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Coordination Chemistry of Amine Bis(phenolate) Titanium Complexes: Tuning Complex Type and Structure by Ligand Modification

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The coordination chemistry of titanium(IV) complexes of amine bis(phenolate) ligands was investigated by synthesizing various types of complexes and analyzing them specroscopically and structurally. Steric effects of tridentate [ONO]- and tetradentate [ONNO]-type ligands were studied by reacting the ligand precursors with titanium tetra(isopropoxide). [ONNO]-type ligands featuring an amine donor located on a pendant arm led to octahedral bis(isopropoxide) complexes, regardless of the steric bulk around the metal. Several such complexes having varying steric crowding were thus synthesized. On the other hand, steric effects were found to play a major role in determining the complex constitution when [ONO]-type ligands, featuring no side donor, were involved. Relatively sterically undemanding ligands led to octahedral bis(homoleptic) complexes, whereas increased steric bulk resulted in the formation of pentacoordinate bis(isopropoxide) complexes. These pentacoordinate complexes readily lead to bis(heteroleptic) complexes by reaction with nonsterically demanding [ONO]- and [ONNO]-type ligand precursors. In the latter case the sidearm nitrogen remains uncoordinated to the metal. The bis(isopropoxide) complexes of the [ONNO]-type ligands may also lead to bis(heteroleptic) complexes, however, these reactions are much slower.

Introduction

Titanium complexes of alkoxide and aryloxide ligands exhibit a rich coordination chemistry and reactivity and find applications in various fields.[1] Especially, the recent interest in the development of nonmetallocene complexes for the polymerization of α-olefins[2] has created a new range of chelating dialkoxo[3] ligands for group IV transition metals. The suitable complexes for this purpose are ones of the LMX_2 type, where L is a dianionic ligand and X is a labile monoanionic group. These complexes appear mostly as either mononuclear or as dinuclear species through bridging of an electron lone pair.[4] Frequently, the synthetic methodology leads to the formation of bis(homoleptic) complexes of the L_2M type.[5] The steric bulk on the ligands may thus have a major effect on the constitution of the complexes formed. Furthermore, the olefin polymerization reactivity of a possible catalyst may strongly depend on the crowding around the metal, as substantial bulk may, on one hand, hinder the approach of an incoming olefin and, on the other hand, decelerate termination processes.[6]

We have recently introduced the versatile amine bis(phenolate) family of ligands to group IV transition metals.[7−9] Various

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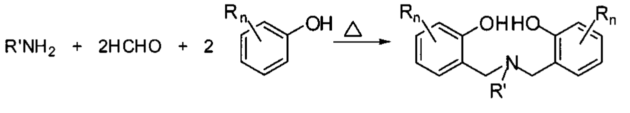
Scheme 1



complex structures and polymerization reactivities were described, demonstrating several differences between [ONO]- and [ONNO]-type ligands, the additional nitrogen donor in the latter being located on a pendant arm. These two types of the amine bis(phenolate) ligands are synthesized in a similar manner (Scheme 1). In the present study, we describe the formation tendency of a variety of titanium complexes, derived from amine bis(phenolate) ligand precursors and titanium tetra(isopropoxide), as a function of steric effects and presence of an extra donor arm.

Experimental Section

General Data. Starting materials for ligand precursor synthesis (**$1H_2$−$6H_2$**) were purchased from Aldrich Inc. and used as received. All experiments requiring a dry atmosphere were performed under a nitrogen atmosphere in a drybox. Ether and pentane were distilled from Na/benzophenone. Anhydrous heptane was purchased from Aldrich Inc. and used without further purification. All solvents were stored in the drybox. Titanium isopropoxide was purchased from Aldrich Inc. and used as received. Mass spectra were determined with a VG M-250 q spectrometer. NMR data were recorded using ARX-500, AVANCE−400, AMX-360, or AC-200 MHz Bruker spectrometers. NMR solvents were sparged with argon and stored over 4 Å molecular sieves. NMR diffusion experiments were performed on the 400 MHz spectrometer at 25 °C, employing the pulse gradient spin−echo sequence (PGSE),[10] and using the parameters published previously.[11] Equimolar solutions of the compounds to be analyzed (**2-Ti-(OiPr)$_2$** + **5-Ti-(OiPr)$_2$** and **5-Ti-(OiPr)$_2$** + **5-Ti-4**) were dissolved in d_6-benzene, and the relative diffusion was measured based on at least two signals of each compound measured in triplicate. The correlation coefficients of each curve (R) were greater than 0.9999. The X-ray diffraction measurements were carried out on a Nonius Kappa CCD diffractometer using Mo Kα (λ = 0.7107 Å) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze cooled to ca. 115 K. The structures were solved by a combination of direct methods and Fourier techniques using the SIR-92 and DIRDIF-96 software,[12] and were refined by full-matrix least-squares with SHELXL-97.[13] Several structures contain partially disordered solvent, which affects to some extent the precision of the structure determination. Elemental analyses were performed in the microanalytical laboratory of the Hebrew University of Jerusalem.

$1H_2$. A solution of 3,4-dimethylphenol (50 mmol), *N,N*-dimethylethylenediamine (25 mmol), and 36% aqueous formaldehyde (50 mmol) was stirred in refluxing methanol for 6 h. The mixture was cooled to room temperature and added to ice water. The solid was filtered, washed with water, and recrystallized from ethyl acetate to give **$1H_2$** in 61% yield. Mp 178−179 °C. ^{1}H NMR ($CDCl_3$): δ 6.75 (s, 2H), 6.66 (s, 2H), 3.55 (s, 4H, CH_2), 2.57 (m, 4H, CH_2), 2.30 (s, 6H, CH_3), 2.15 (s, 6H, CH_3), 2.12 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 154.6, 137.5, 131.1, 126.6, 119.5, 118.1, 56.2 (CH_2), 55.3 ($ArCH_2$), 49.0 (CH_2), 44.9 ($N(CH_3)_2$), 19.6 (CH_3), 18.62 (CH_3). MS (CI): m/z 357 [MH^+, 97], 223 [$(M - CH_2ArO)^+$, 100]. Anal. Calcd for $C_{22}H_{32}N_2O_2$: C, 74.12; H, 9.05; N, 7.86. Found: C, 73.94; H, 9.03; N, 7.67.

$2H_2$.[14] A solution of 2,4-di-*tert*-butylphenol (50 g, 24.2 mmol), *N,N*-dimethylethylenediamine (1.8 mL 16.4 mmol), and 36% aqueous formaldehyde (2.5 mL, 33.6 mmol) in methanol (10 mL) was stirred at RT for 3 days. The mixture was cooled in the freezer overnight, filtered, and washed thoroughly with ice cold methanol to give the bis-adduct as a colorless powder (3.7 g, 58% yield), which could be further purified by recrystallization from methanol. Mp 133 °C. ^{1}H NMR ($CDCl_3$): δ 7.18 (d, J = 2.0 Hz, 2H), 6.90 (d, J = 2.0 Hz, 2H), 3.60 (s, 4H, CH_2), 2.59 (m, 4H, CH_2), 2.31 (s, 6H $N(CH_3)_2$), 1.38 (s, 18H, $C(CH_3)_3$), 1.26 (s, 18H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 153.3, 140.1, 136.0, 124.8, 123.3, 121.6, 56.6 ($ArCH_2$), 56.9 (CH_2), 49.0 (CH_2), 44.8 ($N(CH_3)_2$), 35.0 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 29.5 ($C(CH_3)_3$). Anal. Calcd for $C_{34}H_{56}N_2O_2$: C, 77.81; H, 10.75; N, 5.34. Found: C, 78.08; H, 10.80; N, 5.15.

$3H_2$. A solution of 2,4-dimethylphenol (3.66 g, 30.0 mmol), *N,N*-dimethylethylenediamine (1.65 mL, 15.0 mmol), and 36% aqueous formaldehyde (3.5 mL, 42.0 mmol) in methanol (10 mL) was stirred and refluxed for 24 h. The mixture was cooled, and the product was filtered and washed with ice cold methanol to give the colorless product (4.5 g, 84%). Mp 174 °C (from methanol). ^{1}H NMR ($CDCl_3$): δ 6.84 (s, 2H), 6.67 (s, 2H), 3.58 (s, 4H, CH_2), 2.58 (m, 4H, CH_2), 2.33 (s, 6H, $N(CH_3)_2$) 2.19 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.6, 131.2, 128.3, 127.5, 125.4, 121.6, 56.4, ($ArCH_2$), 56.0 (CH_2), 49.0 (CH_2), 44.9 ($N(CH_3)_2$) 20.4 (CH_3), 16.1 (CH_3). Anal. Calcd for $C_{22}H_{32}N_2O_2$: C, 74.12; H, 9.05; N, 7.86. Found: C, 74.05; H, 9.16; N, 7.83.

$4H_2$. A solution of 3,4-dimethylphenol (50 mmol), 1-aminopropane (25 mmol), and 36% aqueous formaldehyde (50 mmol) was stirred in refluxing methanol for 6 h. The mixture was cooled to room temperature and added to ice water. The solid was filtered, washed with water, and recrystallized from ethyl acetate to give **$4H_2$** in 50% yield. Mp 180−181 °C. ^{1}H NMR ($CDCl_3$): δ 6.80 (s, 2H), 6.60 (s, 2H), 3.64 (s, 4H, CH_2), 2.48 (m, 2H, CH_2), 2.15 (s, 6H, CH_3), 2.14 (s, 6H, CH_3), 1.63 (m, 2H, CH_2), 0.86 (t, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 155.7, 137.1, 132.0, 127.1, 121.2, 117.6, 55.8 (CH_2), 55.2 ($ArCH_2$), 19.9 (CH_2), 19.6 (CH_3), 18.7 (CH_3), 12.0 (CH_3). MS (CI): m/z 328 [MH^+, 100]. Anal. Calcd For $C_{21}H_{29}NO_2$: C, 77.02; H, 8.93; N, 4.28. Found: C, 76.92; H, 8.90; N, 4.04.

$5H_2$. A mixture of 2,4-di-*tert*-butylphenol (5.0 g, 24.2 mmol), 1-aminopropane (1.0 mL, 12.1 mmol), and 36% aqueous formaldehyde (4.0 mL, 48.0 mmol) in methanol (10 mL) was stirred and refluxed for 24 h. The mixture was cooled in the freezer overnight, and the supernatant solution was decanted. The residue was triturated with ice cold methanol, filtered, and washed thoroughly with cold methanol to give the bis-adduct as a colorless powder (2.7 g, 45%), which could be further purified by recrystallization from ethanol. Mp 138 °C. ^{1}H NMR ($CDCl_3$): δ 7.23 (s, 2H), 6.92 (s, 2H), 3.68 (s, 4H, CH_2), 2.51 (m, 2H, CH_2), 1.40 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 0.88 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.4, 141.5, 136.0, 125.0, 123.4, 121.7, 57.2 ($ArCH_2$), 55.5 (CH_2), 34.8 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 29.7 ($C(CH_3)_3$), 19.4 (CH_2), 11.7 (CH_3). Anal. Calcd for $C_{33}H_{53}NO_2$: C, 79.95; H, 10.77; N, 2.83. Found: C, 80.04; H, 11.01; N, 3.03.

$6H_2$. A solution of 2,4-dimethylphenol (5.0 g, 41.0 mmol), 1-aminopropane (1.65 mL, 20.0 mmol), and 36% aqueous formaldehyde (4.1 mL, 49.2 mmol) in methanol (10 mL) was stirred and refluxed for 24 h. The mixture was cooled, and the supernatant solution was decanted. The remaining oil was triturated with cold methanol, filtered, and washed with ice cold methanol to give the colorless product (0.86 g, 13%), which could be further purified by recrystallization from ethanol. Mp 117 °C. ^{1}H NMR ($CDCl_3$): δ 6.86 (s, 2H), 6.71 (s, 2H), 3.68 (s, 4H, $ArCH_2$), 2.49 (m, 2H, CH_2), 2.21 (s, 12H, CH_3), 1.59 (m, 2H, CH_2), 0.86 (t, J = 7.0 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 151.9, 113.0, 128.5, 124.6, 121.4, 56.0 ($ArCH_2$), 55.0 (CH_2), 20.4 (CH_3), 15.9 (CH_3), 19.8 (CH_2), 11.7 (CH_3). Anal. Calcd for $C_{21}H_{29}NO_2$: C, 77.02; H, 8.93; N, 4.28. Found: C, 77.15; H, 9.02; N, 4.35.

1-Ti-(OiPr)$_2$. A solution of **$1H_2$** (0.40 mmol) in ether (5 mL) was added to a solution of titanium tetra(isopropoxide) (0.40 mmol) in ether

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Table 1. Crystal Data and Structure Refinement Parameters for **1a−3a**

	1a	**6a**	**5−6-a**	**5−1-a**
formula	$C_{28}H_{44}N_2O_4Ti$	$C_{42}H_{54}N_2O_4Ti{\cdot}2C_6D_6$	$C_{54}H_{78}N_2O_4Ti{\cdot}3/2C_5H_{10}$	$C_{55}H_{81}N_3O_4Ti{\cdot}C_6D_6$
fw	520.55	854.99	975.30	974.24
temp (K)	120	110	110	110
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P-1$	$P-1$	$P2_1/n$
λ (Å)	0.71070	0.71070	0.71070	0.71070
a (Å)	10.802(1)	12.7240(2)	13.2250(4)	14.7090(4)
b (Å)	23.345(1)	13.3090(2)	15.1930(4)	26.2440(6)
c (Å)	11.384(1)	14.9440(3)	16.3810(6)	15.1640(5)
α (deg)		76.0060(7)	85.406(1)	
β (deg)	102.90(1)	88.5410(7)	79.847(2)	97.9150(9)
χ (deg)		77.743(1)	66.808(2)	
V (Å^3), Z	2798.3(4), 4	2398.70(7), 2	2977.8(2), 2	5797.9(3), 4
ρ (g cm^{-3})	1.236	1.184	1.088	1.116
μ (mm^{-1})	0.340	0.224	0.188	0.193
ref mesd	8448	11173	10000	14459
ref indepd	7207	7761	6877	5569
$R1$ ($I > 2\sigma(I)$)	0.056	0.062	0.060	0.084
$wR2$ ($I > 2\sigma(I)$)	0.161	0.152	0.149	0.182
$R1$ (all data)	0.067	0.010	0.099	0.173
$wR2$ (all data)	0.171	0.137	0.173	0.231
GOF (F^2)	1.000	1.005	0.935	0.959
residual density (e Å^{-3})	0.979/−0.680	1.217/−0.552	0.630/−0.512	0.571/−0.388

(5 mL) at room temperature under a nitrogen atmosphere. The color changed immediately from colorless to yellow. The reaction mixture was stirred for 2 h, and the volatiles were removed under reduced pressure to give **1-Ti-(OiPr)$_2$** quantitatively as a yellow solid. Crystal data are shown in Table 1. ^{1}H NMR (C_6D_6): δ 6.75 (s, 2H), 6.67 (s, 2H), 5.33 (hept, J = 6.1 Hz, 1H, CH), 5.02 (hept, J = 6.1 Hz, 1H, CH), 4.56 (d, J = 13.1 Hz, 2H, ArCH_2), 2.86 (d, J = 13.1 Hz, 2H, ArCH_2), 2.17 (m, 2H, CH_2), 2.14 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 1.60 (m, 2H, CH_2), 1.56 (d, J = 6.1 Hz, 6H, CH_3), 1.29 (d, J = 6.1 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 161.7, 137.7, 130.9, 124.8, 122.6, 118.4, 77.5 (CH), 77.2 (CH), 64.8 (ArCH$_2$), 58.7 (CH$_2$), 50.8 (CH$_2$), 48.7 (N(CH$_3$)$_2$), 26.5 (CH$_3$), 26.4 (CH$_3$), 19.8(CH$_3$), 18.9 (CH$_3$). HRMS (EI, m/z) Calcd for $C_{28}H_{44}N_2O_4Ti$ (M^+), 520.27806; found, 520.27781. Anal. Calcd for $C_{28}H_{44}N_2O_4Ti$: C, 64.61; H, 8.52; N, 5.38. Found: C, 65.16; H, 8.59; N, 5.28.

2-Ti-(OiPr)$_2$. The complex **2-Ti-(OiPr)$_2$** was synthesized quantitatively as a yellow solid, in analogy to **1-Ti-(OiPr)$_2$**, by reacting 0.40 mmol of **2H$_2$** and 0.40 mmol of titanium tetra(isopropoxide). ^{1}H NMR (C_6D_6): δ 7.57 (d, J = 2.4 Hz, 2H), 7.05 (d, J = 2.4 Hz, 2H), 5.22 (hept, J = 6.0 Hz, 1H, CH), 4.81 (hept, J = 6.0 Hz, 1H, CH), 4.23 (d, J = 13.2 Hz, 2H, ArCH_2), 3.10 (d, J = 13.2 Hz, 2H, ArCH_2), 2.26 (m, 2H, CH_2), 2.07 (s, 6H, N(CH_3)$_2$), 1.81 (m, 2H, CH_2), 1.75 (s, 18H, C(CH_3)$_3$), 1.49 (d, J = 6.1 Hz, 6H, CH_3), 1.42 (s, 18H, C(CH_3)$_3$), 0.97 (d, J = 6.1 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 161.2, 138.9, 135.2, 128.3, 124.6, 124.0, 77.5 (CH), 65.2 (ArCH$_2$), 58.4 (CH$_2$), 52.4 (CH$_2$), 49.8 (N(CH$_3$)$_2$), 35.6 (C(CH$_3$)$_3$), 34.3 (C(CH$_3$)$_3$), 32.1 (C(CH$_3$)$_3$), 31.0 (C(CH$_3$)$_3$), 27.2 (CH$_3$), 26.3 (CH$_3$). HRMS (EI, m/z) Calcd for $C_{40}H_{68}N_2O_4Ti$ (M^+), 688.46546; found, 688.46586. Anal. Calcd for $C_{40}H_{68}N_2O_4Ti$: C, 69.74; H, 9.95; N, 4.07. Found: C, 69.94; H, 9.74; N, 3.65.

3-Ti-(OiPr)$_2$. The complex **3-Ti-(OiPr)$_2$** was synthesized quantitatively as a yellow solid, in analogy to **1-Ti-(OiPr)$_2$**, by reacting 0.40 mmol of **3H$_2$** and 0.40 mmol of titanium tetra(isopropoxide). ^{1}H NMR (C_6D_6): δ 6.95 (brs, 2H), 6.68 (brs, 2H), 5.27 (hept, J = 6.1 Hz, 1H, CH), 4.89 (hept, J = 6.1 Hz, 1H, CH), 4.50 (d, J = 13.0 Hz, 2H, ArCH_2), 2.89 (d, J = 13.0 Hz, 2H, ArCH_2), 2.36 (s, 6H, CH_3), 2.27 (s, 6H, CH_3), 2.17 (t, J = 6.0 Hz, 2H, CH_2), 1.98 (s, 6H, CH_3), 1.60 (t, J = 5.6 Hz, 2H, CH_2) 1.51 (d, J = 6.1 Hz, 6H, CH_3), 1.23 (d, J = 6.1 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 160.5, 132.6, 128.8, 126.5, 125.3, 124.9, 77.9 (CH), 65.9 (ArCH$_2$), 59.3 (CH$_2$), 51.8 (CH$_2$), 48.9 (N(CH$_3$)$_2$), 27.3 (CH$_3$), 27.1 (CH$_3$), 21.5 (CH$_3$), 17.65 (CH$_3$). HRMS (EI, m/z) Calcd for $C_{28}H_{44}N_2O_4Ti$ (M^+), 520.27806; found, 520.27899. Anal. Calcd for $C_{28}H_{44}N_2O_4Ti$: C, 64.61; H, 8.52; N, 5.38. Found: C, 65.01; H, 8.72; N, 5.35.

4-Ti-4. The complex **4-Ti-4** was synthesized quantitatively as an orange solid, in analogy to **1-Ti-(OiPr)$_2$**, by reacting 0.40 mmol of **1H$_2$** and 0.20 mmol of titanium tetra(isopropoxide). ^{1}H NMR (C_6D_6): δ 6.94 (s, 2H), 6.81 (s, 2H), 6.50 (s, 2H), 6.44 (s, 2H), 4.72 (d, J = 13.3 Hz, 2H, AX system 1), 4.67 (d, J = 12.8 Hz, 2H, AX system 2), 3.54 (d, J = 12.8 Hz, 2H, AX system 2), 3.45 (d, J = 13.3 Hz, 2H, AX system 1), 3.06 (m, 4H, CH_2), 2.16 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 1.96 (s, 6H, CH_3), 1.41 (m, 4H, CH_2), 0.36 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 142.0, 141.3, 138.0, 137.9, 130.8, 130.7, 126.9, 126.8, 122.2, 121.9, 117.9, 117.4, 59.7 (ArCH$_2$), 59.4 (ArCH$_2$), 53.0 (CH$_2$), 20.4 (CH$_3$), 19.7 (CH$_3$), 14.2 (CH$_2$), 12.0 (CH$_3$). HRMS (EI, m/z) Calcd for $C_{42}H_{54}N_2O_4Ti$ (M^+), 698.35631; found, 698.35621. Anal. Calcd for $C_{42}H_{54}N_2O_4Ti$: C, 72.19; H, 7.79; N, 4.01. Found: C, 72.07; H, 8.02; N, 3.70.

5-Ti-(OiPr)$_2$. The complex **5-Ti-(OiPr)$_2$** was synthesized quantitatively as a yellow solid, in analogy to **1-Ti-(OiPr)$_2$**, by reacting 0.40 mmol of **5H$_2$** and 0.40 mmol of titanium tetra(isopropoxide). ^{1}H NMR (C_6D_6): δ 7.47 (d, J = 2.4 Hz, 2H), 6.93 (d, J = 2.2 Hz, 2H), 5.15 (m, 2H, CH), 3.83 (d, J = 13.4 Hz, 2H, ArCH_2), 3.61 (d, J = 13.4 Hz, 2H, ArCH_2), 2.73 (m, 2H, CH_2), 1.67 (s, 18H, C(CH_3)$_3$), 1.49 (d, J = 6.0 Hz, 6H, CH_3), 1.37 (s, 18H, C(CH_3)$_3$), 1.29 (d, J = 5.9 Hz, 6H, CH_3), 1.6−1.2 (m, 2H, CH_2), 0.42 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (C_6D_6): δ 159.9, 141.3, 135.6, 124.7, 124.5, 123.3, 79.5 (CH), 78.7 (CH), 56.5 (ArCH$_2$), 54.7 (CH$_2$), 35.3 (C(CH$_3$)$_3$), 34.4 (C(CH$_3$)$_3$), 32.0 (C(CH$_3$)$_3$), 30.0 (C(CH$_3$)$_3$), 26.9 (CH$_3$), 26.5 (CH$_3$), 13.7 (CH$_2$), 11.7 (CH$_3$). HRMS (EI, m/z) calcd. for $C_{39}H_{65}NO_4Ti$ (M^+), 659.43931; found, 659.43933. Anal. Calcd for $C_{39}H_{65}NO_4Ti$: C, 70.99; H, 9.93; N, 2.12. Found: C, 70.59; H, 9.55; N, 2.05.

6-Ti-6. The complex **6-Ti-6** was synthesized quantitatively as an orange solid, in analogy to **1-Ti-(OiPr)$_2$**, by reacting 0.40 mmol of **6H$_2$** and 0.20 mmol of titanium tetra(isopropoxide). Crystal data are shown in Table 1. ^{1}H NMR (C_6D_6): δ 6.89 (s, 2H), 6.87 (s, 2H), 6.85 (s, 2H), 6.80 (s, 2H), 4.87 (d, J = 13.3 Hz, 2H, ArCH_2), 4.73 (d, J = 12.6 Hz, 2H, ArCH_2), 3.46 (d, J = 12.6 Hz, 2H, ArCH_2), 3.41 (d, J = 13.3 Hz, 2H, ArCH_2), 3.02 (m, 4H, CH_2), 2.67 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 1.76 (s, 6H, CH_3), 1.29 (m, 4H, CH_2), 0.39 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 161.2, 160.4, 131.9, 131.6, 127.4, 127.0, 126.9, 123.4, 123.2, 122.8, 122.7, 59.4 (ArCH$_2$), 58.6 (ArCH$_2$), 51.5 (CH$_2$), 20.9 (CH$_3$), 17.4 (CH$_3$), 16.9 (CH$_3$), 15.5 (CH$_3$), 13.3 (CH$_2$), 11.2 (CH$_3$). HRMS (EI, m/z) Calcd for $C_{42}H_{54}N_2O_4Ti$ (M^+), 698.35631; found, 698.35614. Anal. Calcd for $C_{42}H_{54}N_2O_4Ti$: C, 72.19; H, 7.74; N, 4.01. Found: C, 72.45; H, 8.18; N, 3.98.

5-Ti-4. A solution of **4H$_2$** (0.40 mmol) in ether (5 mL) was added to a solution of **5-Ti-(OiPr)$_2$** (0.40 mmol Ti) in ether (5 mL) at room temperature under a nitrogen atmosphere. The color changed immediately from yellow to dark yellow and then to orange. The reaction mixture was stirred for 2 h, and the volatiles were removed under reduced pressure to give **5-Ti-4** quantitatively as an orange solid. ^{1}H

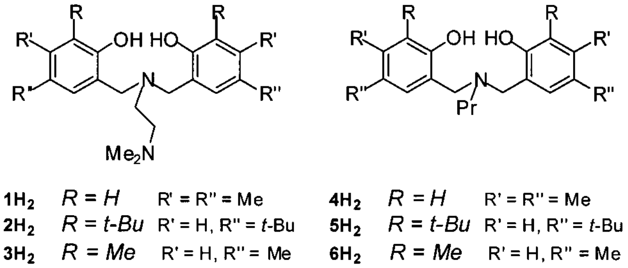
NMR (C_6D_6): δ 7.52 (s, 2H), 7.49 (s, 2H), 7.17 (s, 2H), 7.13 (s, 2H), 6.91 (s, 2H), 6.90 (s, 2H), 6.63 (s, 2H), 6.40 (s, 2H), 5.19 (d, J = 12.3 Hz, 2H, $\mathrm{ArC}H_2$), 5.03 (d, J = 13.2 Hz, 1H, $\mathrm{ArC}H_2$), 4.91 (d, J = 12.9 Hz, 1H, $\mathrm{ArC}H_2$), 3.60 (d, J = 13.4 Hz, 2H, $\mathrm{ArC}H_2$), 3.50 (d, J = 12.9 Hz, 1H, $\mathrm{ArC}H_2$), 3.49 (d, J = 12.8 Hz, 1H, $\mathrm{ArC}H_2$), 3.37 (d, J = 13.0 Hz, 2H, $\mathrm{ArC}H_2$), 3.20 (t, J = 11.7 Hz, 1H, $\mathrm{C}H_2$), 3.03 (t, J = 12.2 Hz, 1H, $\mathrm{C}H_2$), 2.89 (t, J = 8.1 Hz, 2H, $\mathrm{C}H_2$), 2.13 (s, 3H, $\mathrm{C}H_3$), 2.07 (s, 3H, $\mathrm{C}H_3$), 2.00 (s, 3H, $\mathrm{C}H_3$), 1.93 (s, 3H, $\mathrm{C}H_3$), 1.51 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.45 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.39 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.27 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.61−1.31 (m, 4H), 0.57 (t, J = 7.3 Hz, 3H, $\mathrm{C}H_3$), 0.25 (t, J = 7.3 Hz, 3H, $\mathrm{C}H_3$). ^{13}C NMR (C_6D_6): δ 163.1, 163.0, 162.2, 161.8, 141.1, 140.7, 138.5, 137.8, 137.4, 135.6, 135.4, 131.0, 130.7, 127.1, 126.7, 125.5, 125.4, 125.1, 124.6, 124.5, 121.8, 121.7, 118.0, 116.5, 61.7 ($C\mathrm{H_2}$), 59.4 ($C\mathrm{H_2}$), 58.9 ($C\mathrm{H_2}$), 52.8 ($C\mathrm{H_2}$), 50.2 ($C\mathrm{H_2}$), 35.6 ($C\mathrm{(CH_3)_3}$), 35.1 ($C\mathrm{(CH_3)_3}$), 32.7 ($\mathrm{C(}C\mathrm{H_3)_3}$), 31.5 ($\mathrm{C(}C\mathrm{H_3)_3}$), 20.5 ($C\mathrm{H_3}$), 20.3 ($C\mathrm{H_3}$), 19.8 ($C\mathrm{H_3}$), 12.4 ($C\mathrm{H_3}$), 11.8 ($C\mathrm{H_3}$). MS (EI): m/z 866.6 [M$^+$, 25], 731.5 [(M − CH$_2$ArO)$^+$, 100]. Anal. Calcd for $C_{54}H_{78}N_2O_4Ti{\cdot}C_5H_{10}$: C, 75.45; H, 9.66; N, 2.97. Found: C, 75.50; H, 10.18; N, 3.07.

5-Ti-6. The complex **5-Ti-6** was synthesized quantitatively as an orange solid, in analogy to **5-Ti-4**, by reacting 0.40 mmol of **6H$_2$** and 0.40 mmol of **5-Ti-(OiPr)$_2$**. Crystal data are shown in Table 1. ^{1}H NMR (C_6D_6): δ 7.51 (d, J = 2.2 Hz, 1H), 7.46 (d, J = 2.2 Hz, 1H), 7.17 (d, J = 2.2 Hz, 1H), 7.13 (d, J = 2.2 Hz, 1H), 6.88 (s, 1H), 6.82 (s, 2H), 6.74 (s, 1H), 5.07 (m, 4H, $\mathrm{C}H_2$), 3.50 (m, 8H, $\mathrm{C}H_2$), 2.93 (m, 4H, $\mathrm{C}H_2$), 2.25 (s, 3H, $\mathrm{C}H_3$), 2.22 (s, 3H, $\mathrm{C}H_3$), 2.19 (s, 3H, $\mathrm{C}H_3$), 1.84 (s, 3H, $\mathrm{C}H_3$), 1.50 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.46 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.36 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.22 (s, 9H, $\mathrm{C(C}H_3)_3$), 0.58 (t, J = 7.2 Hz, 3H, $\mathrm{C}H_3$), 0.40 (t, J = 7.0 Hz, 3H, $\mathrm{C}H_3$). ^{13}C NMR (C_6D_6): δ 161.5, 161.2, 160.9, 160.7, 140.3, 139.8, 134.9, 134.3, 131.9, 131.4, 128.8, 127.3, 127.2, 127.0, 124.8, 124.6, 124.3, 123.9, 123.8, 123.4, 123.3, 123.0, 122.9, 122.3, 61.1 ($C\mathrm{H_2}$), 60.2 ($C\mathrm{H_2}$), 58.7 ($C\mathrm{H_2}$), 58.6 ($C\mathrm{H_2}$), 52.2 ($C\mathrm{H_2}$), 50.4 ($C\mathrm{H_2}$), 34.9 ($C\mathrm{(CH_3)_3}$), 34.4 ($C\mathrm{(CH_3)_3}$), 34.3 ($C\mathrm{(CH_3)_3}$), 32.0 ($\mathrm{C(}C\mathrm{H_3)_3}$), 31.9 ($\mathrm{C(}C\mathrm{H_3)_3}$), 30.6 ($\mathrm{C(}C\mathrm{H_3)_3}$), 30.5 ($\mathrm{C(}C\mathrm{H_3)_3}$), 20.8 ($C\mathrm{H_3}$), 18.0 ($C\mathrm{H_3}$), 17.0 ($C\mathrm{H_3}$), 13.6 ($C\mathrm{H_2}$), 13.2 ($C\mathrm{H_2}$), 11.8 ($C\mathrm{H_3}$), 11.2 ($C\mathrm{H_3}$). HRMS (EI, m/z) Calcd for $C_{54}H_{78}N_2O_4Ti$ (M^+), 866.54411; found, 866.54137. Anal. Calcd for $C_{54}H_{78}N_2O_4Ti$: C, 74.80; H, 9.07; N, 3.23. Found: C, 74.99; H, 9.31; N, 3.32.

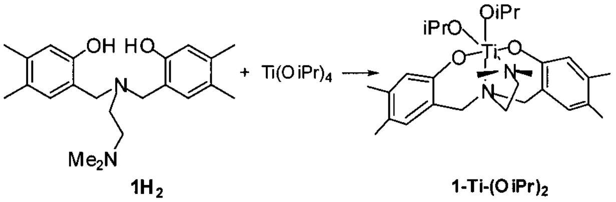
5-Ti-1. The complex **5-Ti-1** was synthesized quantitatively as an orange solid, in analogy to **5-Ti-4**, by reacting 0.40 mmol of **1H$_2$** and 0.40 mmol of **5-Ti-(OiPr)$_2$**. Crystal data are shown in Table 1. ^{1}H NMR (C_6D_6): δ 7.51 (s, 1H), 7.49 (s, 1H), 7.16 (s, 1H), 7.12 (s, 1H), 6.96 (s, 1H), 6.93 (s, 1H), 6.60 (s, 1H), 6.40 (s, 1H), 5.13 (d, J = 11.8, 2H, $\mathrm{C}H_2$), 5.00 (d, J = 11.9, 2H, $\mathrm{C}H_2$), 3.90 (d, J = 12.6, 1H, $\mathrm{C}H_2$), 3.66 (d, J = 12.4, 1H, $\mathrm{C}H_2$), 3.48 (d, J = 12.2, 1H, $\mathrm{C}H_2$), 3.39 (m, 2H, $\mathrm{C}H_2$), 3.21 (m, 1H, $\mathrm{C}H_2$), 2.89 (m, 2H, $\mathrm{C}H_2$), 2.59 (m, 1H, $\mathrm{C}H_2$), 2.36 (m, 1H, $\mathrm{C}H_2$), 2.15 (s, 3H, $\mathrm{C}H_3$), 2.10 (s, 3H, $\mathrm{C}H_3$), 2.01 (s, 3H, $\mathrm{C}H_3$), 1.97 (s, 6H, $\mathrm{N(C}H_3)_2$), 1.94 (s, 3H, $\mathrm{C}H_3$), 1.51 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.45 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.39 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.31 (s, 9H, $\mathrm{C(C}H_3)_3$), 0.25 (t, J = 7.0 Hz, 3H, $\mathrm{C}H_3$), 1.5−1.2 (m, 2H, $\mathrm{C}H_2$). ^{13}C NMR (C_6D_6): δ 162.4, 162.2, 161.5, 161.2, 140.3, 140.0, 137.7, 137.0, 134.9, 126.2, 125.8, 124.8, 124.6, 124.3, 123.8, 121.2, 121.1, 117.2, 115.9, 60.9 ($C\mathrm{H_2}$), 59.2 ($C\mathrm{H_2}$), 58.7 ($C\mathrm{H_2}$), 51.9 ($C\mathrm{H_2}$), 49.6 ($C\mathrm{H_2}$), 47.5 ($C\mathrm{H_2}$), 46.3 ($\mathrm{N(}C\mathrm{H_3)_2}$) 34.9 ($C\mathrm{(CH_3)_3}$), 34.4 ($C\mathrm{(CH_3)_3}$), 32.0 ($\mathrm{C(}C\mathrm{H_3)_3}$), 30.7 ($\mathrm{C(}C\mathrm{H_3)_3}$), 30.6 ($\mathrm{C(}C\mathrm{H_3)_3}$), 19.8 ($C\mathrm{H_3}$), 19.5 ($C\mathrm{H_3}$), 19.0 ($C\mathrm{H_3}$), 13.8 ($C\mathrm{H_2}$), 11.1 ($C\mathrm{H_3}$). MS (EI): m/z 895.3 [M$^+$, 50], 564.2 [100]. Anal. Calcd for $C_{55}H_{81}N_3O_4Ti{\cdot}C_5H_{12}$: C, 74.42; H, 9.68; N, 4.33. Found: C, 74.73; H, 10.16; N, 4.37.

5-Ti-3. The complex **5-Ti-3** was synthesized in 90% yield as an orange solid, in analogy to **5-Ti-4**, by reacting 0.40 mmol of **3H$_2$** and 0.40 mmol of **5-Ti-(OiPr)$_2$**. ^{1}H NMR (C_6D_6): δ 7.51 (s, 1H), 7.49 (s, 1H), 7.46 (s, 1H), 7.17 (s, 1H), 7.12 (s, 1H), 6.88 (s, 1H), 6.82 (s, 1H), 6.74 (s, 1H), 5.08 (m, 4H, $\mathrm{C}H_2$), 3.87 (d, J = 13.2 Hz, 1H, $\mathrm{C}H_2$), 3.62 (d, J = 13.1 Hz, 1H, $\mathrm{C}H_2$), 3.50 (d, J = 12.7 Hz, 1H, $\mathrm{C}H_2$), 3.36 (m, 2H, $\mathrm{C}H_2$), 3.13 (m, 1H, $\mathrm{C}H_2$), 2.91 (m, 2H, $\mathrm{C}H_2$), 2.63 (m, 1H, $\mathrm{C}H_2$), 2.35 (m, 1H, $\mathrm{C}H_2$), 2.24 (s, 3H, $\mathrm{C}H_3$), 2.21 (s, 3H, $\mathrm{C}H_3$), 2.18 (s, 3H, $\mathrm{C}H_3$), 1.97 (s, 6H, $\mathrm{C}H_3$), 1.82 (s, 3H, $\mathrm{C}H_3$), 1.49 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.45 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.35 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.26 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.5−1.0 (m, 2H, $\mathrm{C}H_2$), 0.40 (t, J = 6.9 Hz, 3H, $\mathrm{C}H_3$). ^{13}C NMR (C_6D_6): δ 161.4, 161.2, 160.8, 140.3, 139.8, 134.9, 134.5, 131.8, 131.3, 128.8, 128.6, 127.0, 126.8, 124.8, 124.5, 124.2, 123.8, 123.7, 123.3, 123.2, 122.9, 122.5, 61.1 ($C\mathrm{H_2}$), 60.3 ($C\mathrm{H_2}$), 59.4 ($C\mathrm{H_2}$), 59.1 ($C\mathrm{H_2}$), 51.8 ($C\mathrm{H_2}$), 50.4 ($C\mathrm{H_2}$), 47.5 ($C\mathrm{H_2}$), 46.2 ($C\mathrm{H_3}$), 34.9 ($C\mathrm{(CH_3)_3}$), 34.4 ($C\mathrm{(CH_3)_3}$), 34.3 ($C\mathrm{(CH_3)_3}$), 32.0 ($\mathrm{C(}C\mathrm{H_3)_3}$), 31.9 ($\mathrm{C(}C\mathrm{H_3)_3}$), 30.6 ($\mathrm{C(}C\mathrm{H_3)_3}$), 30.0 ($\mathrm{C(}C\mathrm{H_3)_3}$), 20.8 ($C\mathrm{H_3}$), 20.7 ($C\mathrm{H_3}$), 18.0 ($C\mathrm{H_3}$), 17.0 ($C\mathrm{H_3}$), 13.6 ($C\mathrm{H_2}$), 11.2 ($C\mathrm{H_3}$). MS (EI): m/z 895.4 [M$^+$, 10], 703.3 [100]. Anal. Calcd for $C_{55}H_{81}N_3O_4Ti$: C, 73.72; H, 9.11; N, 4.69. Found: C, 73.48; H, 9.38; N, 4.62.

Scheme 2



Scheme 3



Results and Discussion

The ligands studied are shown in Scheme 2. The [ONO]-type ligands are derived from 1-aminopropane, whereas the [ONNO]-type ligands are derived from *N*,*N*-dimethylethylenediamine. Three ligands of each type are introduced, featuring different substituents on the aromatic rings. Upon binding to the metal, only the group located ortho to the oxygen donor is expected to have any steric influence. The least sterically demanding ligands, derived from 3,4-dimethylphenol, have only hydrogen substituents in the ortho position to the hydroxyl groups (**1** and **4**). The ligands having the bulkiest substituents, namely *t*-Bu groups (**2** and **5**), are derived from 2,4-di-*tert*-butylphenol. Two additional ligands (**3** and **6**), derived from 2,4-dimethylphenol, feature the intermediate size methyl substituents.

[ONNO]-Type Ligands. We previously found that **1H$_2$** (Scheme 2) reacts cleanly with 1 equiv of Ti(OiPr)$_4$ at room temperature, yielding the bis(isopropoxide) complex **1-Ti-(OiPr)$_2$** quantitatively as a yellow crystalline solid (Scheme 3).[7] Reacting **1H$_2$** with 0.5 equiv of Ti(OiPr)$_4$ does not lead to a bis(homoleptic) complex, but instead to **1-Ti-(OiPr)$_2$** accompanied by unreacted free **1H$_2$**.[5a] The **1-Ti-(OiPr)$_2$** is quite stable to hydrolysis, and it does not show any signs of decomposition after several days in air.

The ^{1}H NMR spectrum of **1-Ti-(OiPr)$_2$** is consistent with a single stereoisomer featuring symmetry related aromatic rings, two different isopropoxide groups, and one AX spin system for the two benzylic methylene groups. This points to a rigid chelate of C_s symmetry on the NMR time scale, with the phenolate groups in a trans geometry, as shown in Scheme 3.

Single crystals of **1-Ti-(OiPr)$_2$** suitable for X-ray diffraction were grown from pentane at −35 °C. The X-ray structure of **1-Ti-(OiPr)$_2$** supported the spectroscopic data. A molecular model is shown in Figure 1 (Table 2).

The structure features a mononuclear titanium complex having a slightly distorted octahedral geometry, in which the sidearm nitrogen is bound to the metal, and forces a cis configuration

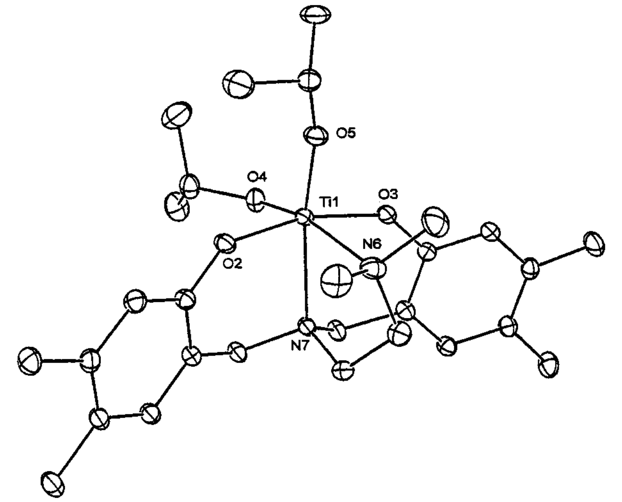


Figure 1. ORTEP drawing of the molecular structure of **1-Ti-(OiPr)$_2$**. (50% probability ellipsoids). The H atoms and disorder were omitted for clarity. Key atoms are labeled.

Table 2. Selected Bond Distances (Å) and Angles (Deg) for **1-Ti-(OiPr)$_2$**

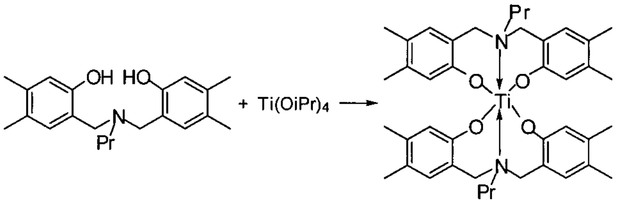
Ti−O2	1.909(5)	Ti−N7	2.317(2)
Ti−O3	1.901(1)	Ti−O4	1.838(1)
Ti−N6	2.383(2)	Ti−O5	1.808(1)
O2−Ti−O3	164.30(6)	N6−Ti−N7	75.58(6)
O4−Ti−O5	104.98(7)		

between the two isopropoxide groups, required for potential α-olefin polymerization catalysts.[15] The phenolate groups of the tetradentate ligand fold back toward the pendant (dimethylamino)ethyl arm, with an angle of ca. 30° between the two planes of the aromatic rings, thus leaving a relatively open cleft for the equatorial isopropoxide group. The relatively short O(^{i}Pr)−Ti bond lengths (1.80 and 1.84 Å) and the wide C(^{i}Pr)−O−Ti angles (135 and 160°) are consistent with π-donation to the metal. The small difference between the two coordinative N−Ti bond lengths (2.38 versus 2.32 Å) may indicate a weaker binding of the sidearm nitrogen to the metal. The inequivalency of the two benzylic methylene hydrogens is also apparent from the structure, one being approximately parallel to the aromatic ring and the other being perpendicular to it. This may explain the 1.70 ppm difference in chemical shifts.

To evaluate the effect of steric bulk on the complex constitution and reveal whether it will affect binding of the side nitrogen to the metal, the ligand precursor **2H$_2$** (Scheme 2) was also synthesized. The precursor **2H$_2$** reacted cleanly with 1 equiv of Ti(OiPr)$_4$, yielding the bis(isopropoxide) complex **2-Ti-(OiPr)$_2$** quantitatively as a yellow crystalline solid. The complex **2-Ti-(OiPr)$_2$** has similar spectroscopic features to **1-Ti-(OiPr)$_2$**, indicating similar symmetry. The sidearm nitrogen is proposed to be bound to the titanium in this complex as well (evidence for this binding is given in the last section).

Intermediate size substituents at the ortho positions to the binding site were also investigated. The tetradentate ligand precursor **3H$_2$** (Scheme 2), featuring methyl substituents at these positions, was reacted with Ti(OiPr)$_4$. In analogy to **1H$_2$** and **2H$_2$**, **3H$_2$** led to a bis(isopropoxide) complex **3-Ti-(OiPr)$_2$** quantitatively, as a yellow crystalline solid, having spectroscopic features similar to the ones obtained for the previous LigTi-(OiPr)$_2$ type complexes.

Scheme 4



4H$_2$ **4-Ti-4**

These [ONNO]-type ligands do not lead to bis(homoleptic) complexes, regardless of the steric bulk surrounding the titanium atom. Thus a series of structurally related titanium bis-(isopropoxide) complexes having varying degree of crowding around the metal were synthesized. In potentially reactive catalysts, the crowding around the metal is of great significance as it may influence the monomer approach.[6]

[ONO]-Type Ligands. The [ONO]-type ligand precursor **4H$_2$** (Scheme 2), was previously found to react very cleanly with 0.5 equiv of Ti(OiPr)$_4$ at room-temperature, giving the bis-(homoleptic) complex **4-Ti-4** quantitatively as an orange crystalline solid (Scheme 4).[7]

The spectral data of **4-Ti-4** indicated the formation of a single isomer, out of several possible ones. The two amine bis-(phenolate) ligands are symmetry related, however, the two halves of each ligand are different, judging from the appearance of two different phenolate groups, yet there is only one type of propyl unit. This complex is also quite rigid on the NMR time scale, judging from the two AX systems, with a *J*-coupling of ca. 13 Hz for the eight benzylic methylene hydrogens.

While the exact geometry of **4-Ti-4** cannot be determined unequivocally by the spectroscopic data alone, its rigidity and apparent C_2 symmetry are consistent with a strong coordination of both nitrogens lone pairs to the metal, thus completing an octahedral geometry around the titanium atom. Changing the molar ratio of the reactants to 1:1 does not lead to a complex of the form LigTi(OiPr)$_2$, but instead to **4-Ti-4** accompanied by unreacted Ti(OiPr)$_4$.[5a] This may be explained by the tendency of the titanium to adopt an octahedral geometry. Since an extra sidearm donor is lacking, the metal compensates for its electron deficiency by binding to two tridentate ligands leading to an octahedral complex. Furthermore, the steric demands of this ligand are low, namely the substituents ortho to the phenolate oxygens are hydrogen atoms.

To evaluate the effect of steric bulk in a tridentate ligand, the bulky [ONO]-type ligand featuring *t*-Bu groups at the ortho positions to the active site (**5**) was also investigated. The precursor **5H$_2$** was found to react cleanly with 1 equiv of Ti(OiPr)$_4$, yielding the bis(isopropoxide) complex **5-Ti-(OiPr)$_2$** quantitatively, as a yellow crystalline solid. Reacting **5H$_2$** with 0.5 equiv of Ti(OiPr)$_4$ did not lead to a bis(homoleptic) complex, but instead, to **5-Ti-(OiPr)$_2$** accompanied by unreacted free **5H$_2$**.[5a] The steric bulk thus prohibits two ligands featuring ortho *t*-Bu substituents from approaching each other to form a bis-(homoleptic) complex, thus yielding a pentacoordinate rather than an octahedral complex.

The spectroscopic features of **5-Ti-(OiPr)$_2$** are similar to those of **1-Ti-(OiPr)$_2$-3-Ti-(OiPr)$_2$**, implying a C_s symmetrical complex with two identical phenolate groups and two different isopropoxide units. To gain information regarding the molecularity of **5-Ti-(OiPr)$_2$** we studied its diffusion in d_6-benzene by NMR.[10,11] Since the diffusion coefficient is proportional to the effective size of the molecule, we measured the diffusion of

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(15) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487.

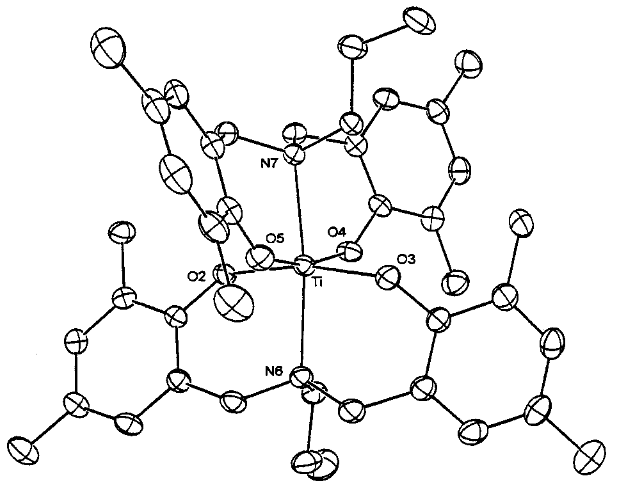
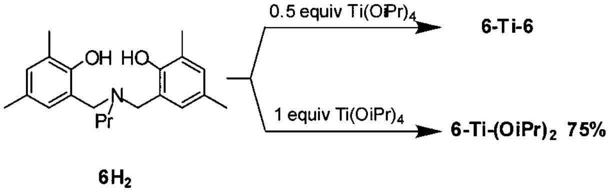


Figure 2. ORTEP drawing of the molecular structure of **6-Ti-6** (50% probability ellipsoids). The H atoms and crystallization solvent were omitted for clarity. Key atoms are labeled.

Scheme 5



5-Ti-(OiPr)$_2$ in comparison to that of **2-Ti-(OiPr)$_2$**. These two compounds featured almost identical difussion coefficients ($0.581 \pm 0.009 \times 10^{-5}$ cm^2 sec^{-1} for **5-Ti-(OiPr)$_2$** and $0.574 \pm 0.009 \times 10^{-5}$ cm^2 sec^{-1} for **2-Ti-(OiPr)$_2$**), implying that they have very similar molecular weights and that **5-Ti-(OiPr)$_2$** does not form a dinuclear complex in solution, which would have allowed completion of an octahedral geometry.[4] This conclusion was further supported by a lower diffusion coefficient ($0.491 \pm 0.003 \times 10^{-5}$ cm^2 sec^{-1}) measured for the heavier complex **5-Ti-4** (see next section). The large steric interactions in **5-Ti-(OiPr)$_2$** probably prohibit the approach of two monomeric pentacoordinate units required for formation of a dimeric structure. The increase of steric bulk is therefore an alternative approach for obtaining a mononuclear bis(isopropoxide) LigTi-(OiPr)$_2$ type complex.

Since replacing hydrogen atoms with *t*-Bu groups prevented formation of a bis(homoleptic) complex, we were interested in revealing whether methyl substituents are bulky enough to cause a similar effect. In contrary to previous observations, when reacting the ligand precursor **6H$_2$** (Scheme 2) with Ti(OiPr)$_4$, the molar ratio of the reactants was found to play a role in determining the reaction product types.

The precursor **6H$_2$** reacted cleanly with 0.5 equiv of Ti(OiPr)$_4$ at room temperature to give the bis(homoleptic) complex **6-Ti-6** quantitatively, as an orange crystalline solid (Scheme 5). The spectroscopic features of **6-Ti-6** are similar to those obtained for the bis(homoleptic) complex **4-Ti-4**, namely two different phenolate groups and one type of propyl unit, indicating a similar symmetry. It therefore seems, that under these conditions, the steric interactions between the methyl groups are not sufficient to prevent the formation of the homoleptic complex.

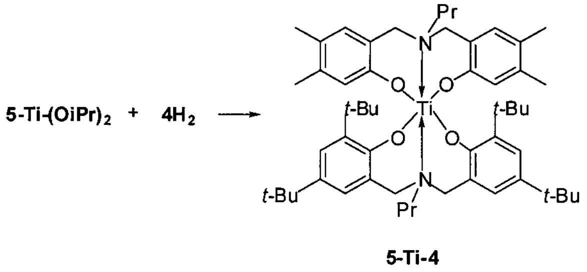
Single crystals of **6-Ti-6** were obtained from slow evaporation of *d*$_6$-benzene at room temperature, and the X-ray structure of **6-Ti-6** is shown in Figure 2 (Table 3).

The structure features a slightly distorted octahedral complex having a mer geometry, i.e., the two phenolate oxygens are in a trans geometry, as was obtained in the [ONNO]Ti(OiPr)$_2$ type complexes. We propose that **4-Ti-4** exhibits a similar structure.

Table 3. Selected Bond Distances (Å) and Angles (Deg) for **6-Ti-6**

Ti−O2	1.899(2)	Ti−O5	1.866(2)
Ti−O3	1.898(2)	Ti−N6	2.266(2)
Ti−O4	1.877(2)	Ti−N7	2.272(2)
O2−Ti−O3	167.46(7)	O2−Ti−O5	93.39(7)
O4−Ti−O5	165.84(7)	N6−Ti−N7	172.25(7)

Scheme 6



However, changing the molar ratio to 1:1 between **6H$_2$** and Ti(OiPr)$_4$ led to an inseparable mixture of two compounds. The minor compound (corresponding to ca. 25% of the ligand) is the homoleptic complex **6-Ti-6** and the major compound is consistent with the bis(isopropoxide) complex **6-Ti-(OiPr)$_2$**, according to ^{1}H NMR (Scheme 5).

The intermediate size of the methyl groups, therefore, enables the formation of both types of products, with the molar ratio of the reactants being the crucial factor.[5a] It is thus plausible that the substituents bulk in **6-Ti-(OiPr)$_2$** decelerates the binding of the second ligand to the metal.

Bis(heteroleptic) Complexes. The intermediate size substituents enable formation of a bis(homoleptic) complex, which cannot be obtained from two ligands having bulkier *t*-Bu groups. To estimate the maximum crowding that the titanium center may withstand, we reacted the pentacoordinate complex **5-Ti-(OiPr)$_2$**, consisting of a sterically demanding ligand, with 1 equiv of the sterically undemanding tridentate ligand precursor **4H$_2$** (Scheme 2). The color changed immediately from yellow to orange, resulting in formation of the bis(heteroleptic) complex **5-Ti-4** quantitatively (Scheme 6).

The ^{1}H NMR spectrum of **5-Ti-4** features four different aromatic rings and eight different benzylic methylene hydrogens, which appear as four AX spin systems. The complex therefore has a C_1 symmetry. These data are consistent with those obtained for **4-Ti-4** and **6-Ti-6**, indicating that the two rings of each ligand are not symmetry related.

It therefore seems that, whenever steric conditions allow, an octahedral complex of the Lig$_2$Ti is preferred over the pentacoordinate LigTi(OiPr)$_2$ complex.

To find out whether additional crowding around the titanium was possible, we reacted the pentacoordinate complex **5-Ti-(OiPr)$_2$** with 1 equiv of the tridentate ligand precursor **6H$_2$** (Scheme 2). The color change from yellow to orange was observed only after a few minutes, yielding the bis(heteroleptic) complex **5-Ti-6** quantitatively.

The spectroscopic data of **5-Ti-6** are similar to those of **5-Ti-4**, indicating a C_1 symmetrical complex. The X-ray structure of **5-Ti-6** supported this notion (Figure 3, Table 4).

The structure features a distorted octahedral complex having an analogous binding mode to the one obtained for **6-Ti-6**. A relatively short distance of 2.5 Å between one of the *t*-Bu hydrogens of **5** and one of the methyl hydrogens of **6** in **5-Ti-6** may explain the reluctance of **5** to form a bis(homoleptic) complex.

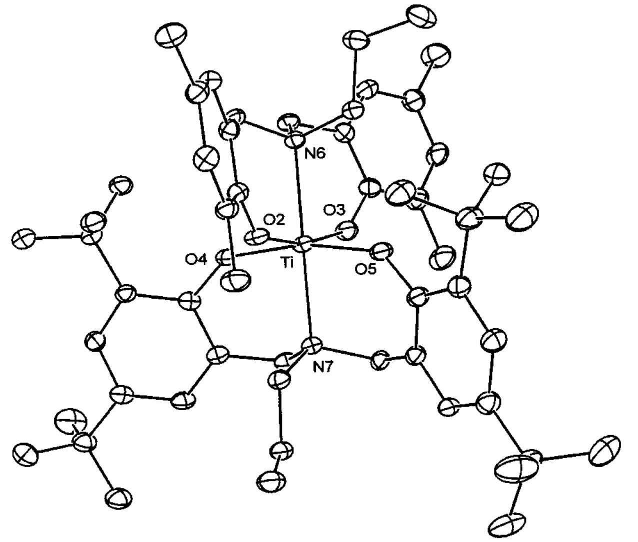


Figure 3. ORTEP drawing of the molecular structure of **5-Ti-6** (50% probability ellipsoids). The H atoms and crystallization solvent were omitted for clarity. Key atoms are labeled.

Table 4. Selected Bond Distances (Å) and Angles (Deg) for **5-Ti-6**

Ti−O2	1.881(2)	Ti−O5	1.913(2)
Ti−O3	1.880(2)	Ti−N6	2.298(2)
Ti−O4	1.904(2)	Ti−N7	2.248(2)
O2−Ti−O3	165.90(9)	O3−Ti−O4	93.80(9)
O4−Ti−O5	166.12(9)	N6−Ti−N7	173.90(9)

Finally, we wanted to investigate whether we could obtain bis(heteroleptic) complexes containing one [ONNO]-type ligand. In such complexes, the sidearm nitrogen may either bind to the titanium, leading to a heptacoordinate metal center,[16] or remain uncoordinated. As the extra donor arm was shown to play a crucial role in reactivity,[8,9] it is valuable to estimate how easy it is to detach it from the metal. As described in the previous section, [ONNO]$_2$Ti type bis(homoleptic) complexes were not obtained at room temperature even when the suitable molar ratio of the reactants was employed. However, reacting the pentacoordinate complex **5-Ti-(OiPr)$_2$,** with the sterically undemanding tetradentate ligand precursor **1H$_2$** at room temperature resulted in an immediate color change from yellow to orange, yielding the bis(heteroleptic) [ONO]Ti[ONNO] type complex **5-Ti-1** quantitatively. The ^{1}H NMR spectrum of **5-Ti-1** has similar features to those of **5-Ti-4** and **5-Ti-6**, indicating a C_1 symmetrical complex.

Single crystals of **5-Ti-1** were obtained by slow evaporation of d_6-benzene, and the X-ray structure of **5-Ti-1** (Figure 4, Table 5) indicated that the side donor arm is not coordinated to the metal, thus a heptacoordinate titanium complex is not formed.

Interestingly, the alternative route toward **5-Ti-1**, namely reacting **1-Ti-(OiPr)$_2$** with **5H$_2$**, did not proceed at room temperature, even after 24 h. Only by conducting the reaction at 110 °C in toluene in a sealed flask for 2 h could **5-Ti-1** be obtained in 95% yield (Scheme 7). Thus the kinetic barrier arises from detaching the donor from the metal, despite its location on a side arm.[17]

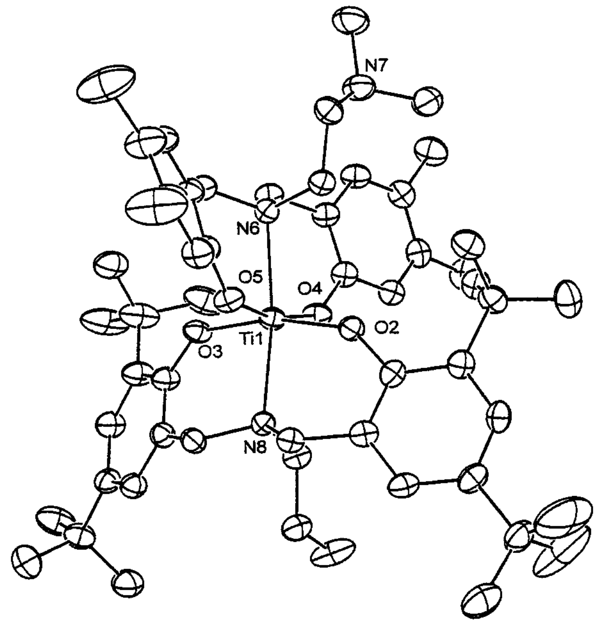
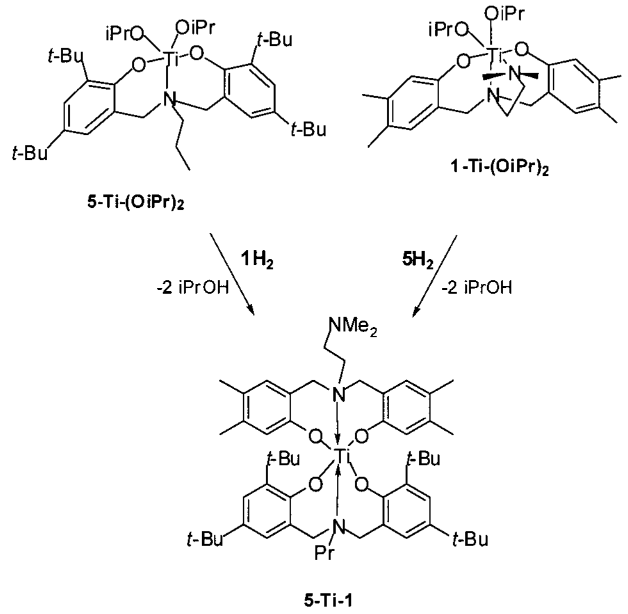


Figure 4. ORTEP drawing of the molecular structure of **5-Ti-1** (50% probability ellipsoids). The H atoms and crystallization solvent were omitted for clarity. Key atoms are labeled.

Table 5. Selected Bond Distances (Å) and Angles (Deg) for **5-Ti-1**

Ti−O2	1.893(3)	Ti−O5	1.885(3)
Ti−O3	1.907(3)	Ti−N6	2.308(4)
Ti−O4	1.865(3)	Ti−N8	2.253(3)
O2−Ti−O3	165.2(1)	O3−Ti−O4	89.5(1)
O4−Ti−O5	165.3(1)	N6−Ti−N8	170.7(1)

Scheme 7



Similar results were obtained when employing the more sterically demanding ligand precursor **3H$_2$**. The bis(heteroleptic) complex **5-Ti-3** was synthesized in two ways: a) by reacting **5-Ti-(OiPr)$_2$** with **3H$_2$** at room temperature, in which the color change from yellow to orange occurred within a few minutes, and b) by reacting **3-Ti(OiPr)$_2$** with **5H$_2$** at 110 °C for 2 h.

Conclusions

We synthesized several types of amine bis(phenolate) titanium complexes, cleanly in quantitative yields, having different steric crowding around the metal. The [ONNO]-type ligands bind to the metal in a tetradentate fashion, leading to octahedral bis-

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(16) Fay, R. C. *Coord. Chem. Rev.* **1996**, *154*, 99.

(17) The substantial difference in reaction rates is a strong indication of the binding of the side donor to the metal. The reaction of **2-Ti-(OiPr)$_2$** with **4H$_2$** proceeds to an appreciable extent only after heating the reaction mixture to 110 °C for 1 h. This indicates that the side donor in **2-Ti-(OiPr)$_2$** is indeed bound to the metal.

(isopropoxide) complexes regardless of the steric bulk of the aromatic ring substituents. Thus, a series of three such complexes having different steric hindrance was synthesized. On the other hand, in the [ONO]-type ligand family, steric interactions play a major role in determining the constitution of the resulting complexes. Small substituents lead to bis(homoleptic) complexes having an octahedral geometry. Increasing the bulk of the substituents leads to deceleration or even prevention of the corresponding octahedral complex formation. The resulting pentacoordinate complexes may be used as convenient starting materials for the preparation of bis(heteroleptic) complexes of [ONO]- and [ONNO]-type ligands; in the latter case, the side amine donor is not coordinated to the metal. The slow formation of bis(heteroleptic) complexes from [ONNO]-Ti(OiPr)$_2$ type complexes indicates that the sidearm donor is strongly bound to the metal.

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles for **1-Ti-(OiPr)$_2$**, **6-Ti-6, 5-Ti-6**, and **5-Ti-1** This material is available free of charge via the Internet at http://pubs.acs.org.

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