Synthesis, Structure, and Reactivity of Hydroxylaminato Alkyltitanium Complexes

Mahesh K. Mahanthappa, Adam P. Cole, and Robert M. Waymouth*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

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Alkyltitanium complexes bearing hydroxylaminato ligands were synthesized by two methods: (i) reaction of the stable nitroxide radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) with $TiCl_3$ to generate (TEMPO)$TiCl_3$ (**1**) followed by alkylation with $PhCH_2MgCl$ to furnish (TEMPO)$Ti(CH_2Ph)_3$ (**2**), and (ii) protonolysis of $Ti(CH_2Ph)_4$ (**3**) with hydroxylamines to yield $(R_2NO)_2Ti(CH_2Ph)_2$ (R = CH_2Ph (**4**), Et (**5**)). ^1H NMR studies of these compounds demonstrate that the hydroxylaminato ligands exhibit both η^1- and η^2-binding modes with varying degrees of hemilability. X-ray crystallographic analysis of **5** shows that titanium adopts a six-coordinate "propeller" conformation in which the hydroxylamine anions are η^2-bound. The reaction of the complex **2** with $B(C_6F_5)_3$ at 20 °C forms 1 equiv of toluene and a cationic benzyltitanium complex exhibiting strong η^6-$PhCH_2B(C_6F_5)_3$ anion coordination, in which one of the TEMPO methyl groups has undergone C−H bond activation as evidenced by ^1H, ^{13}C NMR, gHSQC, gHMBC, and gROESY experiments. Complexes **2**−**5** exhibit very low activities for propylene polymerization.

Introduction

Cyclopentadienyl ligands have figured prominently in early transition metal chemistry. Recent attention has focused on other monoanionic ligands to support early transition metals, motivated in part by a desire to develop new classes of olefin polymerization catalysts[1] and to uncover new modes of reactivity.[2] Hemilabile ligands[3−5] have also attracted attention in the development of new ligands for catalysis. Recent computational studies have suggested that hemilability is the source of a novel mechanism of stereoselectivity for bis-phenoxyimine titanium complexes that produce syndiotactic polypropylene upon activation with MAO.[1s,t,6] Homoleptic complexes of titanium and zirconium containing hydroxylamine ligands were previously shown to exhibit hemilability; however, no catalytic activity has been reported for these compounds.[7]

Recently, we reported the synthesis of titanium compounds containing a monoanionic ligand derived from the stable nitroxide radical TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl).[8] Crystallographic studies of those complexes demonstrate that the TEMPO-derived ligand adopts either η^1- or η^2-binding modes depending on the nature of the ancillary ligation at titanium. Furthermore, we also demonstrated that the bond strength of the TEMPO−Ti interaction can be modulated by the ligation environment, thus permitting the homolysis of the TEMPO−Ti bond in Cp_2TiCl-(TEMPO) under mild conditions.[9] Herein, we describe the synthesis of three titanium coordination complexes containing hydroxylamine ligands, the structure of the first hydroxylaminato-titanium complex with alkyl ligands, NMR studies of the reactions of two of these complexes with $B(C_6F_5)_3$, and preliminary investigations of their propylene polymerization activity.

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Results

Synthesis of (Hydroxylaminato)titanium Complexes. The synthesis of TEMPO$TiCl_3$ (**1**) was carried out by reaction of TEMPO with $TiCl_3$ in toluene or by

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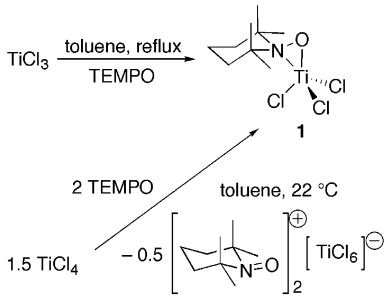
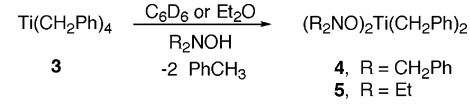
Scheme 1. Synthesis of TEMPOTiCl$_3$



the reaction of TEMPO with $TiCl_4$ in toluene as previously reported[8,10] (Scheme 1). Recrystallization from toluene gives analytically pure **1** in high yields. The ^{1}H NMR spectrum of **1** in toluene-d_8 at room temperature reveals that the methyl groups of the TEMPO ligand are magnetically inequivalent, as expected on the basis of the previously published X-ray structure, which demonstrated the η^2-binding mode of TEMPO.[8] The proton NMR chemical shifts exhibit a strong temperature dependence consistent with a fluxional process over the temperature range from −70 to 80 °C. Upon warming a toluene-d_8 solution of **1** to 27 °C, the diastereotopic methyl proton resonances are first to coalesce into a single broad peak due to their relatively small chemical shift difference ($\Delta\delta$ = 36 Hz), implying that piperidine-ring inversion is taking place; heating the sample further causes the spectrum to simplify to three broad resonances consistent with (η^1-TEMPO)$TiCl_3$. Therefore, TEMPO is a hemilabile ligand capable of stabilizing an unusual five-coordinate Ti species at room temperature, while retaining access to a coordinatively less saturated species at higher temperatures. Attempts to measure the activation energy of the $\eta^1 \leftrightarrow \eta^2$ interconversion by NMR line shape analysis were hampered by temperature-dependent chemical shifts resulting in overlapping resonances.

Attempts to alkylate **1** with MeLi, MeMgBr, and $AlMe_3$ in ethereal solvents yielded dark intractable products; however, treatment of **1** with $PhCH_2MgCl$ in ether followed by extraction with pentane cleanly yielded orange microcrystals of (TEMPO)Ti(CH_2Ph)$_3$ (**2**). The ^{1}H NMR spectrum of **2** in C_6D_6 at 22 °C consists of broad and poorly defined peaks corresponding to the TEMPO ligand (δ 0.40−1.50 ppm), a single sharp peak at δ 3.29 ppm for the benzylic methylene groups, and aromatic resonances associated with the benzyl ligands at low field. The equivalence of the benzyl resonances is consistent with an η^1-bound nitroxide or fast interconversion of the benzyl ligands at 22 °C. Variable-temperature ^{1}H NMR studies demonstrate that the signals associated with the TEMPO ligand sharpen at 60 °C to three broad resonances, consistent with the η^1-bound form. Throughout the temperature range from 22 to 70 °C, the benzylic protons in the ^{1}H NMR spectrum appear as a sharp singlet, indicating their chemical equivalence. On the basis of the last observation, we conclude that broadening of the TEMPO resonances in complex **2** at room temperature is most consistent with a η^1-coordination with slow ring inversion of the piperidine moiety due to ligation to the sterically bulky Ti(CH_2Ph)$_3$ fragment.

Scheme 2. Synthesis of Bis(hydroxylaminato)TiR$_2$



To investigate the influence of hydroxylamine structure on the resulting coordination geometry,[7,11,12] we attempted to synthesize related complexes of the type (R_2NO)Ti(CH_2Ph)$_3$ (R = alkyl or aryl). Doxsee[13] and Tilley[14] previously demonstrated that aryl and alkyl nitroso compounds insert into titanacyclobutenes and zirconacyclopentadienes, respectively, to furnish titanium and zirconium complexes having hydroxylaminato ligands. On the basis of these precedents, we examined the reaction of Ti(CH_2Ph)$_4$ (**3**) with 2 equiv of PhNO in Et_2O at −60 °C. Warming the solution to room temperature and removal of volatile components yielded a sticky brown solid, whose ^{1}H NMR spectrum indicated the complete consumption of **3** to form a mixture of products. Recrystallization of this mixture from hexanes yielded only small amounts of an unidentified brown paramagnetic solid.

We pursued a second synthetic approach toward mono-hydroxylaminato alkyltitanium complexes based on protonolysis of **3** with R_2NOH (R = CH_2Ph, Et) (Scheme 2). Stoichiometric reaction of **3** and $(PhCH_2)_2NOH$ in C_6D_6 yields 0.5 equiv of $[(PhCH_2)_2NO]_2Ti(CH_2Ph)_2$ and 0.5 equiv of **3**, with no evidence for the formation of a mono-hydroxylaminato product. Treatment of **3** with 2 equiv of R_2NOH in Et_2O at −60 °C cleanly generates (R_2NO)$_2$Ti(CH_2Ph)$_2$ (R = CH_2Ph (**4**), Et (**5**)), which was isolated in moderate yields after recrystallization from toluene or hexanes. The high-field region of the ^{1}H NMR spectrum of **4** consists of a sharp singlet for the Ti-CH_2Ph methylene protons and a pair of doublets for the diastereotopic benzylic protons adjacent to nitrogen. These observations are consistent with the η^2-binding of the R_2NO moiety to titanium in a high-symmetry environment. ^{1}H NMR analysis of **5** in C_6D_6 yields a deceptively simple spectrum consisting of an apparent triplet (δ 0.814 ppm) corresponding to the terminal methyl groups of the diethylhydroxylaminato ligand, a sharp singlet for the benzylic Ti-CH_2Ph protons, and a set of multiplets for the diastereotopic methylene protons adjacent to nitrogen. (See Supporting Information for the ^{1}H NMR spectrum of **5**.) Evaluation

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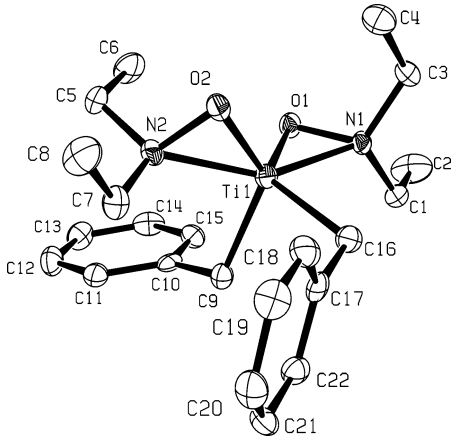

Figure 1. ORTEP diagram for $(Et_2NO)_2Ti(CH_2Ph)_2$ (**5**) with thermal ellipsoids at the 50% probability level.

of the coupling constants shows that the apparent high-field "triplet" is an overlapping doublet of doublets with $\Delta^3 J_{H-H} = 0.5$ Hz, which explains the appearance of the diastereotopic hydroxylamine methylene groups as complex multiplets (δ 2.85−3.05 ppm). The ^{1}H NMR spectrum of **5** also implies a highly symmetric structure in which the hydroxylaminato ligands are η^2-bound to titanium. Variable-temperature ^{1}H NMR study of complex **5** in C_6D_6 shows that the resonances corresponding to the diastereotopic methylene hydrogens adjacent to nitrogen broaden but do not coalesce completely upon heating to 70 °C, indicating that the η^2-binding mode of these ligands is maintained at elevated temperatures. The strength of the η^2-binding interaction in **5** sharply contrasts the hemilability of the hydroxylaminato ligands in **1** and $(R_2NO)_4Ti$ (R = Et, CH_2Ph),[7] all of which exhibit coalescence temperatures below 45 °C. (The coalescence temperature of **4** was not measured.)

X-ray Crystallographic Analysis of $(Et_2NO)_2TiBn_2$ (5). Slow cooling of a saturated hexanes solution of **5** to −45 °C yielded crystals suitable for single-crystal X-ray analysis. The structure of **5** is shown in Figure 1, and selected metrical parameters for this structure are given in Table 1, along with analogous dimensions for some related complexes. (Details of the data acquisition conditions and structure refinements are given in the Supporting Information.)

Crystallographic analysis of **5** shows that titanium adopts a six-coordinate "propeller" conformation, in which the hydroxylaminato ligands bind in a η^2-cisoid manner with a *cis* disposition of the Ti-benzyl moieties. The Ti−O, Ti−N, and N−O bond lengths observed in **5** are comparable to those previously found in **1**,[8] $CpTiCl_2(\eta^2\text{-}ONMe_2)$ (**6**),[12] and $(R_2NO)_4Ti$ (R = Me,[11] Et[7]), with the exception of the Ti−O oxygen bond length in $(Et_2NO)_4Ti$, which is ∼0.1 Å longer. The Ti−C bond lengths are in the range of those found in other titanium benzyl complexes such as $Ti(CH_2Ph)_4$ (**3**)[15] and $Cp^*Ti(CH_2Ph)_3$.[16] The benzylic hydrogen atoms, whose locations were inferred from Fourier difference maps, do not display any interactions with titanium as previously observed in **3**.[15] The O(1)−Ti(1)−O(2) and N(1)−Ti−N(2) bond angles in **5** are substantially wider than those found in the homoleptic complexes $(\eta^2\text{-}R_2NO)_4Ti$ (R = Me, Et). The widening of these angles is accompanied by the expansion of the O(1)−Ti(1)−N(2) and O(2)−Ti(1)−N(1) bond angles, with attendant contraction of the C(9)−Ti(1)−C(16) bond angle to 93.32(15)°. The Ti−O−N and Ti−N−O bond angles, however, do not differ greatly from those previously observed in **1** and in homoleptic hydroxylaminato-titanium complexes. Comparison of the structure of **5** to other known titanium complexes having two η^2-bound monoanionic ligands demonstrates that the ligation environment is closely related to that of the homoleptic complex[11] in which two of the η^2-hydroxylaminato ligands have been replaced by benzyl groups.

Reaction of 2 with $B(C_6F_5)_3$. At room temperature, the reaction of **2** and $B(C_6F_5)_3$ proceeds cleanly in C_6D_6, liberating 1 equiv of toluene to generate a red solution. Upon removal of the volatile components and redissolution of the red oil in C_6D_6, ^{1}H NMR analysis described below yields a spectrum consistent with the zwitterionic structure **6** shown in Figure 2 resulting from abstraction of a benzyl ligand by $B(C_6F_5)_3$ and cyclometalation of one of the TEMPO methyl groups. (See Supporting Information for the ^{1}H NMR spectrum of **6**.) The ^{1}H NMR spectrum reveals the presence of three diastereotopic pairs of methylene resonances at δ −0.84 and 0.92 ppm (protons 1a,b), δ 1.75 and 2.90 ppm (protons 8a,b), and δ 3.05 and 3.24 ppm (protons 12a,b). (See Figure 2 for the numbering of the H atoms in **6**.) The last pair of lines is broadened due to coupling of these benzylic hydrogens (12a,b) to the quadrupolar boron nucleus in the $PhCH_2B(C_6F_5)_3$ anion. The diastereotopic doublets at δ −0.84 and 0.92 ppm are assigned to the cyclometalated TEMPO methylene group (protons 1a,b), while the remaining three inequivalent methyl groups (2, 6, and 7) occur as sharp singlets (δ 0.73, 0.99, 1.16 ppm, respectively). The constrained conformation of the azoxatitanacyclopentane enforces a rigid conformation on the piperidine ring, evidenced by the well-defined multiplets in the range δ 0.80−1.80 ppm assigned to the diastereotopic methylene protons (hydrogens 3−5) in the ligand backbone. The aromatic region of the ^{1}H NMR spectrum displays a distinct set of lines at δ 6.63, 6.59, 6.03, 5.90, and 5.69 ppm as a pair of doublets and three triplets having equal peak integrals. These five aromatic resonances, correlated by ^{1}H,^{1}H-gCOSY, occur at characteristic upfield shifts associated with a $PhCH_2B(C_6F_5)_3$ counterion (protons 13−17) η^6-bound to titanium through the phenyl ring.[17−20]

Two-dimensional proton−carbon correlation NMR spectroscopy experiments were used to verify the connectivity of **6** and to assign completely the ^{13}C NMR spectrum. ^{1}H,^{13}C-gHSQC and ^{1}H,^{13}C-gHMBC analyses of **6** in C_6D_6 provide support for the η^6-bound $PhCH_2B(C_6F_5)_3$ anion as demonstrated by the boron quadrupolar broadened ^{13}C spectral line at δ 34.82 ppm for benzylic carbon 12 and the downfield *ipso* carbon resonance at δ 159.7 ppm (δ 148.5 ppm for the unbound anion).[19] Methylene carbon 8 of the Ti-CH_2Ph occurs at δ 84.0

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 5 and Related Hydroxylaminato-titanium Complexes

	5	$TEMPOTiCl_3$	$Ti(ONMe_2)_4$	$Ti(ONEt_2)_4$	$CpTiCl_2(ONMe_2)$
			Bond Lengths		
Ti−O	1.889(3)	1.839(3)	1.918(1)	1.980(3)	1.866(1)
	1.891(2)		1.976(1)		
Ti−N	2.104(3)	2.112(4)	2.230(1)	2.108(5)	2.128(2)
	2.134(3)		2.095(1)		
N−O	1.436(3)	1.433(4)	1.432(1)	1.402(7)	1.418(2)
	1.427(4)		1.424(1)		
$Ti-CH_2$	2.145(4)				
	2.136(3)				
			Bond Angles		
Ti−O−N	77.18(16)	79.4(2)	82.1(1)	75.0(2)	79.5(1)
	78.69(16)		74.1(1)		
O−Ti−N	41.73(10)	41.8(1)	39.5(1)	40.0(2)	40.9
	40.96(11)		40.8(1)		
Ti−N−O	61.09(14)	58.8(2)	58.4(1)	65.1(2)	59.6(1)
	60.35(14)		65.1(1)		
O−Ti−O′	110.77(11)		101.2(1)	90.1(1)	
O−Ti−N′	115.64(11)		89.8(1)	87.0(2)	
N−Ti−O′	120.09(12)		91.9(1)	90.7(2)	
N−Ti−N′	150.99(12)		104.8(1)	103.9(3)	
O−N−C	110.2(3)	110.6(4)	110.5(1)	110.6(4)	110.6(2)
	110.0(3)	110.3(4)	107.7(1)	108.9(4)	109.2(2)
C−Ti−C	93.32(15)				
reference		8	11	7	12

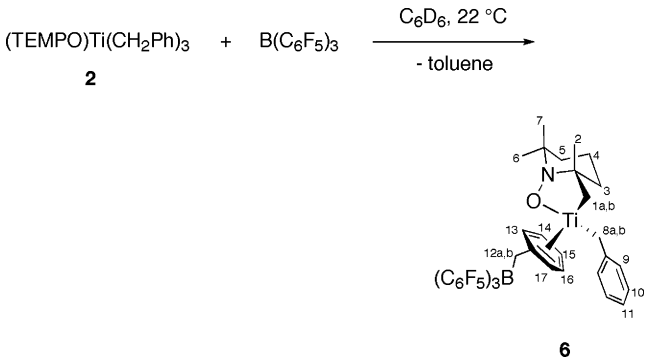

Figure 2. Proposed structure of zwitterion **6** based on one- and two-dimensional NMR experiments.

ppm with a corresponding *ipso* carbon resonance at δ 149.0 ppm in the ^{13}C NMR spectrum. The downfield occurrence of the resonance for benzylic carbon 8 along with the upfield shift of *ortho* protons 9 (δ 6.37 ppm) could be consistent with partial η^2-benzyl coordination to titanium; however, the observed symmetry of the aromatic ring (proton 9−11) rules out this possibility.[20,21] Evidence for TEMPO cyclometalation derives from gHMBC signals correlating methyl group 2 with a quaternary carbon (δ 79.7 ppm) and cyclometalated carbon 1 (δ 90.4 ppm), as well as a correlation between carbon 1 and TEMPO backbone carbon 3 (δ 38.4 ppm). Horton previously reported analogous NMR evidence for a similar C−H activation process upon reaction of $[(Me_3Si)_2N]_2Zr(CH_2Ph)_2$ with $B(C_6F_5)_3$ to yield a cationic cyclometalated zirconium compound strongly complexed by a η^6-$PhCH_2B(C_6F_5)_3$ anion.[19,22] Rothwell also observed that bis(2,6-di-*tert*-butylphenoxy)$Zr(CH_2Ph)_2$ undergoes cyclometalation of one of the *tert*-butyl groups upon reaction with $B(C_6F_5)_3$ to yield $[\eta^1$-$(2,6\text{-}tBu_2C_6H_3O)][\kappa^2$-O-$C_6H_3$-6-*t*Bu-$CMe_2CH_2]Zr[\eta^6$-$PhCH_2B(C_6F_5)_3]$ as verified by X-ray crystallography.[23]

Analysis of **6** by $^1H,^1H$-ROESY at −15 °C in toluene-d_8 is also consistent with the proposed structure shown in Figure 2, in that proton 1a of the cyclometalated TEMPO correlates with both the piperidine backbone (protons 3 and 4) and benzyl protons 8a and 9. Proton 1b correlates with benzylic protons 12a,b of the coordinated η^6-$PhCH_2B(C_6F_5)_3$ anion and aromatic protons 13, 16, and 17. Hydrogen 8a exhibits complementary ROE interactions with TEMPO methyl group 6, along with weaker correlations to protons 13 and 14 of the benzylborate counterion. Diastereotopic partner hydrogen 8b also interacts with the protons 1a,b. Finally, the aromatic protons 9−11 of Ti-CH_2Ph (δ 6.37, 6.96, and 7.13 ppm, respectively) interact with the aromatic protons 13−17 of the borate counterion.

Reaction of 5 with $B(C_6F_5)_3$. Reaction of **5** with $B(C_6F_5)_3$ in C_6D_6 yields a red species **7**, which exhibits poor hydrocarbon solubility. The ^1H NMR spectrum of this complex reveals the presence of two types of terminal methyl groups (apparent triplets at δ 0.80 and 0.68 ppm) and four pairs of diastereotopic methylene protons (multiplet δ 2.69−2.92 ppm) from the diethylhydroxylaminato ligands along with some minor impurities. (See Supporting Information for the ^1H NMR spectrum of **7**.) In contrast to zwitterion **6**, **7** shows no evidence for a η^6-bound $PhCH_2B(C_6F_5)_3$ counterion or η^2-benzyl binding to titanium; instead, a single sharp ^1H NMR resonance for the boron-bound benzylic methylene group (δ 3.24 ppm) is observed and no unusual upfield aromatic resonances are found. Complex **7** appears less prone to C−H activation of the hydroxylaminato ligands, although some toluene is observed in the spectrum along with unassigned multiplets (δ 1.15−1.35, 0.87 ppm). From these observations, we conclude that ionic species **7** is present as a loosely bound ion pair in which fluxionality of the five-coordinate titanium center yields a symmetric ^1H NMR spectrum. Attempts to characterize this complex further were hampered by

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its low solubility in aromatic hydrocarbon solvents and decomposition upon exposure to CD_2Cl_2.

Complexes **4** and **5** both exhibited very low activity (5−8 kg PP/mol·Ti·h) for propylene polymerization in the presence of methylaluminoxane (MAO). The activities of these complexes were lower than that of $Ti(CH_2Ph)_4$ but yielded low-tacticity polypropylenes ([*mmmm*] = 18.5−22.1%) with a microstructure similar to that obtained with $Ti(CH_2Ph)_4$, implying that the hydroxylamine ligands may not be stable to the MAO activator. Attempted activation of **2**, **4**, or **5** with $B(C_6F_5)_3$ and triisobutylaluminum as a scavenging agent did not yield an active polymerization catalyst at room temperature; the zwitterion **6** was similarly inactive.

Conclusion

We have demonstrated the synthesis of a series of complexes of the structural type $(R_2NO)_nTi(CH_2Ph)_{4-n}$ (n = 1, 2) by benzylation of the corresponding metal halides or by protonolysis of $Ti(CH_2Ph)_4$ with stable *N*,*N*-dialkylhydroxylamines. Structural characterization of $(Et_2NO)_2Ti(CH_2Ph)_2$ shows that it adopts a propeller conformation in the solid state due to the η^2-binding mode of the hydroxylaminato ligands. In conjunction with our previous structural study of (TEMPO)$TiCl_3$, this work demonstrates that the binding mode of the *N*,*N*-dialkylhydroxylaminato ligands depends on both the steric requirements of the ligand and ancillary ligation at the metal center. Variable-temperature ^{1}H NMR studies show that all of these anionic ligands exhibit varying degrees of hemilabile binding. Reaction of (TEMPO)$Ti(CH_2Ph)_3$ with $B(C_6F_5)_3$ generates a novel zwitterionic complex in which the TEMPO moiety undergoes C−H activation of one of the methyl groups. Preliminary investigations of the polymerization behavior of these complexes upon activation with MAO and $B(C_6F_5)_3$ demonstrate that they generate low-activity propylene polymerization catalysts.

Experimental Section

Materials. Standard Schlenk techniques and a MBraun Labmaster 100 drybox were used to handle all oxygen- and moisture-sensitive compounds. Toluene and pentane were dried and deoxygenated by passage through columns containing alumina Q-5 (Engelhard).[24] Hexanes, diethyl ether, benzene-d_6, and toluene-d_8 were vacuum transferred from Na/K alloy, and CD_2Cl_2 was dried over CaH_2. TEMPO (Aldrich) was doubly sublimed at 1×10^{-5} Torr prior to use to remove oily residues, and *N*,*N*-diethylhydroxylamine (Aldrich) was vacuum transferred from oil-free KH to remove traces of water. $C_6H_5CH_2MgCl$ (1.0 M) in diethyl ether and *N*,*N*-dibenzylhydroxylamine were also purchased from Aldrich. $TiCl_4$ (99.8%) from Strem was used without further purification. $B(C_6F_5)_3$ from Albemarle Corporation was purified by recrystallization from pentane to remove hydrated impurities. Methylaluminoxane (unmodified), supplied by Albermale as a 10 wt % solution in toluene, was dried under vacuum (5×10^{-6} Torr) at 45 °C to remove solvent and residual trimethylaluminum prior to use. $TiCl_3$[25] and $Ti(CH_2C_6H_5)_4$[26] were synthesized using known procedures. Gaseous and liquid propylene (polymer grade, 99.5%) were supplied by Scott Specialty Gases and were dried by passage through alumina and deoxygenated by passage through Q-5 (Engelhard).

^{1}H NMR spectra were recorded on Unity Inova 300, Varian XL-400, Gemini 400, and Unity Inova 500 spectrometers and were referenced relative to the residual protiated solvent peaks in the samples. ^{13}C NMR spectra were obtained at 125 MHz using a Varian Unity Inova 500 spectrometer or at 100 MHz using a Varian Gemini 400 spectrometer. gCOSY, gHSQC, gHMBC, and gROESY were performed on a Unity Inova 500 spectrometer using pulse sequences from the Varian Chempack without modification. gCOSY spectra were measured at 22 °C in C_6D_6 with a proton spectral width of −3 to 13 ppm, 256 real points in the t1 dimension, and 3248 points in the t2 dimension; the data were processed using 90° weighted sine-bell squared functions in both dimensions with 128 points of linear prediction and were zero-filled to a two-dimensional matrix of 2048 × 2048. gHSQC experiments were performed at 20 °C in C_6D_6 with a proton spectral width of −2 to 12 ppm and a carbon spectral width of −30 to 170 ppm, 256 complex points in t1, 1792 points in t2; data were processed using 90° shifted sine-bell squared function weighting in both dimensions with 128 points of linear prediction used in the t1 dimension and zero-filled to a two-dimensional matrix of 2048 × 2048. gHMBC experiments were performed at 20 °C in C_6D_6 with a proton spectral width of −8 to 8 ppm and a carbon spectral width of −15 to 220 ppm, 256 real points in t1, 2048 points in t2; data were processed using 90° shifted sine-bell squared function weighting in both dimensions with 128 points of linear prediction used in the t1 dimension and zero-filled to a two-dimensional matrix of 2048 × 1024. gROESY experiments were performed at −15 °C in toluene-d_8 with a proton spectral width of −1.8 to 8.2 ppm, 150 real points in t1, 2048 points in t2, with a mixing time of 0.3 s; data were processed using 90° shifted sine-bell squared function weighting in both dimensions with 128 points of linear prediction used in the t1 dimension and zero-filled to a two-dimensional matrix of 2048 × 1024.

Elemental analyses were carried out at Desert Analytics Laboratory (Tuscon, AZ).

TEMPOTiCl$_3$: Method 1. At room temperature, TEMPO (0.612 g, 3.91 mmol) was quickly added to a slurry of $TiCl_3$ (1.000 g, 6.49 mmol) in 25 mL of toluene to generate an orange-brown solution. Heating the reaction to reflux for 5 min yielded a yellow solution and a dark precipitate, which was allowed to cool with stirring over 12 h. The contents of the flask were allowed to settle, the brilliant yellow supernatant solution was decanted to a clean Schlenk tube, and the solvent was removed under reduced pressure to yield a yellow solid, which was washed with 30 mL of pentane and dried in vacuo. Yield: 0.547 g (45% based on TEMPO).

TEMPOTiCl$_3$: Method 2. TEMPO (2.47 g, 15.8 mmol) in 40 mL of toluene was quickly added over 90 s to a solution of $TiCl_4$ (1.30 mL, 11.8 mmol) in 25 mL of toluene to generate a yellow solution and an orange-yellow precipitate in an exothermic reaction. After 2 h of stirring at room temperature, the reaction was Schlenk filtered through Celite to give a yellow solution, which was concentrated in a vacuum to 25 mL and cooled to −45 °C to induce crystallization. Decanting the supernatant solution, washing the resulting solid with pentane, and drying it in a vacuum yielded a product identical to the one produced by method 1 above as verified by ^{1}H and ^{13}C NMR. Yield: 1.219 g (50%). ^{1}H NMR (C_6D_6, 400 MHz, 18 °C): δ 0.80 (s, CH_3, 6H), 0.89 (s, CH_3, 6H), 0.95−1.80 (mult, −CH_2-CH_2-CH_2−, 6H). ^{1}H NMR (C_6D_6, 400 MHz, 72 °C): δ 0.966 (s, CH_3, 12H), 1.24 (br s, 4H, −N-C(CH_3)$_2$-CH_2−, 4H), 1.50 (br s, −CH_2-CH_2-CH_2−). ^{13}C{^{1}H} NMR (C_6D_6, 400 MHz, 18 °C): δ 67.1, 37.4, 30.8, 24.0, 16.0. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 69 °C): δ 67.38, 37.79, 27.07 (br), 16.20. Anal. Calc for $C_9H_{18}NOTiCl_3$: C 34.82, H 5.84, N 4.51. Found: C 34.42, H 6.18, N 4.51.

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TEMPOTi($CH_2C_6H_5$)$_3$ (2). A slurry of TEMPOTiCl_3 (0.617 g, 2.00 mmol) in 25 mL of diethyl ether was cooled to −10 °C, and 6.0 mL of 1.0 M $C_6H_5CH_2MgCl$ was added over 6 min to provide an orange solution with a lightly colored precipitate. The cold bath was removed and the reaction allowed to stir at room temperature for 10 h. Removal of the solvent under reduced pressure yielded an oily solid, which was extracted with pentane (3 × 40 mL). The combined pentane extracts were filtered through Celite and concentrated in a vacuum to 10 mL; cooling to −45 °C produced orange crystals. This crude product was further recrystallized from ∼30 mL of hexanes at −45 °C. Yield: 0.317 g (33%). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ (ppm) 7.12−7.16 (t, 4H, *m*-C_6H_5), 6.80−6.90 (m, 6H, *o*,*p*-C_6H_5), 3.29 (s, 6H, Ti-CH_2Ph), 1.55 (s, 12H, −CH_3), 1.20−1.40 (br, 4H, −N-CMe$_2$-CH_2−), 0.50−0.70 (br, 2H, CH_2-CH_2-CH_2−); ^{1}H NMR (300 MHz, C_6D_6, 70 °C): δ (ppm) 7.20 (t, 4H, *m*-C_6H_5), 7.04 (d, 4H, *o*-C_6H_5), 6.90 (t, 2H, *p*-C_6H_5), 3.47 (s, 6H, Ti-CH_2Ph), 1.27 (br s, 6H, −CH_2-CH_2-CH_2−), 0.81 (s, 12H, −N-C(CH_3)$_2$−). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 50 °C): δ (ppm) 149.15, 128.23, 126.57, 122.38, 93.57, 63.96, 39.00, 29.79, 16.77. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 70 °C): δ (ppm) 149.52, 128.59, 127.16, 122.87, 93.98, 63.94, 39.08, 26.89, 16.91. Anal. Calc for $C_{30}H_{39}NOTi$: C 75.46, H 8.23, N 2.93. Found: C 75.76, H 8.01, N 2.98.

((PhCH$_2$)$_2$NO)$_2$Ti(CH_2Ph)$_2$ (4). A solution of (PhCH$_2$)$_2$NOH (0.209 g, 0.980 mmol) in 20 mL of ether was added slowly to Ti(CH_2Ph)$_4$ (0.205 g, 0.497 mmol) in 20 mL of diethyl ether at −30 °C, causing the solution to immediately lighten in color. The cold bath was removed, and the reaction was allowed to stir for 15.5 h at room temperature. The reaction solvent was concentrated to 10 mL, causing a yellow solid to settle out of solution. The yellow supernatant solution was decanted, and the resulting yellow solid was dried in vacuo. Analytically pure yellow-orange crystals were obtained after two recrystallizations from toluene. Yield: 0.105 g (32%). Higher yields (∼75%) of this material can be obtained by removal of the ethereal solvent from the reaction mixture followed by two recrystallizations from toluene at −45 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ (ppm) 7.30−7.50 (m, 20H, ON(CH$_2$*Ph*)$_2$), 7.06 (d, 4H, Ti(CH$_2$-*o*-Ph)), 7.16 (t, 4H, Ti(CH$_2$-*m*-Ph)), 6.83 (t, 2H, Ti(CH$_2$-*p*-Ph)), 4.21 (d, 4H, TiON(CH_2Ph)$_2$), 4.07 (d, 4H, TiON(CH_2-Ph)$_2$), 2.70 (s, 4H, TiCH_2Ph). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 19 °C): δ (ppm) 149.10, 133.24, 131.01, 128.44, 128.40, 128.23, 126.97, 121.58, 78.16, 61.64. Anal. Calc for $C_{42}H_{42}N_2O_2Ti$: C 77.05, H 6.47, N 4.28. Found: C 77.14, H 6.50, N 4.43.

(Et$_2$NO)$_2$Ti(CH_2Ph)$_2$ (5). Et$_2$NOH (0.30 mL, 2.91 mmol) was added dropwise over 5 min to Ti(CH_2Ph)$_4$ (0.608 g,1.47 mmol) in 40 mL of hexanes at −30 °C. The cold bath was removed upon finishing the addition, and the reaction was allowed to stir for 6 h at room temperature. The reaction solvent was concentrated to 12 mL and cooled to −45 °C to produce a yellow precipitate, which was isolated by decanting the supernatant solution. The crude product was recrystallized from hexanes at −45 °C to produce crystals suitable for single-crystal X-ray analysis. Yield: 383 mg (64%). ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ (ppm) 7.19 (app t, $^3J_{H-H}$ = 7 Hz, 4H, TiCH_2-*m*-Ph), 7.15 (app d, $^3J_{H-H}$ = 7.0 Hz, 4H, TiCH_2-*o*-Ph), 6.89 (tt, $^3J_{H-H}$ = 7 Hz, $^5J_{H-H}$ = 1.5 Hz, 4H, TiCH_2-*p*-Ph), 2.85−3.05 (m, 8H, (CH$_3$CH_2)$_2$NO-Ti), 2.71 (s, 4H, Ti-CH_2Ph), 0.814 (dd, $^3J_{H-H}$ = 7.0 and 7.5 Hz, 12H, Ti-ON(CH$_2$CH_3)). ^{1}H NMR (400 MHz, $CDCl_3$, 19 °C): δ (ppm) 7.10 (app t, 2H, TiCH_2-*m*-Ph), 6.89 (app d, 4H, TiCH_2-*o*-Ph), 6.80 (app d, 4H, TiCH_2-*p*-Ph), 3.08−3.26 (m, 8H, (CH$_3$CH_2)$_2$NO-Ti), 2.50 (s, 4H, Ti-CH_2Ph), 1.07 (app t, 12H, Ti-ON(CH$_2$CH_3)). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 20 °C): δ (ppm) 149.22, 127.90, 126.72, 121.51, 75.76, 52.06, 9.77. Anal. Calc for $C_{22}H_{34}N_2O_2Ti$: C 65.02, H 8.43, N 6.89. Found: C 64.75, H 8.47, N 6.82.

Reaction of 2 with B(C_6F_5)$_3$ (6). A solution of **2** (0.0072 g, 15 μmol) in 1.5 mL of C_7D_8 was added to a solution of B(C_6F_5)$_3$ (0.0082 g, 16 μmol) in 1.5 mL of C_7D_8 to obtain a dark red solution of zwitterionic complex **6**. The solvent was removed in vacuo to yield a ruddy oil, which was redissolved in C_6D_6. ^{1}H NMR (500 MHz, C_6D_6, 22 °C): δ (ppm) 7.13 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, overlap with solvent, TiCH_2-*m*-Ph), 6.96 (t, 1H, $^3J_{H-H}$ = 7.0 Hz, TiCH_2-*p*-Ph), 6.63 (d, 1H, $^3J_{H-H}$ = 8.0 Hz, BCH_2-*o*-Ph), 6.59 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, BCH_2-*o*-Ph), 6.37 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, TiCH_2-*o*-Ph), 6.03 (app t, 1H, $^3J_{H-H}$ = 7.0 Hz, BCH_2-*m*-Ph), 5.90 (app t, 1H, $^3J_{H-H}$ = 7.0 Hz, BCH_2-*m*-Ph), 5.69 (t, 1H, $^3J_{H-H}$ = 8.0 Hz, BCH_2-*p*-Ph), 3.24 (m, 1H, BCH_2Ph), 3.05 (m, 1H, BCH_2Ph), 2.90 (d, 1H, $^2J_{H-H}$ = 11.5 Hz, TiCH_2Ph), 1.75 (d, 1H, $^2J_{H-H}$ = 11.5 Hz, TiCH_2Ph), 1.53 (dt, 1H, $^3J_{H-H}$ = 13.0 Hz, $^2J_{H-H}$ = 3.65 Hz, ONC(CH$_3$)$_2$CH_2−), 1.45 (dt, 1H, $^3J_{H-H}$ = 13.0 Hz, $^2J_{H-H}$ = 3.65 Hz, ONC-(CH$_3$)$_2$CH_2−),1.18−1.36 (m, 3H, CH$_2$CH_2-CH_2), 1.16 (s, 3H, ONC(CH_3)$_2$−), 1.00−1.08 (m, 1H, CH$_2$CH_2-CH$_2$), 0.99 (s, 3H, ONC(CH_3)$_2$−), 0.92 (d, 1H, $^2J_{H-H}$ = 11.5 Hz, O-NC(CH$_3$)(CH$_2$-Ti)), 0.73 (s, 3H, ONC(CH_3)(CH$_2$-Ti)), −0.84 (d, 1H, $^2J_{H-H}$ = 11.5 Hz, O-NC(CH$_3$)(CH$_2$Ti)). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C): δ (ppm) 159.74 (*ipso* B-CH_2Ph),149.58 (*ipso* B-C_6F_5), 148.99 (*ipso* Ti-CH_2Ph), 147.64 (B-*o*-C_6F_5), 138.55 (B-*m*-C_6F_5), 136.48 (B-*p*-C_6F_5), 132.31, 132.02 (BCH_2-*o*-Ph), 130.75 (BCH_2-*m*-Ph), 129.60 (BCH_2-*p*-Ph), 129.29 (TiCH_2-*o*-Ph), 126.21 (TiCH_2-*m*-Ph), 125.91 (BCH_2-*m*-Ph), 124.22 (TiCH_2-*p*-Ph), 90.38 (NC-(CH$_3$)(*C*H$_2$Ti)−), 84.03 (Ti*C*H$_2$Ph, $^1J_{C-H}$ = 124 Hz), 79.72 (N*C*(CH$_3$)(CH$_2$Ti)−), 64.58 (N*C*(CH$_3$)$_2$−), 39.20, 38.42 (−*C*H$_2$-CH$_2$*C*H$_2$−), 34.82 (br, B*C*H$_2$Ph), 28.81, 26.83, 19.37 (−*C*H$_3$), 16.48 (−CH$_2$*C*H$_2$CH$_2$−).

Generation of [(η^2-Et$_2$NO)$_2$Ti(CH_2Ph)][PhCH$_2$B(C_6F_5)$_3$]. A solution of **5** (0.0127 g, 31.2 μmol) in 1.5 mL of C_6D_6 was added to a solution of B(C_6F_5)$_3$ (0.0153 g, 29.2 μmol) at room temperature. ^{1}H NMR (500 MHz, C_6D_6, 22 °C): δ (ppm) 6.88−7.14 ppm (m, 10H, BCH$_2$*Ph*, TiCH_2*Ph*), 3.24 (s, 2H, BCH_2Ph), 2.68−2.92 (m, 8H, ON(CH_2CH$_3$)$_2$), 2.68 (s, 2H, TiCH_2Ph), 0.797 (dd, $^3J_{H-H}$ = 7.5 and 7.0 Hz, ON(CH$_2$CH_3)$_2$), 0.675 (dd, $^3J_{H-H}$ = 7.5 and 7.0 Hz, ON(CH$_2$CH_3)$_2$).

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Supporting Information Available: ^{1}H NMR spectra of complexes **5**−**7**, text giving the experimental details associated with data collection and refinement, and tables of crystal data, positional parameters, anisotropic thermal factors, bond distances, bond angles, and torsional angles for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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