Synthesis, Structure, and Polymerization Activity of a Titanium Complex with a Chelating [(Hydroxy-*κO*)amino-*κN*]phenolato(2−)-*κO* Ligand

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

A novel titanium complex with a chelating nitroxide ligand, dichloro-2-{[(hydroxy-*κO*)phenylamino-*κN*)phenylmethyl}phenolato(2−)-2*κO*}(tetrahydrofuran)titanium (**1**), was synthesized and characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography. In the presence of methylaluminoxane (MAO), **1** displayed moderate activity for the polymerization of propylene.

Introduction. – The past two decades have witnessed major advances in olefin polymerizations utilizing well-defined metallocene complexes [1–4]. These advances have led to new insights on the role of catalyst structure on the polymerization behavior of transition-metal catalysts [5–7]. More recently these advances have been extended to other classes of coordination complexes [8][9]. Considerable success has been achieved for Group-4 transition metals with ligands such as salicylaldiminato [10–14], phosphinoamide and ketimide [15–17], 8-quinolinolato [18], benzamidinato [19][20], *β*-diketonato [21], and diketiminato [22], or dianionic chelating ligands, such as bridged bis[phenolato] [23–31], *Schiff* base [32–34], aryl diamide [35], and aminodiolato ligands [36]. These new advances have re-invigorated coordination chemistry in the search for new classes of olefin-polymerization catalysts.

We have recently demonstrated that hydroxylaminato ligands derived from stable nitroxide radicals ($R_2N–O^{\cdot}$) are an intriguing class of hemi-labile ancillary ligands for early transition metals [37–43]. These ligands adopt both η^2 and η^1 (*i.e.*, *κN*, *κO* and *κO*) coordination modes, depending on the nature of the hydroxylamine ligand and the ancillary ligation at the Ti-atom. For example, the X-ray structure of [TiCl$_3$(tempo) (tempo = 2,2,6,6-tetramethylpiperidin-1-yloxy) reveals an η^2 coordination of the tempo group to the Ti-atom, while in the complexes [TiCl$_2$(Cp)(tempo)] and [TiCl(Cp)$_2$(tempo)], (Cp = cyclopentadienyl), tempo adopts an η^1 coordination to the metal [39][40]. The solution measurements indicate that the $\eta^1 \rightleftharpoons \eta^2$ interconversion of [TiCl$_3$(tempo)] is facile at room temperature [38]. Mono(cyclopentadienyl)titanium derivatives such as [Ti(Cp*)Me$_2$(ONEt$_2$)]/Ph$_3$C[B(C$_6$F$_5$)$_4$] (Cp* = pentamethylcyclopentadienyl) exhibit very high activities for propylene polymerization, generating high-molecular-mass atactic polypropylenes [43]. Herein, we report the synthesis, structure, and polymerization behavior of a novel Ti complex with a chelating nitroxide ligand.

Results and Discussion. – The synthesis of dichloro{2-{[(hydroxyl-κO)phenyl-amino-κN]phenylmethyl}phenolato(2−)-κO}(tetrahydrofuran)titanium (**1**) was carried out in one pot by the phenylation and deprotonation of the 2-hydroxysalicylaldehyde-derived *N*-phenylimine *N*-oxide, *i.e.*, of 2-[(oxidophenylimino)methyl]phenol (generally a nitrone RH=N(=R)−R′), with 2 equiv. of PhLi in THF followed by *in situ* addition of neat TiCl$_4$ (*Scheme 1*). Complex **1** was isolated as orange-red crystals in good yield by recrystallization in THF/Et$_2$O 3:1 at −50°. The ^{1}H-NMR spectrum of both the crude and purified product displayed only one diastereoisomer of **1**, as indicated by the appearance of a single resonance for the benzylic methine H-atom at δ 5.68. No fluxional behavior was observed for this complex in CDCl$_3$ at room temperature.

Scheme 1
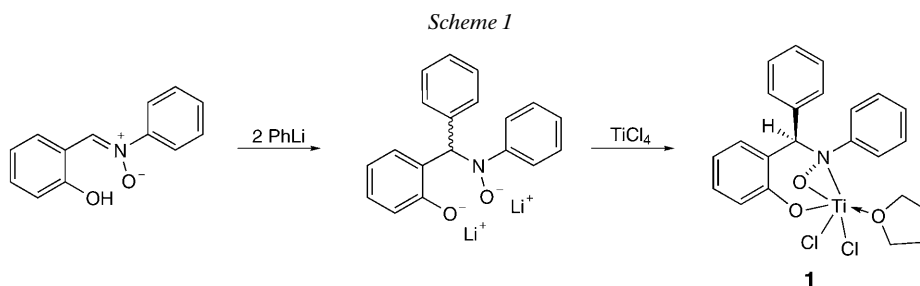
Complex **1** is very soluble in CH$_2$Cl$_2$, but virtually insoluble in toluene. This complex is moderately air-sensitive, but it is thermally stable up to 80° under vacuum. An attempt to remove the coordinated THF under vacuum by heating **1** at 100° in the solid state resulted in decomposition. An attempt to prepare the THF-free analog of **1** by substituting Et$_2$O as the solvent in the synthesis produced only unidentified products. These observations suggest that THF is required for successful isolation of **1**, as also reported for the synthesis of another 6-coordinate titanium complex bearing a pyridinediylbis[phenolato] ligand [29].

The X-ray structure of **1** illustrates a distorted octahedral geometry about the Ti center and reveals a η^2 coordination of the nitroxide functionality (*Figure*). That only one diastereoisomer was observed in solution or in the solid state indicates that the configurations of N and Ti are controlled by the stereogenic benzylic C-atom (C(1)). The nitroxide O-atom and the phenyl group in α-position to the N-atom adopt an *anti*-periplanar conformation, presumably to avoid an eclipsed conformation of the phenyl groups. The long N(1)−O(1) bond distance, 1.428 Å, is indicative of a fully reduced nitroxide moiety, comparable to other known hydroxylaminato-coordinated group-4 transition metal complexes [40][42][44−46]. The small N(1)−Ti−O(1) bond angle (87.71°) causes the extension of the Cl−Ti−Cl bond angle (114.76°). The coordinating THF molecule is *trans* to the phenolato group.

In the presence of methylaluminoxane (MAO), complex **1** exhibited modest activity for the polymerization of propylene. Polymerization in the presence of *Akzo-Nobel* MMAO or PMAO-IP in liquid propylene at 20° over a period of 30 min with a Ti concentration ranging from 0.15 to 0.29 mM yielded 0.27–0.32 g of a low tacticity polypropylene ([*mmmm*]=23%) with productivities in the range of 10.4–27.8 kg PP Ti-mol^{-1}
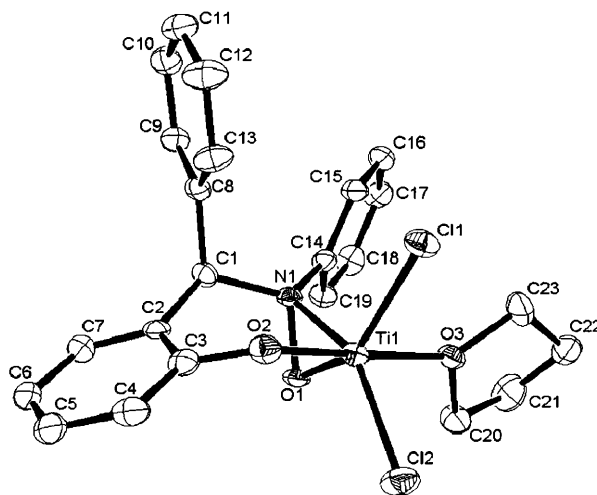
Figure. *X-Ray crystal structure of* **1**. Selected bond distances [Å] and angles [°]: Ti(1)−O(1) 1.882, Ti(1)−O(2) 1.817, Ti(1)−O(3) 2.167, Ti(1)−Cl(1) 2.289, Ti(1)−Cl(2) 2.290, N(1)−O(1) 1.428, Cl(1)−Ti(1)−Cl(2) 114.76, O(2)−Ti(1)−O(3) 177.25, N(1)−Ti(1)−O(1) 41.85, N(1)−Ti(1)−O(2) 87.71, O(1)−Ti(1)−O(2) 94.18, N(1)−Ti(1)−Cl(1) 99.75.

h^{-1}. This is significantly lower than that observed with $[Ti(Cp^*)Me_2(ONEt_2)]/Ph_3C$-$[B(C_6F_5)_4]$ (153000 kg PP Ti-mol^{-1} h^{-1}) [43]. Fractionation of the polymer yielded 22% of an Et$_2$O-soluble fraction (M_n 1,120,000, M_w/M_n 1.89), 58% of a heptane-soluble fraction (M_n 771,400, M_w/M_n 2.4), and 20% of a heptane-insoluble fraction. ^{13}C-NMR Analysis of each of these fractions revealed the Et$_2$O-soluble fraction to be atactic ([*mmmm*] = 12%), whereas the heptane-soluble fraction ([*mmmm*] = 22%) and heptane-insoluble fraction ([*mmmm*] = 34%) exhibited higher tacticities. Differential-scanning-calorimetry (DSC) analysis of the bulk polymer revealed a T_g at −7°, and no definitive T_m, although upon cooling, a small exotherm was observed at 74°.

In an attempt to probe the nature of the catalytically active cationic species in the polymerization of propylene (= prop-1-ene), **1** was treated with trimethylaluminum (*Scheme 2*). Upon reaction with 3 equiv. of AlMe$_3$ at room temperature in (D$_6$)benzene, the solution immediately became dark brown/black, and gas evolution was observed. ^{1}H-NMR Analysis of the solution revealed the disappearance of the resonance assigned to the doubly-benzylic methine H-atom, the presence of methane, and a multitude of unidentified products. Reaction of **1** with *Akzo-Nobel* PMAO-IP, containing no residual AlMe$_3$, also resulted in the immediate formation of a dark-brown solution, much like that observed in the reaction with AlMe$_3$.

Attempts to prepare benzyltitanium derivatives of **1** were unsuccessful. Treatment of **1** with benzylmagnesium chloride (BzMgCl) in THF yielded toluene and 1,1′-(ethane-1,2-diyl)bis[benzene] (bibenzyl) along with many unidentified products (*Scheme 3*). Similarly, treatment of TiCl$_4$ with 2 equiv. of BzMgCl to give 'Bz$_2$TiCl$_2$', followed by addition of a solution of the dilithium salt of the alkylated nitrone also gave toluene, bibenzyl, and unidentified products. Lastly, addition of the nitrone, to TiCl$_4$ followed by sequential treatment with 2 equiv. of PhLi and 2 equiv. of BzMgCl still did not yield the

desired dialkylated product. These observations suggested that the high acidity of the benzylic methine H-atom can lead to the decomposition of complex **1** upon deprotonation in the presence of metal alkylmetal compounds[1]).

Scheme 2
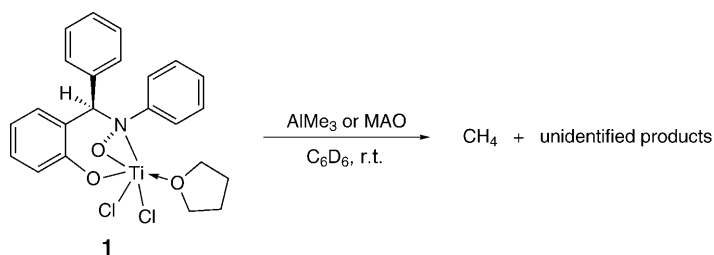
Scheme 3
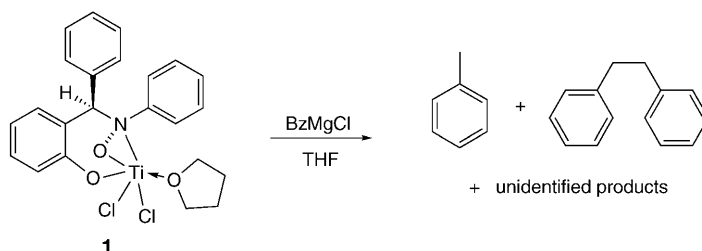
Experimental Part

General. All manipulations were performed under N_2 in a glove box or by using standard *Schlenk* techniques. All solvents were dried according to known techniques. The 2-hydroxysalicylaldehyde-derived *N*-phenylimine *N*-oxide, 2-[(oxidophenylimino)methyl]phenol, was prepared according to [47]. Differential scanning calorimetry (DSC): *Perkin-Elmer-DSC-7* apparatus; polymer samples were annealed at 180° for 10 min, and then cooled to −20° at a rate of 10°/min; heating curves were measured with a heating rate of 20°/min from −20 to 180°. Gel-permeation chromatography (GPC): analyses of the Et_2O and heptane-soluble fractions of polypropylene by *Symyx*. ¹H- and ¹³C-NMR Spectra: *Varian-Mercury-400* or *Varian-XL-400* NMR spectrometers; δ in ppm referenced to the residual H-atoms of the deuterated solvent; ¹³C-NMR of polypropylene at 100° with a *Varian-Inova-300* NMR spectrometer equipped with a 10-mm broad-band probe; polymer samples were prepared in 10-mm tubes in 3 ml of 1,1,2,2-tetrachloroethane containing 0.5 ml of 1,1,2,2-tetrachloro(1,2-D₂)ethane. Elemental analysis was performed by *Desert Analytics Laboratory* (AZ, USA).

Dichloro{2-{[(hydroxy-κO)-phenylamino-κN]phenylmethyl}phenolato(2−)-κO}(tetrahydrofuran)titanium (**1**). A suspension of 2-[(oxidophenylimino)methyl]phenol (2.13 g, 10 mmol) in THF (100 ml) at −70° was treated with 1.8M PhLi in cyclohexane/Et_2O (21.6 mmol, 12 ml) under N_2. The mixture was stir-

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[1])   Crude samples of two other derivatives of **1** were prepared by alkylation of the 3,5-di(*tert*-butyl)-salicylaldehyde-derived *N*-phenylimine *N*-oxide with [(trimethylsilyl)methyl]lithium or [1,1′-biphenyl]-2-yllithium followed by addition of $TiCl_4$. Similar reactivities were observed for both of these complexes, forming methane upon reaction with $AlMe_3$. For both of these complexes, the rate of decomposition was clearly decreased as evidenced by the slowed darkening of the solution, occurring over several minutes in comparison to several seconds in the reaction of **1** with $AlMe_3$.

red for 2 h, allowing to warm to r.t., and then immediately cooled back to $-70°$. Neat $TiCl_4$ (10 mmol) was added, and the mixture was stirred for 3 h, allowing to warm to r.t. The volatiles were evaporated and the red solid residue was extracted by CH_2Cl_2 at $0°$ and filtered to remove LiCl. The crude material was **1** with < 95% purity (by ^{1}H-NMR). The solvent was evaporated to leave a red residue, which, upon recrystallization from THF/Et₂O 3 : 1 at $-50°$, yielded **1** (1.06 g, 22%). Red microcrystals. ^{1}H-NMR ($CDCl_3$): 1.44 (*s*, 4 H, THF); 3.73 (*s*, 4 H, THF); 5.66 (*s*, 1 H); 6.82 (*m*, 3 H); 7.02–7.26 (*m*, 11 H). ^{13}C-NMR ($CDCl_3$): 140.0; 137.2; 129.5; 128.9; 128.4; 128.3; 127.9; 124.1; 114.1; 80.9 (THF); 70.0 (THF); 24.9; several signals of arom. C-atoms overlap. Anal. calc.: C 57.52, H 4.83, N 2.92; found: C 57.08, H 4.95, N 2.81.

Propylene-Polymerization Procedure. Methylaluminoxane (MAO; *Akzo Nobel*, MMAO type-4 soln. in toluene, dried *in vacuo* prior to use, 500 mg) or *Akzo-Nobel* PMAO-IP (MAO containing no residual $AlMe_3$) was added to a soln. of **1** (12.8 mg, 0.027 mmol) in toluene (10 ml). The soln. was stirred for 5 min upon which time the soln. had become dark brown (for both MMAO and PMAO) and was then transferred to an injection tube. A 300-ml *Parr* reactor was dried in an oven, evacuated, and flushed with N_2 three times prior to use. Liquid propylene (90 ml) was passed through *Q5* and alumina into the *Parr* reactor and brought to $20°$. The injection tube was pressurized with Ar, and the contents were injected into the reactor with mechanical stirring. After 30 min, the reaction was quenched with MeOH (10 ml). Excess MeOH (150 ml) and 12M aq. HCl (*ca.* 1 ml) were added and stirred overnight. The precipitated polymer was isolated by filtration, rinsed with MeOH, and dried *in vacuo* at $60°$ overnight.

X-Ray Data Collection for **1** *and Reduction.* A suitable crystal of **1** with approximate dimensions $0.20 × 0.14 × 0.05$ mm was mounted on a quartz fiber using *Paratone N* hydrocarbon oil. All measurements were made with a *Bruker-Siemens-SMART* [48] CCD area detector with graphite monochromated Mo$K_α$ radiation (λ 0.71069 Å). Data were integrated by the program SAINT [49] with box parameters of $0.86 × 0.76$. No decay correction was applied. The structure was solved by direct methods [50] and expanded by *Fourier* technique [51]. The non-H-Atoms were refined anisotropically. H-atoms were located by difference *Fourier* synthesis and were constrained to idealized geometries in a riding (AFIX) refinement. Scattering factors were taken from the International Tables for Crystallography [52]. All calculations were performed with the CrystalStructure crystallographic software package [53][54], except for refinement, which was performed with SHELXL-97 [50].

Crystal data of **1**: $C_{23}H_{23}Cl_2NO_3Ti$, M 480.25, orthorhombic; $a = 11.050(2)$ Å, $b = 8.0319(12)$ Å, $c = 25.751(4)$ Å, $β = 101.579(2)°$, $V = 2238.9(5)$ Å³, T 125 K, space group $P2_1/C$ (No. 14), $Z = 4$, $μ(MoK_α) = 6.5$ cm⁻¹; 10355 total reflections, 3721 unique reflections used in all calculations. Final $wR(F^2) = 0.061$ (all data).

CCDC-612954 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK.

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