_2(THF)]^+[B(C_6F_5)_4]^-$ (**8**) is straightforward and selective. The pattern of ^{1}H resonances for the ligand was similar to that of **7**; the only difference is the presence of a singlet at 1.85 ppm for the Ti-Me and two broad singlets at 3.77 and 2.08 ppm for the methylene protons of coordinated THF, found in a rapid equilibrium with uncoordinated THF. The Lewis acid-catalyzed ring-opening reaction of THF was not observed at room temperature after overnight aging of the solution at room temperature.

2. Dynamic NMR Behavior of the Solution Structures 3–6. The fluxional behavior of the hemilabile heteroscorpionate ligand has been studied in the solution structures of **3**–**6** by VT ^{1}H NMR spectroscopy. The strong *trans* effect exerted by the amido groups in **3** produces partial dissociation of the ligand, and the equilibrium between the tetrahedral and octahedral forms of **3** in benzene-d_6 or dichloromethane-d_2 solution was observed in the temperature range 193–303 K (Scheme 2). The integral ratio of the ^{1}H resonances diagnostic of the two species permitted the equilibrium constant K_{eq} to be evaluated at different temperature according to eq 1:

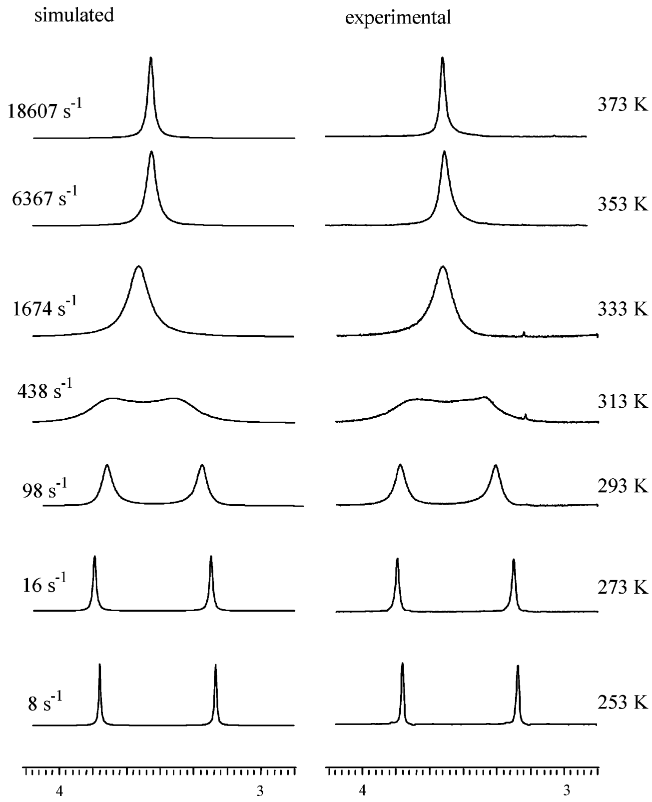

Figure 4. Experimental and simulated ^{1}H NMR spectra showing the resonances for the $-$NMe$_2$ group of (*bpzmp*)-Ti(NMe$_2$)Cl$_2$ (**5**) in TCDE.

$$K_{eq} = [T]/[O] = I_T/I_O \qquad (1)$$

in which [T] and [O] stand for the concentration of the tetrahedral (T) and octahedral (O) species and I_T and I_O for the intensities of the H^4 of the pyrazolyl resonances assumed as diagnostic of the tetrahedral and octahedral forms, respectively. The thermodynamic parameters, namely, the standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) values of 4.0 ± 0.6 kcal·mol^{-1} and 18.9 ± 2.6 cal mol^{-1} K^{-1}, were respectively determined. The $\Delta H°$ value is smaller than expected for the dissociation reaction of the two neutral imino parts of the ligand and likely accounts for the reorganization energy from the octahedral to the tetrahedral coordination sphere. In the latter the relief of interligand steric repulsion, documented by the high $\Delta S°$ value, stabilizes the species with lower coordination number.

Replacement of Cl for NMe$_2$ increased the coordination energy of the heteroscorpionate ligand as a result of lower *trans* effect of the halide vs the amide. The stereorigid octahedral environment is stable up to 373 K, where no fluxional behavior of the ligand was detected by ^{1}H NMR spectroscopy. Noteworthy, a higher energetic barrier to rotation of the amide group about the Ti–N bond was observed in **5**, in agreement with the shorter bond distance detected in the X-ray molecular structure (Figure 4). Two broad ^{1}H NMR signals at 4.23 and 3.58 ppm have been detected for the two nonequivalent methyls of $-$NMe$_2$, whose coalescence was observed at 323 K. No broadening of the *bpzmp* signals was observed at this temperature, suggesting that the rotation about the Ti–N bond does not involve

Table 3. Ethylene and Propylene Polymerization Results

entry[a]	precatalyst	temp (°C)	Al/Ti	monomer	time (min)	yield (g)	$M_w \times 10^3$
1	(*bpzmp*)$TiCl_3$/MAO	25	100	E	15	0.50	796
2	(*bpzmp*)$TiCl_3$/MAO	25	300	E	15	0.98	1163
3	(*bpzmp*)$TiCl_3$/MAO	25	500	E	15	1.04	1116
4	(*bpzmp*)$TiCl_3$/MAO	25	500	E	60	1.43	1140
5	(*bpzmp*)$TiCl_3$/Al−Bu_3/[Ph_3C][B(C_6F_5)$_4$]	25	20	E	30	0.93	36
6[b]	(*bpzmp*)$TiCl_3$/AliBu$_3$/[Ph_3C][B(C_6F_5)$_4$]	−40	20	E	30	0.54	368
7[c]	(*bpzmp*)$TiMe_3$/[Ph_3C][B(C_6F_5)$_4$]	25		E	60	0.35	730
8[d]	(*bpzmp*)$TiCl_3$/MAO	25	500	P	60	2.69[e]	178
9[c]	(*bpzmp*)$TiMe_3$/[Ph_3C][B(C_6F_5)$_4$]	25		P	60	0.06[f]	24

[a] Polymerization conditions: precatalyst = 20 μmol ([Ti] = 2.5×10^{-4} M); 80 mL of toluene; monomer pressure = 6 atm; cocatalyst = 10 mmol of MAO (Al/Zr molar ratio = 500); alternatively, 20 μmol of [Ph_3C][B(C_6F_5)$_4$] (B/Ti = 1) and 400 μmol of Al-^{i}Bu$_3$ (Al/Ti = 20). [b] 40 mL of toluene ([Ti] = 5.0×10^{-4} M); monomer pressure = 1 atm. [c] Precatalyst = 40 μmol ([Ti] = 5.0×10^{-4} M); cocatalyst = 40 μmol of [Ph_3C][B(C_6F_5)$_4$] (B/Ti = 1), 0.1 mL (0.4 mmol) of Al-^{i}Bu$_3$ as scavenger. [d] Precatalyst = 40 μmol ([Ti] = 5.0×10^{-4} M); cocatalyst = 20 mmol of MAO (Al/Zr molar ratio = 500). [e] Microstructure: *mm* = 0.46, *mr* = 0.28, *rr* = 0.26; 13% of region-errors. [f] Microstructure: *mm* = 0.36, *mr* = 0.33, *rr* = 0.31; 9% of region-errors.

ligand dissociation. A rate constant of 98 s^{-1} was evaluated for this isomerization at 293 K by comparison of the experimental and simulated VT ^{1}H NMR spectra obtained with a full line shape calculation program.[24] An activation free energy ($\Delta G^‡$) of 12.7 ± 0.1 kcal·mol^{-1} and the corresponding $\Delta H^‡$ and $\Delta S^‡$ of 13.6 ± 0.2 kcal mol^{-1} and 3.1 ± 0.5 cal mol^{-1} K^{-1} were determined at 293 K. Noteworthy, previous theoretical studies carried out on the group 4 hydrotris(pyrazol-1-yl)borate complexes TpM(NMe_2)$_3$ (M = Ti or Zr) showed that the NMe_2 rotation in the octahedral complex is almost barrierless (1−2 kcal mol^{-1}) because of the extreme flatness of the potential-energy curve as a result of a compromise between the electronic and steric factors.[25]

The methyl complex **6** was configurationally not stable. The methyl ^{1}H signals are broad at room temperature in 1,1,2,2-tetrachloroethane-d_2 solution because of rapid exchange between the axial and equatorial positions, and the coalescence of these two signals was observed at 333 K. The VT ^{1}H NMR analysis was carried out in the slow exchange region because of thermal decomposition of **6** at temperature higher than 333 K. $\Delta H^‡$ and $\Delta S^‡$ values of 22.3 ± 1.1 kcal·mol^{-1} and −19.6 ± 3.7 cal mol^{-1} K^{-1} were calculated, respectively, and the rate constant of 3 s^{-1} with $\Delta G^‡$ of 28.1 ± 0.1 kcal·mol^{-1} was found at 293 K.

3. Olefin Polymerization Catalyzed by 2 and 6. Preliminary ethylene polymerization experiments catalyzed by **2** and **6** were carried out in toluene at room temperature using MAO or [Ph_3C][B(C_6F_5)$_4$] as cocatalyst. The results are summarized in Table 3.

The chloride derivative **2** activated with MAO showed good activity in ethylene polymerization and exhibits activity values comparable to that of CpTiCl$_3$ or TpTiCl$_3$[5] but lower than the heteroscorpionate complex (*bdmpza*)TiCl$_3$.[13] The polymerization activity increases as the Al/Ti molar ratio is increased from 100 to 300 and gives a plateau at higher ratios; the same trend was observed for the average molecular mass M_w's, which reach the value of about 1×10^6 Da or higher at an Al/Ti ratio of 500. All polyethylene samples are linear and show a melting point of 135 °C. The molecular weight distributions of the polymer samples from runs 1−6 are broad and multimodal curves with PDI (M_w/M_n) values in the range 2.1−16 (depending on the condition) and thus larger than 2, as expected for a single-site catalyst. The broad PDIs are consistent with a variable concentration of the active sites during the polymerization time, probably as a result of the reaction or leaching of the ligand promoted by the excess of MAO. Hydridotris(pyrazol-1-yl)borate titanium complexes, for which the olefin polymerization mechanism was studied in great detail,[6] exhibited similar PDI values and performances in ethylene polymerization. The decrease of the polymerization activity with time (entry 3: $A = 35$ g$_{PE}$ mmol^{-1} h^{-1} atm^{-1}; entry 4: $A = 12$ g$_{PE}$ mmol^{-1} h^{-1} atm^{-1}) confirms the poor thermal stability of the active species under polymerization conditions, in agreement with the ^{1}H NMR monitoring of the reaction of the methyl complex **6** with [Ph_3C][B(C_6F_5)$_4$]. Second, the octahedral and the tetrahedral forms of the catalyst, resulting from the dissociation of the nitrogen donors of the pyrazolyl groups, exhibit different propagation and termination rate constants, also contributing to the enlargement of the PDIs. The high molecular weight of the polymers precluded ^{1}H NMR analysis of the end groups of the polymer chain; however the elevated values of the molecular mass suggest for the terminating reaction a prevailingly chain transfer of the polymer chain to the acidic aluminum center of the cocatalyst or of the scavenger employed.

In situ alkylation of **2** with Al-^{i}Bu$_3$ (Al/Ti molar ratio of 20) followed by reaction with 1 equiv of [Ph_3C][B(C_6F_5)$_4$] produced ethylene polymerization catalysts with activity values comparable to that of the MAO-based catalyst. The excess of trialkyl aluminum compound produces an increase of the chain transfer rate, and low molecular weight polyethylene was correspondingly obtained. When the polymerization temperature was lowered to −40 °C, a significant increase of the molecular weight, of about 1 order of magnitude, was observed, in agreement with a reduced chain transfer rate to aluminum. The broad PDI ($M_w/M_n = 8.2$) confirms the decomposition of the catalyst also at very low temperature.

A control polymerization experiment in the presence of **6** activated with 1 equiv of [Ph_3C][B(C_6F_5)$_4$] was carried out to assess the nature of the active species. Polyethylene with the same molecular mass of run 1 was obtained but in lower yield. The broad PDI ($M_w/M_n = 4.5$) and low yield confirm the poor thermal

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stability of the active species in the presence of the trialkylaluminum compounds.

Propylene polymerization runs catalyzed by **2** were also carried out: the corresponding results are listed in Table 3. The **2**/MAO catalyst exhibited low but significant activity in propene polymerization, and high molecular weight polypropylene was thus produced: it is worth noting that corresponding data for the hydridotris(pyrazol-1-yl)borate titanium complex and (*bdmpza*)-$TiCl_3$ were not reported. The crude polymer was substantially stereoirregular in the ^{13}C NMR analysis, in agreement with the symmetry of the catalyst precursor ($mm = 0.46$, $mr = 0.28$, $rr = 0.26$; entry 8). However a small fraction of crystalline stereoregular polymer was isolated by exhaustive fractionating with hot heptane (16 wt % of the raw polymer). This fraction stayed isotactic during ^{13}C NMR analysis ($mm = 58$), and the relative intensity of the stereoirregualr methyl pentads ($mmmr{:}mmrr{:}mrrm = 2{:}2{:}1$) showed that it is produced via an enantiomorphic site polymerization mechanism. Considering that traces of isotactic polypropylene by enantiomorphic site mechanism are often produced via Ziegler−Natta catalysis when group 4 metal complexes carrying labile ligands are treated with excess MAO, we propose that the stereoregular fraction arises from side reactions of the titanium precursor with MAO. Actually $ZrCl_4$-MAO gave isotactic polypropylene with the same ^{13}C NMR fingerprint and comparable yield under the same conditions.[26] To confirm this hypothesis, we carried out propene polymerization catalyzed by the methyl complex **6** activated with $[Ph_3C][B(C_6F_5)_4]$. The crude polymer was completely atactic with relative intensities of the monomer triads of $mm = 0.36$, $mr = 0.33$, and $rr = 0.31$ (entry 9), as expected from the symmetry of the catalyst precursor.

Conclusion

A series of novel titanium complexes **2**−**6** of the tridentate *N,N,O* heteroscorpionate ligand (3,5-$^tBu_2$-2-phenoxo)bis(3,5-Me_2-pyrazol-1-yl)methane have been prepared and the corresponding solution structures investigated by NMR spectroscopy. All complexes exhibit in the solid state an octahedral geometry in which the ligand is κ^3-coordinated to the metal. A fluxional coordinative behavior of the *bpmpz* ligand was monitored with different ancillary ligands (−Cl, $-NMe_2$, −Me). The amide ligands in **3** exert a strong *trans* effect toward pyrazolyl groups that are involved in a dissociative equilibrium producing the tetrahedral isomer of **3** as the major species at room temperature. The chloride-amide mixed coordination sphere complexes **4** and **5** are configurationally more stable, and the octahedral form is the main species in benzene solution. The methyl complex (*bpzmp*)$TiMe_3$ was successfully obtained and was thermally more stable than the corresponding alkyl derivatives of mono-tris(pyrazolyl)borate or mono-cyclopentadienyl titanium complexes. A site exchange of the nonequivalent methyl groups of the octahedral form was monitored by EXSY ^1H NMR spectroscopy.

Complexes **2** and **6** are active olefin polymerization catalysts after activation with excess MAO or treatment with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in the presence of Al-$^iBu_3$ as alkylating agent and/or scavenger. The **2**-MAO catalyst was more active and produces linear high molecular weight polyolefins characterized by broad PDIs. A similar trend was found for other non-Cp Ti complexes, such as the hydrotrispyrazolyl borate titanium complex by Jordan et al. and (*bdmpza*)$TiCl_3$ by Otero et al. The methyl complex **6** activated with the trityl salt is moderately active in ethylene polymerization and fairly active in propene polymerization: linear polyethylene and atactic polypropylene were respectively produced in the polymerization experiments. The reaction of **6** with $[Ph_3C][B(C_6F_5)_4]$ permitted the synthesis of the ionic species **7**, proposed as a model of the active species in this class of olefin polymerization catalysts.

Experimental Section

3.1. General Information. All organic preparations were carried out under aerobic conditions. Organometallic manipulations were performed in dry nitrogen or argon atmospheres using standard Schlenk line techniques and a glovebox. Solvents were distilled from the appropriate drying agents (sodium/benzophenone for hydrocarbon solvents, CaH_2 for ethyl ether and THF). The *bpzmp*-H ligand was synthesized according to the literature procedure.[14] $TiCl_4$, $Ti(NMe_2)_4$, MeLi, MeMgCl (Aldrich), $[CPh_3][B(C_6F_5)_4]$ (Boulder SPA Company), and $B(C_6F_5)_3$ (Strem Chemicals) were used as received. Me_3SiCl (Aldrich) was distilled from CaH_2. Ethylene (S.O.N., polymerization grade) was dried by passing over activated 4 Å molecular sieves. Methylalumoxane (MAO) (Witco, 10 wt % solution in toluene) was dried in a vacuum at 50 °C to remove the uncoordinated $AlMe_3$, washed with hexane, and used as solid. Elemental analyses were performed with a Perkin-Elmer 240-C. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 and Bruker Avance 400 operating at 300 and 400 MHz for ^1H, respectively. The ^1H NMR chemical shifts were referred to TMS as external standard using the residual protio impurities of the deuterated solvents as reference.

GPC analyses of the polymers were carried out with a PL-GPC210 chromatograph equipped with 4 PL-Gel Mixed A columns, RALLS light-scattering detector PD2040, H502 viscometer (Viscotek) refractive detector, and DM400 data manager (Viscotek). The GPC measurements were conducted at 140 °C, using 1,2,4-trichlorobenzene as solvent and narrow MWD polystyrene standard samples for the molecular weight calibration.

Differential scanning calorimetry (DSC) measurements were carried out with a TA Instrument DSC 2920 at a heating rate of 10 °C/min.

Synthesis of (*bpzmp*)$TiCl_3$ (2). *bpzmp*-H (**1**) (2.72 g, 6.66 mmol) was deprotonated by treatment with NaH (0.159 g, 6.66 mmol) in toluene at room temperature. The toluene solution of the sodium salt of **1** (140 mL, 6.66 mmol) was slowly added to a solution of $TiCl_4$ (6.66 mmol) in toluene (20 mL) at room temperature, and the resulting red suspension was stirred overnight at this temperature. The solvent was filtered off by cannula, and the residue was washed with hexane (50 mL), dried in vacuo, and then exhaustively extracted with dichloromethane (100 mL). The red-brown dichloromethane solution was concentrated at 50 mL and layered with hexane (1:1 v/v) to yield 2.088 g of **2** as a bright red microcrystalline powder (62%). Anal. Found: C, 53.23; H, 6.30; N, 9.92. Calc for $C_{25}H_{35}Cl_3N_4OTi$: C, 53.45; H, 6.28; N, 9.97. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.33 (s, 9H, 5-^tBu-Ph), 1.57 (s, 9H, 3-^tBu-Ph), 2.52 (s, 6H, 3-CH_3-Pz), 2.73 (s, 6H, 5-CH_3-Pz), 6.10 (s, 2H, Pz-*H*), 7.17 (d, 1H, $J = 2.1$ Hz, 6-*H*-Ar), 7.18 (s, 1H, −C*H*−), 7.47 (d, 1H, $J = 2.1$ Hz, 4-*H*-Ar). Selected $^{13}C\{^1H\}$ NMR data: δ

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[26] Proto, A.; Capacchione, C.; Motta, O.; De Carlo, F. *Macromolecules* **2003**, *36*, 5942. Similar results were obtained with a $TiCl_4$/MAO catalytic system in our laboratory.

12.4, 17.2, 31.5, 35.2, 36.0, 71.1, 109.3, 124.4, 127.4, 128.2, 140.5, 141.0, 147.4, 154.1, 161.4.

Synthesis of (*bpzmp*)Ti(NMe$_2$)$_3$ (3). A solution of *bpzmp*-H (**1**) (0.500 g 1.22 mmol) in toluene (20 mL, 0,061 M) was slowly added to a solution of Ti(NMe$_2$)$_4$ (2.88 mL, 1.22 mmol) in toluene (30 mL, 0.0407 M) at room temperature. Evolution of dimethylamine was soon observed. The resulting orange solution was stirred overnight at room temperature. All volatiles were then removed in vacuo, and the solid was extracted with hexane (40 mL). The orange-red filtrate was concentrated, and a bright red crystalline solid was isolated after cooling of the hexane solution at −10 °C. Yield: 0.438 g (61%). The crystalline sample spontaneously and slowly releases the hexane molecules clathrated in the lattice. To achieve good elemental analysis, the sample was evacuated overnight at 50 °C and then analyzed. Anal. Found: C, 63.06; H, 9.02; N, 16.73. Calc for $C_{31}H_{53}N_7OTi$: C, 63.36; H, 9.09; N, 16.68. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): δ 1.18 (s, 9H, 5-^{t}Bu-Ph), 1.43 (s, 9H, 3-^{t}Bu-Ph), 1.83 (bs, 6H, 5-C*H*$_3$-Pz), 2.12 (s, 6H, 3-C*H*$_3$-Pz), 3.06 (bs, 18H, TiN-C*H*$_3$), 5.82 (s, 2H, Pz-*H*), 6.54 (brs, 1H, 6-*H*-Ar), 7.30 (d, 1H, J = 2.4 Hz, 4-*H*-Ar) 7.76 (brs, 1H, −C*H*−). Selected ^{13}C{^{1}H} NMR data (63 MHz, CD$_2$Cl$_2$, 25 °C): δ 10.9, 14.5, 29.9, 31.8, 34.6, 35.7, 45.2, 72.9, 107.4, 124.2, 124.7, 126.0, 138.7, 141.1, 147.8, 159.7.

Synthesis of (*bpzmp*)Ti(NMe$_2$)$_2$Cl (4) (reaction in a NMR tube). Me$_3$SiCl (3.15 μL, 25.5 μmol) dissolved in benzene-d_6 (0.3 mL) was added to a solution of (*bpzmp*)Ti(NMe$_2$)$_3$ (0.015 g, 25.5 μmol) in benzene-d_6 (0.3 mL) in a NMR tube. The color of the resulting solution changed from orange-red to dark red in a few minutes. Spectroscopic data for (*bpzmp*)Ti(NMe$_2$)$_2$Cl (**4**) in the C_s symmetric form: ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 1.34 (s, 9H, 5-^{t}Bu-Ph), 1.57 (s, 9H, 3-^{t}Bu-Ph), 1.74 (s, 3H, 3-C*H*$_3$-Pz), 2.47 (s, 3H, 5-C*H*$_3$−Pz), 3.73 (s, 12H, TiN−C*H*$_3$), 5.37 (s, 2H, Pz-*H*), 6.80 (s, 1H, −C*H*-), 7.02 (d, 1H, J = 2.7 Hz, 6-*H*-Ar), 7.65 (d, 1H, J = 2.7 Hz, 4-*H*-Ar). Spectroscopic data for (*bpzmp*)Ti(NMe$_2$)$_2$Cl (**4**) in the C_1 symmetric form: ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 1.28 (s, 9H, 5-^{t}Bu-Ph), 1.38 (s, 9H, 3-^{t}Bu-Ph), 1.68 (s, 3H, C*H*$_3$-Pz), 1.82 (s, 3H, C*H*$_3$-Pz), 1.89 (s, 3H, C*H*$_3$-Pz), 2.50(s, 3H, C*H*$_3$-Pz), 3.25 (bs, 6H, TiN-C*H*$_3$), 3.67 (s, 6H, TiN-C*H*$_3$), 5.23 (s, 1H, Pz-*H*), 5.46 (s, 1H, Pz-*H*), 6.75 (s, 1H, −C*H*−), 6.97 (d, 1H, J = 2.7 Hz, 6-*H*-Ar), 7.63 (d, 1H, J = 2.7 Hz, 4-*H*-Ar).

Synthesis of (*bpzmp*)Ti(NMe$_2$)Cl$_2$ (5). A solution of Me$_3$SiCl (0.22 mL, 1.204 mmol) in toluene (5 mL) was slowly added to a solution of (*bpzmp*)Ti(NMe$_2$)$_3$ (0.380 g, 0.602 mmol) in toluene (15 mL) and left under stirring at room temperature for 5 h. During this time the color of the solution changed slowly from orange to dark red. All volatiles were then removed in vacuo, and the residue was washed with hexane (10 mL) and extracted with toluene (30 mL). The red-brown toluene solution was concentrated to 15 mL and layered with hexane (20 mL). A bright red crystalline solid was isolated by filtration. Yield: 0.180 g (52%). The crystalline sample spontaneously and slowly released the toluene molecules clathrated in the lattice. To achieve good elemental analysis, the sample was evacuated overnight at 70 °C and then analyzed. Anal. Found: C, 56.70; H, 7.20; N, 12.34. Calc for $C_{27}H_{41}Cl_2N_5OTi$: C, 56.85; H, 7.24; N, 12.28. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 1.32 (s, 9H, 5-^{t}Bu-Ph), 1.60 (s, 9H, 3-^{t}Bu-Ph), 1.62 (s, 3H, C*H*$_3$-Pz), 1.77 (s, 3H, C*H*$_3$-Pz), 2.14 (s, 3H, C*H*$_3$-Pz), 3.02 (s, 3H, C*H*$_3$-Pz), 3.56 (bs, 6H, TiN-C*H*$_3$), 4.21 (s, 6H, TiN-C*H*$_3$), 5.13 (s, 1H, Pz-*H*), 5.38 (s, 1H, Pz-*H*), 6.77 (s, 1H, −C*H*−), 7.01 (d, 1H, J = 2.0 Hz, 6-*H*-Ar), 7.58 (d, 1H, J = 2.0 Hz, 4-*H*-Ar). Selected ^{13}C{^{1}H} NMR data: 11.5, 11.6, 15.3, 16.6, 32.0, 34.7, 36.4, 71.8, 108.3, 108.9, 124.2, 126.0, 127.5, 128.9, 129.7, 138.7, 139.9, 140.2, 142.4, 152.8, 154.2 161.4.

Synthesis of (*bpzmp*)TiMe$_3$ (6). Method 1: Metathesis with MeLi. An 80 mL sample of a diethyl ether solution of methyllithium (1.7 M, 2.57 mmol) was added to a slurry of (*bpzmp*)TiCl$_3$ (0.400 g, 0.79 mmol) in diethyl ether (1.7 mL) at −80 °C. The mixture was stirred for 1 h at −80 °C and then left to slowly reach room temperature (overnight). All volatiles were removed in vacuo, and the black-green residue was extracted with hexane (80 mL). The pale yellow filtrate was concentrated to 15 mL and cooled at −10 °C, affording a yellow microcrystalline powder. Yield: 0.040 g (10%). ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_2$, 25 °C): δ 1.30 (s, 9H, 5-^{t}Bu-Ph), 1.52 (s, 9H, 3-^{t}Bu-Ph), 1.55 (s, 6H, Ti-eq-*CH*$_3$), 1.78 (s, 3H, Ti-ax-*CH*$_3$), 2.35 (s, 6H, 5-C*H*$_3$-Pz), 2.47 (s, 6H, 3-C*H*$_3$-Pz), 5.96 (s, 2H, Pz-*H*), 7.04 (s, 1H, −C*H*−), 7.08 (bs, 1H, 6-*H*-Ar), 7.40 (bs, 1H, 4-*H*-Ar). Selected ^{13}C{^{1}H} NMR data (400 MHz, CD$_2$Cl$_2$, 25 °C): δ 12.2 (3-*C*H$_3$-Pz), 15.0 (5-*C*H$_3$-Pz), 30.2 (3-^{t}Bu-Ph), 31.6 (5-^{t}Bu-Ph), 54.8 (Ti-ax-*C*H$_3$), 68.4 (Ti-eq-*C*H$_3$), 71.9 (−*C*HPz$_2$−), 108.3 (4-*C*-Pz), 124 (6-*C*-Ar), 126.6 (4-*C*-Ar).

Method 2: One-Pot Synthesis. A solution of methyllithium (4.88 mmol) in diethyl ether (3.5 mL 1.4 M) was added to a solution of TiCl$_4$ (0.13 mL, 1.22 mmol) in diethyl ether (25 mL) at −80 °C, and the resulting yellow solution was left under stirring at −80 °C in argon atmosphere for 7 h. A precooled (−80 °C) solution of **1** (0.500 g 1.22 mmol) in diethyl ether (25 mL, 0.049 M) was then added to the reaction mixture. The resulting solution was slowly allowed to reach room temperature (overnight). All volatiles were removed in vacuo, and the black-green residue was extracted with hexane (80 mL). The pale yellow filtrate was concentrated to 20 mL and cooled at −10 °C to give a yellow solid, which was isolated by filtration and dried in vacuo. Yield: 0.170 g (28%).

Synthesis of [(*bpzmp*)TiMe$_2$][B(C$_6$F$_5$)$_4$] (7) (reaction in a NMR tube). [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.010 g, 11.2 μmol) was dissolved in benzene-d_6 (0.5 mL) and added to a solution of (*bpzmp*)TiMe$_3$ (0.005 g, 11.2 μmol) in benzene-d_6 (0.5 mL) in a NMR tube at room temperature. After a few minutes a red oil separated from the reaction mixture. The mother liquor was filtered off and the red oil analyzed in chlorobenzene-d_5 solution. ^{1}H NMR (400 MHz, C$_6$D$_5$Cl, 25 °C): δ 1.54 (s, 9H, 5-^{t}Bu-Ph), 1.91 (s, 9H, 3-^{t}Bu-Ph), 2.14 (s, 6H, Ti-C*H*$_3$), 2.25 (s, 6H, 3-C*H*$_3$-Pz), 2.32 (s, 6H, 5-C*H*$_3$-Pz), 5.60 (s, 2H, Pz-*H*), 7.00 (s, 1H, −C*H*−), 7.88 (d, 1H, J = 1.7 Hz, 4-*H*-Ar).

Synthesis of [(*bpzmp*)TiMe$_2$(THF)][B(C$_6$F$_5$)$_4$] (8) (reaction in a NMR tube). [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.010 g, 11.2 μmol) was dissolved in benzene-d_6 (0.5 mL) and added at room temperature to a solution of (*bpzmp*)TiMe$_3$ (0.005 g, 11.2 μmol) in benzene-d_6 (0.5 mL) containing tetrahydrofuran (0.9 μL, 11.5 μmol). After a few minutes a red oil separated from the reaction mixture. The mother liquor was filtered off and the red oil analyzed in chlorobenzene-d_5 solution. ^{1}H NMR (400 MHz, C$_6$D$_5$Cl, 25 °C): δ 1.58 (s, 9H, 5-^{t}Bu-Ph), 1.85 (s, 6H, Ti-C*H*$_3$), 1.97 (s, 9H, 3-^{t}Bu-Ph), 2.08 (s, 6H, 3-C*H*$_3$-Pz), 2.20 (s, 6H, 5-C*H*$_3$-Pz), 3.77 (b, OC*H*$_2$CH$_2$-THF), 4.46 (b, OCH$_2$C*H*$_2$-THF), 5.62 (s, 2H, Pz-*H*), 7.04 (s, 1H, −C*H*−), 7.90 (d, 1H, J = 2.2 Hz, 4-*H*-Ar). Selected ^{13}C{^{1}H} NMR data: δ 11.5 (3-*C*H$_3$-Pz), 25.7 (5-*C*H$_3$-Pz), 30.5 (3-^{t}Bu-Ph), 31.5 (5-^{t}Bu-Ph), 70,8 (−*C*HPz$_2$−), 78.9 (Ti-*C*H$_3$), 109.3 (4-*C*-Pz), 128,4 (4-*C*-Ar).

Polymerization Procedure. The polymerization runs employing MAO cocatalyst were carried out using the following procedure. A 500 mL Büchi glass reactor equipped with a mechanical stirrer was charged with toluene (80 mL) containing the appropriate precatalyst and MAO. The evacuated reactor was fed with ethylene at 6 atm, and the monomer pressure was kept constant by feeding on demand. After the specific reaction time, the polymerization was stopped by venting the reactor and pouring the polymerization mixture into ethanol acidified with aqueous HCl. The polymer was recovered by filtration, washed with an excess of fresh ethanol, and dried in a vacuum at 80 °C.

The polymerization runs employing [Ph$_3$C][B(C$_6$F$_5$)$_4$] cocatalyst were carried out using the following procedure. A sealed glass vial containing the appropriate amount of precatalyst and [Ph$_3$C][B(C$_6$F$_5$)$_4$] was introduced into a 500 mL Büchi glass autoclave equipped with a mechanical stirrer. The autoclave was evacuated and charged with a toluene (80 mL) and Al-^{i}Bu$_3$ (0.4 mL, 1.60 mmol) used as scavenger. After equilibration of the solution with ethylene at 6 atm, the polymerization run was started by breaking the vial with the mechanical stirrer. The run was terminated by venting the reactor and pouring the polymerization mixture into ethanol acidified with aqueous HCl. The polymer was recovered by filtration, washed with an excess of fresh ethanol, and dried in a vacuum at 80 °C.

Crystal Structure Determinations. The crystal data for **2**, **3**, and **5** were collected using a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. The data sets were integrated with the Denzo-SMN package[27] and corrected for Lorentz−polarization and absorption effects (SORTAV).[28] The structures were solved by direct methods (SIR97)[29] and refined using full-matrix least-squares with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. The crystals of **3** contain molecules of hexane lying in centers of symmetry, while those of **5** contain disordered molecules of toluene. Furthermore, the ^{t}Bu groups linked to C4 in **5** are disordered, and the three methyl groups were refined over two positions with occupancy of 0.5.

All calculations were performed using SHELXL-97[30] and PARST[31] implemented in the WINGX[32] system of programs. The crystal data and refinement parameters are summarized in Table 1.

Supporting Information Available: ^{1}H NMR spectra of **1**−**8**, 2D NMR experiments, determination of the thermodynamic parameters for the equilibrium between the octahedral and tetrahedral isomers of (*bpzmp*)Ti(NMe$_2$)$_3$ (**3**), determination of the kinetic parameters for the rotation of the amide group about the Ti−N bond in (*bpzmp*)TiCl$_2$(NMe$_2$)$_3$ (**5**) and for the rotation of methyl groups in (*bpzmp*)TiMe$_3$ (**6**); full crystallographic data given in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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