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Titanium Complexes of Chelating Bis(phenolato) Ligands with Long Titanium−Sulfur Bonds. A Novel Type of Ancillary Ligand for Olefin Polymerization Catalysts†

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Summary: The sulfide-linked bis(phenol) tbmpH$_2$ (tbmp = 2,2′-thiobis(6-tert-butyl-4-methylphenolato)) gives a series of titanium complexes of the formula [Ti(tbmp)X$_2$]$_2$ or [Ti(tbmp)(L)X$_2$] (L = two-electron ligand, X = one-electron ligand). The molecular structures of [Ti(tbmp)(OiPr)$_2$]$_2$ and of [Ti(tbmp){C$_6$H$_4$(CH$_2$NMe$_2$)-2}Cl] were determined by single-crystal X-ray structural analyses. An unusually long titanium−sulfur bond of ∼270 pm is observed in both complexes which contain a six-coordinate titanium center. Variable-temperature NMR spectroscopy shows a fluxional coordination of the chelating aryl group in [Ti(tbmp){C$_6$H$_4$(CH$_2$NMe$_2$)-2}Cl].

Up to now, the development of new homogeneous Ziegler−Natta polymerization catalysts has relied on the use of metallocenes containing specifically substituted cyclopentadienyl ligands.[1] A new trend has been the incorporation of non-cyclopentadienyl ancillary ligands such as amido,[2] alkoxo,[3] and related polydentate[4] ligands. Titanium complexes of the formula [Ti(tbmp)X$_2$] derived from the sulfide-linked bis(phenol) tbmpH$_2$ (tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolato); X = Cl, O*i*Pr), activated with methyl aluminoxane, were first reported by Kakugo et al. to effectively polymerize ethylene, propylene, styrene, and dienes, as well as to copolymerize ethylene with styrene.[5,6] These titanium complexes were found to be more active than the mononuclear eight-electron complexes of the type [Ti(mbmp)X$_2$] (mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)).[7] Nevertheless, no data are available as yet in the literature on the structure and reactivity of group 4 metal complexes containing the tbmp ligand.[6,8] We have carried out single-crystal X-ray structural analyses on a series of titanium complexes with the tbmp ligand. In each of the complexes studied, a tridentate O,O,S-coordination with a long titanium−sulfur bond was found.[9] The consequence of this quite unexpected bonding situation is the predominance of six-coordination of the tetravalent titanium center due to the enhanced electrophilicity of the 10-electron [Ti(tbmp)X$_2$] unit.

As summarized in Scheme 1, the bis(phenol) tbmpH$_2$ smoothly reacts with a variety of simple titanium precursors to give derivatives of the type [Ti(tbmp)X$_2$]$_2$ or [Ti(tbmp)(L)X$_2$] (L = two-electron ligand, X = one-electron ligand), each containing a tridentate tbmp ligand. A single-crystal X-ray diffraction study of the sparingly soluble, red-orange di(isopropoxo) complex [Ti(tbmp)(O*i*Pr)$_2$]$_2$ (**1**)[10] shows the presence of a centrosymmetric dimer with a Ti$_2$O$_2$ lozenge (Figure 1).[11] The coordination sphere around the titanium center in **1** can be described as octahedral: The oxygen atoms of the bis(phenolato) ligand (O1, O2) and of two bridging O*i*Pr groups (O3, O3A) form the equatorial plane, while the

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† Dedicated to Professor G. E. Herberich on the occasion of his 60th birthday.

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(10) Crystal data for **1**: C$_{28}$H$_{42}$O$_4$STi, M_r = 522.6 g mol^{-1}, 0.36 × 0.24 × 0.15 mm, monoclinic, $C2/c$ (No. 15), a = 1760.7(2) pm, b = 2038.5(2) pm, c = 1651.9(1) pm, β = 100.061(9)°, V = 5837.8(9) × 10^{-30} m^3, Z = 8, ρ_{calc} = 1.189 mg m^{-3}, Cu Kα (λ = 154.178 pm), empirical absorption correction, T = 298 K, ω-scan, 3.0° < θ < 60.0°, F(000) = 2240, μ(Cu Kα) = 33.8 cm^{-1}. Number of reflections measured, 4545, 4329 independent reflections of which 3631 were assigned observed with $I > 2\sigma(I)$. The structure was solved (direct methods) and refined against all F^2 data, resulting in $wR2$ = 0.1697 and R = 0.059 (based on F_o^2).

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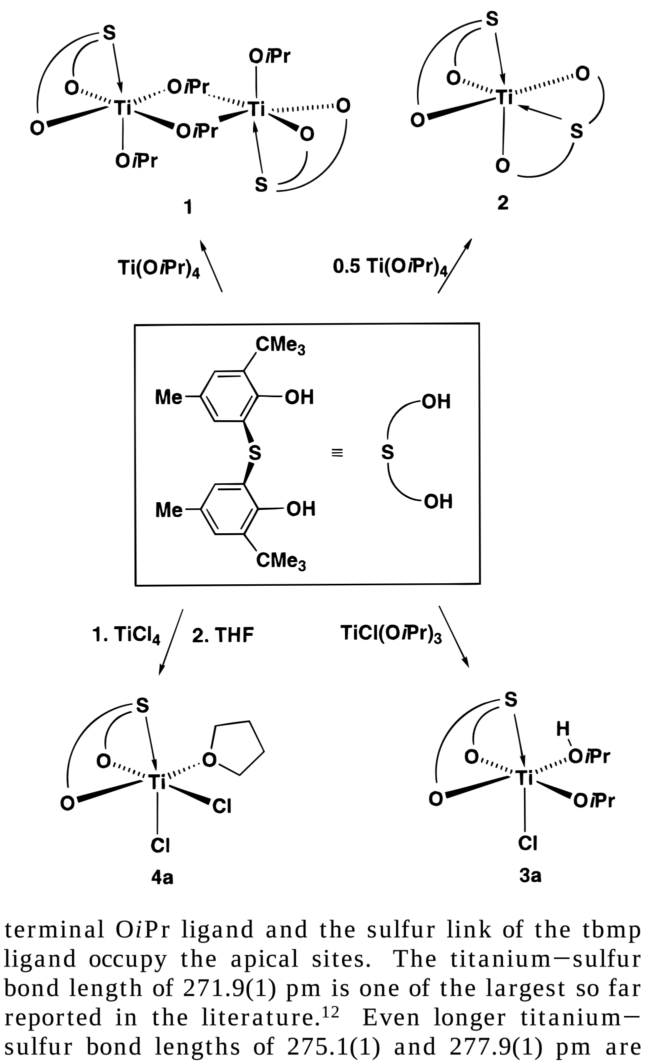
S0276-7333(96)00609-7 CCC: $12.00

Scheme 1



terminal O*i*Pr ligand and the sulfur link of the tbmp ligand occupy the apical sites. The titanium−sulfur bond length of 271.9(1) pm is one of the largest so far reported in the literature.[12] Even longer titanium−sulfur bond lengths of 275.1(1) and 277.9(1) pm are found[13] in the orange C_2-symmetric bis(chelate) complex Ti(tbmp)$_2$ (**2**),[6b] which also contains a distorted octahedral titanium center. The orange chloro isopropoxo complex [Ti(tbmp)Cl(O*i*Pr)] (**3**) and the dark brown dichloro complex [Ti(tbmp)Cl$_2$] (**4**)[5,6b] are presumably both dimeric but can be readily converted into better soluble adducts with Lewis basic solvents. Thus, the mononuclear 2-propanol adduct of **3** [Ti(tbmp)Cl(O*i*Pr) (HO*i*Pr)] (**3a**) completes its sixth coordination site at the tetravalent titanium center (titanium−sulfur bond length 269.3(1) pm) by coordination of a 2-propanol ligand.[13]

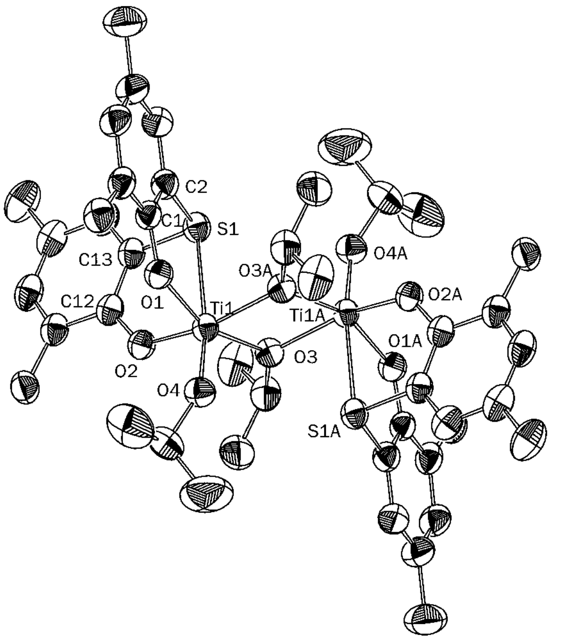
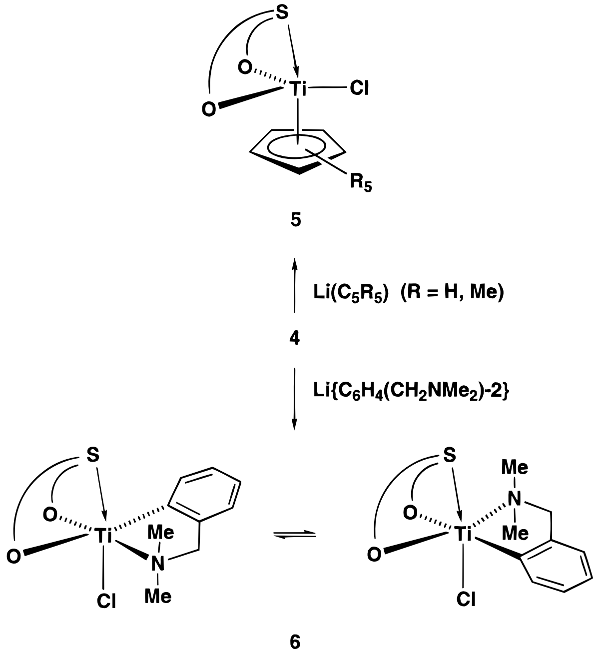


Figure 1. ORTEP diagram of the molecular structure of complex **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms as well as carbon atoms of the *tert*-butyl groups are omitted for the sake of clarity. Selected bond lengths (pm) and bond angles (deg): Ti−O1 189.9(2), Ti−O2 188.5(2), Ti−S1 271.9(1), Ti1−O3 201.8(2), Ti1−O3a 202.9(2), Ti1−O4 176.4(2), O1−Ti1−O2 92.3(1), O3−Ti1−O3a 73.70(9), O4−Ti1−S1 171.81(8), C1−O1−Ti1 132.8(2), C12−O2−Ti1 132.0(2), Ti1−O3−Ti1a 106.30(9), C3−S1−C2 100.8(2).

Scheme 2



The pronounced tendency of the titanium center in tbmp complexes to adopt a six- rather than a four- or five-coordination is in line with the difficulty we encountered during attempts to synthesize dialkyl derivatives of the type [Ti(tbmp)R$_2$]. Metathesis of **1**−**4** with a variety of alkylating reagents such as LiMe or MgMeCl resulted in the formation of intractable materials, in stark contrast to the facile formation of complexes of the type [Ti(mbmp)R$_2$].[7a,d] On the other hand, complexes **5** and **6** with the more electron-donating cyclopentadienyl ligand $C_5R'_5$ (R′ = H (**5a**), Me (**5b**))[13] and the chelating phenyl ligand $C_6H_4(CH_2NMe_2)$-2 can be straightforwardly prepared and isolated (Scheme 2). The crystallographically characterized complex [Ti(tbmp){$C_6H_4(CH_2NMe_2)$−2}Cl] (**6**) also exhibits an octahedral coordination (Figure 2). The only diastereomer obtained contains the chelating aryl group and the two oxygen atoms of the tbmp ligand (O1, O2) in the equatorial plane, while the sulfur and the chlorine atoms are at the apical positions (titanium−sulfur bond length 270.4(1)

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[12] Coordination of thioether at a tetravalent titanium center is exceedingly rare: (a) Olmstead, M. M.; Kessler, R. M.; Hope, H.; Yanuck, M. D.; Musker, W. K.; *Acta Crystallogr.* **1987**, *C43*, 1890. (c) Nadasdi, T. T.; Huang, Y.; Stephan, D. W. *Inorg. Chem.* **1993**, *32*, 347.

[13] Fokken, S.; Okuda, J.; Massa, W.; Kang, H.-C., unpublished results.

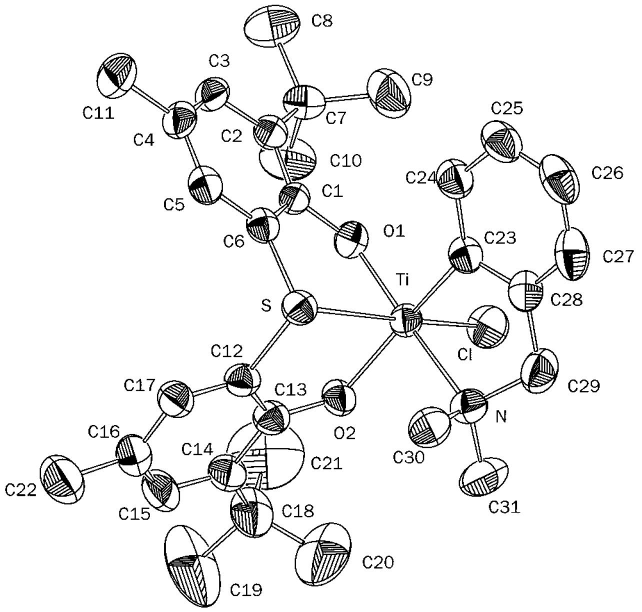

Figure 2. ORTEP diagram of the molecular structure of complex **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (pm) and bond angles (deg): Ti−Cl 225.1(1), Ti−S 270.4(1), Ti−O1 183.1(3), Ti−O2 187.9(3), Ti−N 228.5(4), Ti−C23 214.3(4), Cl−Ti−S 175.50(5), O2−Ti−C23 149.5(2), O1−Ti−N 163.9(1), Ti−N−C29 106.7(3), Ti−O1−C1 135.6(3), Ti−O2−C13 135.3(2), C6−S−C12 103.4(2).

pm).[14] In solution, the chiral complex **6** reveals fluxional behavior ($\Delta G^{\ddagger}$ (15 °C) = 62.3(4) kJ mol^{-1}) on the NMR time scale: The reversible dissociation of the aryl ligand's NMe$_2$ group, followed by the rotation about the titanium−carbon bond and complexation cause the apparent C_s symmetry of the molecule above the coalescence temperature.

We have confirmed the enhanced activity of some of the above tbmp complexes as compared to analogous mbmp complexes upon activation with methyl aluminoxane, *e.g.*, in the syndiospecific polymerization of styrene and copolymerization of ethylene with styrene.[15] The increased polymerization activity of the tbmp complexes may be ascribed to the substantially higher electrophilicity of four- or five-coordinate environments in the catalytically active species [Ti(tbmp)R(L)$_n$]$^+$ (n = 0, 1), despite the additional thioether coordination of the tridentate tbmp ligand.[16]

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl. Pentane and hexane were purified by distillation from sodium/triglyme benzophenone ketyl. 2,2′-Thiobis(6-*tert*-butyl-4-methylphenol) was prepared according to a procedure described in ref 8b. All other chemicals were commercially available and used as received unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200 or AM 400 spectrometer. Mass spectra were obtained on a Finnigan 8230 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department.

[Ti(tbmp)(O*i*Pr)$_2$]$_2$ (1). An ethereal solution of tbmpH$_2$ (1.22 g, 3.38 mmol in 10 mL) was layered on top of an ethereal solution of titanium tetra(isopropoxide) (1.0 mL, 3.38 mmol in 5 mL). After standing for 15 h at room temperature, precipitation of orange crystals was complete. The mother liquor was filtered off, and the crystals were washed with 10 mL of diethyl ether to give 1.75 g of product (99%). The low solubility in any common organic solvents precluded the recording of NMR spectra. Single crystals suitable for X-ray diffraction could be obtained by this method: EI MS m/z 522 (100, M$^+$/2), 463 (53, M$^+$/2 − O*i*Pr). Anal. Calcd for $C_{28}H_{42}O_4STi$: C, 64.35; H, 8.10. Found: C, 64.01, H, 8.18.

[Ti(tbmp)(C$_5$H$_5$)Cl] (5a). Precooled diethyl ether (15 mL) was added to a solid mixture of [Ti(tbmp)Cl$_2$] (**4**; 554 mg, 1.17 mmol) and [Li(C$_5$H$_5$)] (84 mg, 1.17 mmol) at −78 °C, and the reaction mixture was allowed to warm slowly to room temperature. After being stirred for 4 h at room temperature, the orange mixture was filtered, the filter bed was extracted with 2 × 20 mL of diethyl ether, and the combined filtrates were concentrated under vacuum to one-third of the volume. Addition of 10 mL of hexane precipitated 510 mg of black red microcrystals (87%): ^{1}H NMR (CDCl$_3$, 25 °C) δ 1.25 (s, 18 H, 6-C(CH$_3$)$_3$), 2.21 (s, 6 H, 4-CH$_3$), 6.76 (s, 5 H, C$_5$H$_5$), 6.98 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, 5-H), 7.27 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, 3-H); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C) δ 20.8 (4-CH$_3$), 29.8 (6-C(*C*H$_3$)$_3$), 35.2 (6-*C*(CH$_3$)$_3$), 119.4 (C$_5$H$_5$), 128.3 (C-2), 129.9 (C-5), 130.4 (C-4), 131.7 (C-3), 138.4 (C-6), 167.1 (C-1); EI MS m/z 504 (86, M$^+$), 439 (100, M$^+$ − C$_5$H$_5$). Anal. Calcd for $C_{27}H_{33}ClO_2STi$: C, 64.22; H, 6.59. Found: C, 64.35; H, 6.49.

[Ti(tbmp)(C$_5$Me$_5$)Cl] (5b). This compound was prepared in a manner analogous to that described for the synthesis of **5a** and isolated as red microcrystals (84%): ^{1}H NMR (CDCl$_3$, 25 °C) δ 1.35 (s, 18 H, 6-C(CH$_3$)$_3$), 2.25 (s, 15 H, C$_5$(CH$_3$)$_5$), 2.26 (s, 6 H, 4-CH$_3$), 7.05 (d, $^4J_{HH}$ = 1.9 Hz, 2 H, 5-H), 7.23 (d, $^4J_{HH}$ = 1.9 Hz, 2 H, 3-H); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C) δ 13.5 (C$_5$(*C*H$_3$)$_5$), 20.7 (4-CH$_3$), 30.1 (6-C(*C*H$_3$)$_3$), 34.8 (6-*C*(CH$_3$)$_3$), 124.3 (C-2), 129.2 (C-5), 130.1 (C-4), 130.3 (*C*$_5$(CH$_3$)$_5$), 130.4 (C-3), 138.1 (C-6), 165.6 (C-1); EI MS m/z 574 (89, M$^+$), 439 (100, M$^+$ − C$_5$Me$_5$). Anal. Calcd for $C_{32}H_{43}ClO_2STi$: C, 66.83; H, 7.54. Found: C, 67.05; H, 7.64.

[Ti(tbmp){C$_6$H$_4$(CH$_2$NMe$_2$)−2}Cl] (6). Precooled diethyl ether (20 mL) was added to a mixture of [Ti(tbmp)Cl$_2$] (**4**; 475 mg, 1.0 mmol) and [Li{C$_6$H$_4$(CH$_2$NMe$_2$)−2}] (155 mg, 1.0 mmol) at −78 °C, and the reaction mixture was allowed to warm slowly to room temperature. After being stirred for 4 h at room temperature, the orange mixture was filtered, the filter bed was extracted with 2 × 10 mL of diethyl ether, and the combined filtrates were concentrated under vacuum. Cooling to −78 °C afforded red rhombic crystals in two crops. Yield 473 mg (82%): ^{1}H NMR (CDCl$_3$, +60 °C) δ 1.38 (s, 18 H, 6-C(CH$_3$)$_3$), 2.23 (s, 6 H, 4-CH$_3$), 2.84 (s, 6 H, NMe$_2$), 4.01 (s, 2 H, CH$_2$), 6.83 (m, 1 H, C$_6$H$_4$), 7.00−7.15 (overlapping m, 6 H,

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[14] Crystal data for **6**·0.5Et$_2$O: $C_{33}H_{45}ClO_{2.5}NTi$, M_r = 611.2 g mol^{-1}, 0.4 × 0.5 × 0.8 mm, monoclinic, $P2_1/c$ (No. 14), a = 1869.3(5) pm, b = 1046.3(5) pm, c = 1822.2(4) pm, β = 109.87(2)°, V = 3352(4) × 10^{-30} m^3, Z = 4, ρ_{calc} = 1.21 mg m^{-3}, Mo Kα (λ = 71.073 pm), empirical absorption correction, T = 298 K, ω-scan, 3.0° < θ < 24.0°, F(000) = 1300, μ(Mo Kα) = 4.2 cm^{-1}. Number of reflections measured, 10816, 5229 independent of which 3317 were assigned observed with $I > 2\sigma(I)$. The structure was solved (direct methods) and refined, resulting in R = 0.049, Rw = 0.056.

[15] The productivity values (g of syndiotactic polystyrene/(mmol of Ti h)) in syndiospecific styrene polymerization under standardized conditions (styrene 43.7 mmol, methyl aluminoxane 7.5 mmol, titanium complex 0.05 mmol in 10 mL of toluene, T = 80 °C, reaction time 2 h) are as follows: Ti(mbmp)Cl$_2$ (0.25; M_w = 46 230, M_w/M_n = 3.2); **4** (3.50; M_w = 20 250, M_w/M_n = 2.0), **3** (18.00; M_w = 55 770, M_w/M_n = 4.8); **1** (7.50; M_w = 49140, M_w/M_n = 6.1). Fokken, S.; Masoud, E.; Okuda, J., unpublished results.

[16] The nature of the soft thioether coordination at the hard titanium(IV) center is unknown.[12,17] Tetrahydrothiophene has been used by Teuben et al. as a weakly coordinating Lewis base in metallocenium alkyl cations: Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Cat.* **1990**, *62*, 277.

[17] Theoretical calculation (RHG/3-31G level) of a model compound [Ti(OCH$_2$CH$_2$SCH$_2$CH$_2$O)Cl$_2$] also predicts the presence of a long titanium−sulfur coordination of 273 pm; Kawamura-Kuribayashi, H., unpublished results.

C_6H_4, 3-H, 5-H), 7.47 (m, 1 H, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, +60 °C) δ 20.8 (4-CH_3), 29.6 (C(CH_3)$_3$), 35.1 (*C*(CH_3)$_3$), 50.2 (N(CH_3)$_2$), 69.5 (CH_2), 124.1 (C_6H_4), 125.3 (C_6H_4), 128.3 (C_6H_4), 129.5 (C-2), 129.9 (C_6H_4), 130.1 (C-5), 131.6 (C-4), 133.0 (C-3), 138.8 (C-6), 142.5 (C_6H_4), 164.0 (C-1), 196.7 (*ipso*-C_6H_4); ^1H NMR ($CDCl_3$, −20 °C) δ 1.35, 1.41 (s, 2 × 9 H, 6-C(CH_3)$_3$), 2.24, 2.26 (s, 2 × 3 H, 4-CH_3), 2.63, 3.03 (s, 2 × 3 H, N(CH_3)$_2$), 3.52 (d, $^2J_{HH} = 13.1$ Hz, 1 H, CH_2), 4.67 (d, $^2J_{HH} = 13.1$ Hz, 1 H, CH_2), 6.83 (m, 1 H, C_6H_4), 7.00−7.17 (overlapping m, 6 H, C_6H_4, 3-H, 5-H), 7.45 ("d", 1 H, C_6H_4); $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C) δ 20.7, 21.0 (4-CH_3), 29.0, 29.4 (C(*C*H_3)$_3$), 35.0, 35.1 (*C*(CH_3)$_3$), 49.5, 50.7 (N(CH_3)$_2$), 68.9 (CH_2), 124.3 (C-2), 124.4 (C_6H_4), 125.1 (C_6H_4), 128.3 (C_6H_4), 129.7 (C-5), 129.8 (C-2′), 130.0 (C_6H_4), 130.9 (C-5′), 131.0 (C-4), 131.7 (C-4′), 132.2 (C-3), 132.6 (C-3′), 136.7 (C-6), 137.7 (C-6′), 142.6 (C_6H_4), 163.0 (C-1), 164.9 (C-1′), 195.4 (*ipso*-C_6H_4); EI MS m/z 573 (20, M^+), 439 (3, $M^+ - C_6H_4CH_2NMe_2$). Anal. Calcd for $C_{31}H_{40}ClNO_2STi$: C, 64.86; H, 7.02; N, 2.44. Found: C, 64.82; H, 7.01; N, 2.41.

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Supporting Information Available: Listings of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **1** and **6** (23 pages). Ordering information is given on any current masthead page.

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