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Imido and Amido Titanium Complexes that Contain a [OSSO]-Type Bis(phenolato) Ligand: Synthesis, Structures, and Hydroamination Catalysis

Bing Lian,[a] Thomas P. Spaniol,[a] Patricia Horrillo-Martínez,[b] Kai C. Hultzsch,[b][‡] and Jun Okuda*[a]

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Salt metathesis reaction of the imido complex [Ti(NR)$Cl_2(NC_5H_5)_3$] (R = *t*Bu, C_6H_3*i*Pr_2-2,6) with 1 equiv. of the lithium salt of the corresponding [OSSO]-type bis(phenol) [edtbpH_2: (HOC_6H_2-*t*Bu_2-4,6)$_2$(SCH_2CH_2S); *rac*-(cydtbp)H_2: (HOC_6H_2-*t*Bu_2-4,6)$_2$($S_2C_6H_{10}$-1,2)] afforded imido titanium complexes [Ti(edtbp)(N*t*Bu)(NC_5H_5)] (**1**), [Ti(edtbp)(NC_6H_3-*i*Pr_2-2,6)(NC_5H_5)] (**2**), and [Ti{*rac*-(cydtbp)}(N*t*Bu)(NC_5H_5)] (**3**). The bis(dimethylamido)titanium complex [Ti(edtbp)-(NMe_2)$_2$] (**4**) was synthesized by protonolysis of [Ti(NMe_2)$_4$] with bis(phenol) edtbpH_2. Reaction of [Ti(NMe_2)Cl_3] with the lithium salt of the bis(phenol) gave the chloro dimethylamido complex [Ti(edtbp)(NMe_2)Cl] (**5**) in high yield. All complexes were characterized by NMR spectroscopy and elemental analysis. Additionally, complexes **1** and **5** were studied by X-ray diffraction analysis. Imido titanium complex **1** shows moderate activity in the intramolecular hydroamination reaction of 5-phenylpent-4-ynylamine. Complexes **1**–**3** catalyze the intramolecular hydroamination of aminoalkenes.

Introduction

The catalytic hydroamination, constituting the addition of N–H across the carbon–carbon multiple bond, has become an attractive carbon–nitrogen bond forming process in the recent past.[1] In particular, group 4 metal systems exhibit the catalytic performance distinct from other metal systems.[2] We have recently introduced configurationally rigid titanium complexes containing a linked bis(phenolato) [OSSO]-type ligand that polymerize styrene isospecifically,[3a–3d,3g] and oligomerize α-olefins regioselectively.[3e] Living polymerization of methyl methacrylate could be achieved with the titanium enolate complex.[3f] The helical configuration around the metal center ensures the isospecific polymerization of styrene and related monomers.[4] To explore the suitability of this [OSSO]-type titanium system for hydroamination reactions, we have prepared both imido- and amidotitanium complexes containing this [OSSO]-type ligand and investigated their hydroamination reactivity. In the course of the preparation of this article, Doye et al. reported that the amido titanium and zirconium catalysts generated in situ with this type of ligand catalyze the hydroamination of alkynes and alkenes.[2l]

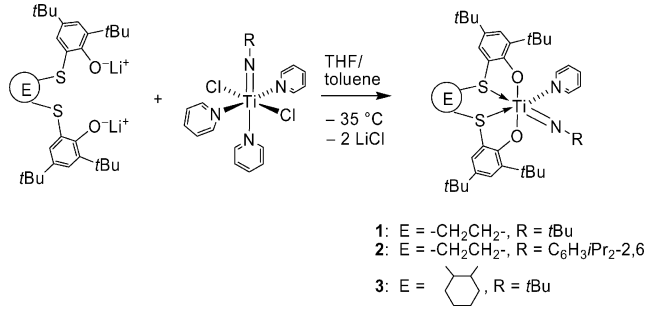
[a] Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
Fax: +49-241-80-92644
E-mail: jun.okuda@ac.rwth-aachen.de
[b] Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestr. 42, 91054 Erlangen, Germany
[‡] New address: Rutgers, The State University of New Jersey, Department of Chemistry and Chemical Biology, 610 Taylor Road, Piscataway, NJ 08854-8087, USA

Results and Discussion

Imido and Amidotitanium Complexes

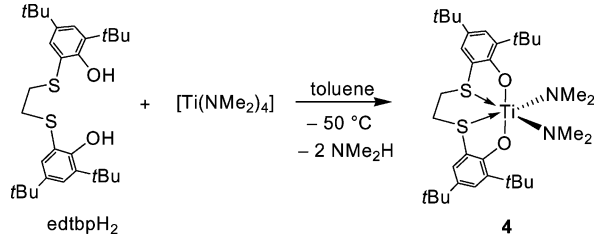
Reaction of the imido precursor [Ti(NR)$Cl_2(NC_5H_5)_3$] (R = *t*Bu, C_6H_3*i*Pr_2-2,6) with one equiv. of the lithium salt of the bis(phenol) [edtbpH_2: (HOC_6H_2-*t*Bu_2-4,6)$_2$-(SCH_2CH_2S); *rac*-(cydtbp)H_2: (HOC_6H_2-*t*Bu_2-4,6)$_2$-($S_2C_6H_{10}$-1,2)] generated in situ in THF/toluene mixture at –35 °C led to the formation of the imido titanium complexes **1**–**3** (Scheme 1). The new complexes were isolated as crystals in high yield (80–87%) and characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis. The ^{1}H NMR spectrum of both [Ti(edtbp)(N*t*Bu)-(NC_5H_5)] (**1**) and [Ti(edtbp)(NC_6H_3*i*Pr_2-2,6)(NC_5H_5)] (**2**) in C_6D_6 at room temperature shows an ABCD spin system for the SCH_2CH_2S bridge with four sets of signals [**2**: δ = 2.60 (dm), 2.48 (dm), 2.24 (td), and 2.13 ppm (td)]. The ^{1}H-^{13}C HMQC spectrum gives the correlation of the ^{1}H NMR resonances with two ^{13}C NMR resonances at δ = 37.74 (2.60 and 2.24 ppm) and 35.07 ppm (2.48 and 2.13 ppm), respectively. In the ^{1}H NMR spectrum of **2** four singlets for the four *tert*-butyl groups are found (δ = 1.89, 1.71, 1.32, and 1.23 ppm), indicating a rigid C_1-symmetric molecular structure in solution. According to ^{1}H NMR spectroscopic studies, dissociation of the pyridine ligand in the imido titanium complexes **1**–**3** is slow up to 100 °C.

The bis(dimethylamido)titanium complex **4** was synthesized under dimethylamine elimination from [Ti(NMe_2)$_4$] and bis(phenol) edtbpH_2 in 1:1 molar ratio (Scheme 2) and isolated as red crystals in 85% yield. The ^{1}H NMR spectrum of **4** in C_6D_6 shows an AB spin pattern for the



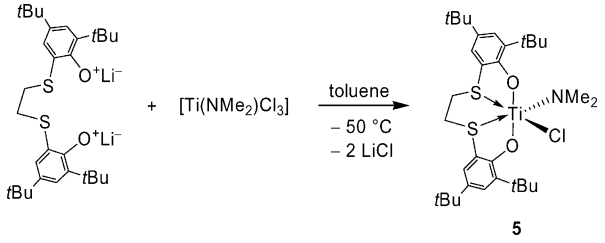
Scheme 1.

SCH_2CH_2S bridge (δ = 2.56 and 2.16 ppm) and one singlet at δ = 3.53 ppm for all 4 methyl groups of the dimethylamido groups. This is in agreement for the bis(dimethylamido)titanium complex generated in situ.[21] These NMR spectra data suggest a C_2-symmetric molecular structure in solution.



Scheme 2.

Treating Li_2(edtbp) with one equiv. of [Ti(NMe_2)Cl_3] in toluene gave the chloro dimethylamido complex [Ti(edtbp)(NMe_2)Cl] (**5**) as red crystals in 81% yield (Scheme 3). In the ^{1}H NMR spectrum of **5**, an ABCD spin system for the SCH_2CH_2S bridge was observed with resonances at δ = 2.52 (dt), 2.38 (dt), 2.22 (td), and 1.97 ppm (td) which correlate in the HMQC 2D NMR spectrum with two ^{13}C NMR resonances at δ = 37.87 (2.52 and 2.22 ppm) and 37.80 ppm (2.38 and 1.97 ppm), respectively. One singlet at δ = 3.68 ppm was observed for the two equivalent methyl groups of the dimethylamido group.



Scheme 3.

X-ray Crystal Structures of 1 and 5

Single crystals of complexes **1** and **5** were obtained from pentane and have been characterized by X-ray diffraction analysis. Details of the crystal structure determination are given in Table 3 (see Exp. Sect.). The molecular studies of **1** and **5** in the solid state as well as selected interatomic distances and angles are shown in Figure 1 and Figure 2. Complexes **1** and **5** are monomeric in the solid state.

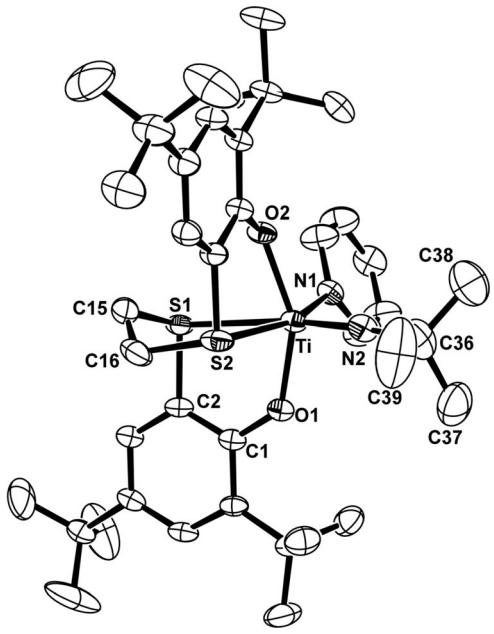


Figure 1. Molecular structure of complex [Ti(edtbp)(N*t*Bu)(NC_5H_5)] (**1**) (hydrogen atoms were omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti–O1, 1.965(2); Ti–O2, 1.985(2); Ti–S1, 2.7853(10); Ti–S2, 2.5826(10); Ti–N1, 2.202(2); Ti–N2, 1.705(3); N2–C36, 1.442(4); O1–C1, 1.327(3); O1–Ti–O2, 151.96(9); S1–Ti–S2, 80.73(3); N1–Ti–N2, 102.66(11); Ti–N2–C36, 173.6(3); O2–Ti–S1, 79.73(7); O2–Ti–S2, 77.62(6); O2–Ti–N2, 104.14(11); O2–Ti–N1, 91.70(9).

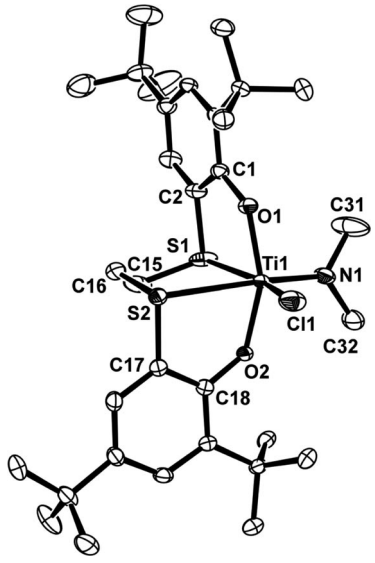


Figure 2. Molecular structure of complex [Ti(edtbp)(NMe_2)Cl] (**5**) (hydrogen atoms were omitted for clarity). Only one of the two crystallographically independent atoms are shown. Selected bond lengths [Å] and angles [°]: Ti1–O1, 1.887(2); Ti1–O2, 1.8852(19); Ti1–S1, 2.5997(10); Ti1–S2, 2.7229(9); Ti1–N1, 1.877(3); Ti1–Cl1, 2.3129(10); N1–C31, 1.450(5); N1–C32, 1.441(4); O1–Ti1–O2, 156.64(9); S1–Ti1–S2, 78.31(3); N1–Ti1–Cl1, 103.86(11); C31–N1–Ti1, 124.9(2); C32–N1–Ti1, 125.9(2); C31–N1–C32, 109.3(3); O1–Ti1–S1, 77.19(7); O1–Ti1–N1, 97.85(10).

Table 1. Titanium···sulfur distances in [OSSO]-type bis(phenolato) titanium complexes.

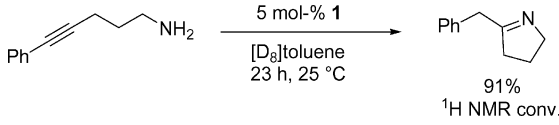
Compound	Ti–S1 [Å] (*trans* group)	Ti–S2 [Å] (*trans* group)	Ref.
[Ti(etbmp)Cl_2]	2.647(3) (Cl)	2.647(3) (Cl)	[3b]
[Ti(edtbp)Me_2]	2.8056(7) (Me)	2.8417(7) (Me)	[3e]
[Ti(edtbp)$(CH_2Ph)_2$]	2.8836(7) (η^2-CH_2Ph)	2.7472(7) (η^1-CH_2Ph)	[3c]
[Ti{(*R*,*R*)-(cytbmp)}(O*i*Pr)$_2$]	2.674(4) (O*i*Pr)	2.673(4) (O*i*Pr)	[3g]
[Ti(edtbp)MeCl]	2.6986(8) (Me)	2.6756(8) (Cl)	[3f]
[Ti(edtbp)Me{O(*i*PrO)C=CMe_2}]	2.6389(15) [O(*i*PrO)C=CMe_2]	2.7327(14) (Me)	[3f]
[Ti(edtbp)Me($OCMe_2CMe_2CO_2$*i*Pr)]	2.7156(8) ($OCMe_2CMe_2CO_2$*i*Pr)	2.7227(8) (Me)	[3f]
[Ti(edtbp)(N*t*Bu)(NC_5H_5)] (**1**)	2.7853(10) (N*t*Bu)	2.5826(10) (NC_5H_5)	this work
[Ti(edtbp)(NMe_2)Cl] (**5**)	2.7229(9) (NMe_2)	2.5997(10) (Cl)	this work

The octahedrally coordinated titanium center in complex **1** is coordinated by two *trans*-oxygen atoms, two *cis*-sulfur donor atoms, and the *cis*-arranged pyridine and *tert*-butylamido ligands (Figure 1). The Ti(edtbp) moiety adopts a C_2-symmetric helical framework similar as observed in the previous study.[3a] The O1–Ti–O2 [151.96(9)°] bond angle is slightly narrower than that of analogous Ti(edtbp) complexes, in the range of 156.7(2) –157.82(10)°,[3] indicating the formation of a fairly open titanium coordination sphere. The bond angle of S1–Ti–S2 [80.73(3)°] is slightly wider than the value of a similar complex [78.37(8)°];[3b] the Ti–S bond length [2.7853(10) Å and 2.5826 (10) Å] in **1** is comparable to the values in a reported dichloro complex [2.647(3) Å].[3b] The Ti–N2 bond length [1.705(3) Å] is much shorter than the value of a coordinated Ti–N1 bond [2.202(2) Å] in **1**. The bond angle of Ti–N2–C36 [173.6(3)°] is close to linear and comparable to the reported values,[5] indicating that N*t*Bu group donates four electrons to the titanium metal center.

The solid-state structure of dimethylamido complex **5** also features a six-coordinate titanium center with a C_2-symmetric helical Ti(edtbp) fragment (Figure 2). The O1–Ti–O2 [156.64(9)°] bond angle is close to that of Ti(edtbp) complexes [156.7(2)–157.82(10)°].[3] The Ti–N1 [1.877(3) Å] bond length is comparable to the values of similar amidotitanium complexes [1.862(3)–1.917(5) Å].[6,2k] The nitrogen atom is trigonal with the sum of angles around N1 atom close to 360° (calculated: 360.1°), indicating strong π-electron donation to the Ti center. Notably, the elongated Ti–S2 [2.7229(9) Å] bond length as compared to that of Ti–S1[2.5997(10) Å] is caused by the stronger electron-donating *trans*-dimethylamido group in the solid state. Detailed comparisons of the *trans*-influence on the Ti–S bond length are shown in Table 1.

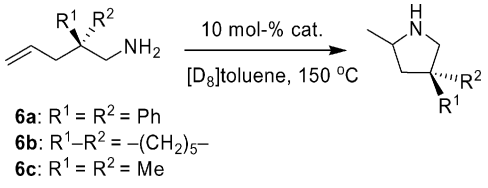
Intramolecular Hydroamination of Aminoalkyne and Aminoalkene

Complex **1** was selected for the catalytic study in the intramolecular hydroamination of 5-phenylpent-4-ynylamine (Scheme 4). By combination of 5 mol-% of catalyst **1** with substrate in toluene solution at room temperature, over 91% conversion was observed to give the cyclic imine product within 23 h. In comparison with the reported activity of a titanocene catalyst Cp_2TiMe_2 (98% yield, 110 °C, 6 h),[7a] the imidotitanium catalyst with a [OSSO]-type bis(phenolato) ligand shows higher activity under rather mild reaction conditions. However, the activity of catalyst **1** is still lower than the known bis(amidinato)titanium catalyst [Ti(C_6F_5C(O)N*t*Bu)$_2$(NMe_2)$_2$] (97% yield, 25 °C, 15 min).[7b] The intermolecular hydroamination with this type of catalyst has been investigated by Doye et al.[2l]



Scheme 4.

Catalysts **1**–**3** have been studied in the intramolecular hydroamination of aminoalkenes (Scheme 5). Results are summarized in Table 2. Only trace amounts of desired cyclization product was observed after short reaction times at 150 °C (entries 5 and 7). High conversions (85–94%) are achieved at prolonged reaction times of 14–22 d (entries 3, 4 and 6). As commonly observed,[1i] the *gem*-diphenyl activated[8] substrate **6a** reacts faster than the aminoalkene **6b** using the rigid complex **3** with a cydtbp ligand (Table 2, entry 3 vs. entry 6). However, the opposite is true for the more flexible edtbp complex **1** (entry 1 vs. entry 4). Although catalysts **1**–**3** are active in the intramolecular hy-



Scheme 5.

Table 2. Intramolecular hydroamination of aminoalkenes using catalysts **1**–**3**.[a]

Entry	Substrate	Complex	Time [d]	% Conv.[b]
1	**6a**	**1**	29	61
2	**6a**	**2**	23	78
3	**6a**	**3**	14	85
4	**6b**	**1**	16	92
5	**6b**	**2**	20 h	< 1
6	**6b**	**3**	22	94
7	**6c**	**1**	21 h	< 1

[a] Reaction conditions: substrate: 0.2 mmol, catalyst: 0.02 mmol (10 mol-%), solvent: 0.5 mL [D_8]toluene, temperature: 150 °C. [b] Determined by ^{1}H NMR spectroscopy.

droamination of aminoalkenes, their catalytic activities are rather low in comparison with titanium catalysts reported in the literature, e.g. [Ti(NMe_2)$_4$] (substrate **6a**, 5 mol-% cat., 92% yield, 24 h, 110 °C).[2e]

Conclusions

We have isolated imido and amido titanium complexes that contain a tetradentate [OSSO]-type bis(phenolato) ligand. The imido complexes were found to be catalytically active in the intramolecular hydroamination of aminoalkynes and aminoalkenes. The moderate catalytic activities of these imido catalysts were probably caused by the sterically crowded titanium center with the strongly coordinated pyridine ligand. Further studies will be undertaken to achieve enantioselective hydroamination reactions[1b,1e,1f,1h] using optically pure [OSSO]-type group 4 metal catalysts.[3d,3g]

Experimental Section

General: All experiments were carried out under purified argon using standard Schlenk techniques or a glove box (<1 ppm O_2, 1 ppm H_2O). Toluene, pentane, diethyl ether, dichloromethane, and THF were purified from the MBraun SPS-800 system prior to use. Deuterated solvents were purchased from Aldrich and purified before use. All other chemicals were commercially available and used after appropriate purification. Compounds (HOC_6H_2-*t*Bu_2-4,6)$_2$(SCH_2CH_2S) (edtbpH_2),[3a] *rac*-(2,3-*trans*-butanediyl-1,4-dithiabutanediyl)-2,2′-bis{4,6-di-*tert*-butylphenol} [*rac*-(cydtbp)H_2],[3d] [Ti(N*t*Bu)Cl_2(NC_5H_5)$_3$],[5] [Ti(NC_6H_3*i*Pr_2-2,6)Cl_2(NC_5H_5)$_3$],[5] [Ti(NMe_2)Cl_3],[9] 5-phenylpent-4-ynylamine,[10a] 2,2-diphenylpent-4-enylamine (**6a**),[10b] *C*-(1-allylcyclohexyl)methylamine (**6b**)[10c] and 2,2-dimethylpent-4-enylamine (**6c**)[10d] were synthesized according to literature methods. NMR spectra were recorded on Bruker DRX 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz) and Varian 200 spectrometers in Teflon-valved NMR tubes at 25 °C unless stated otherwise. ^{1}H and ^{13}C NMR chemical shifts were determined using residual solvent resonances and are reported vs. $SiMe_4$. Assignment of signals was made from ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC 2D NMR experiments. Coupling constants are given in Hertz. Elemental analyses were performed by the Microanalytical Laboratory of this department.

[Ti(edtbp)(N*t*Bu)(NC_5H_5)] (1): To a solution of [Ti(N*t*Bu)Cl_2(NC_5H_5)$_3$] (1.25 g, 2.92 mmol) in THF (20 mL) was slowly added at –35 °C a solution of Li_2(edtbp) in 30 mL of toluene, generated in situ from edtbpH_2 (1.47 g, 2.92 mmol) and *n*BuLi (2.34 mL, 2.5 M in hexane, 5.85 mmol). The reaction mixture was warmed to room temperature and stirred for 6 h. After removal of all volatiles under vacuum, the residue was recrystallized from pentane to give [Ti(edtbp)(N*t*Bu)(NC_5H_5)] (**1**) as orange crystals (1.67 g, 82%). A crystal of **1** suitable for X-ray diffraction analysis was selected. ^{1}H NMR ([D$_6$]benzene): δ = 9.28 (dt, $^3J_{HH}$ = 4.6, $^4J_{HH}$ = 1.7 Hz, 2 H, *o*-H, NC_5H_5), 7.63 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.61 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.43 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.20 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 6.70 (tt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.7 Hz, 1 H, *p*-H, NC_5H_5), 6.48 (tm, $^3J_{HH}$ = 6.4 Hz, 2 H, *m*-H, NC_5H_5), 2.72 (dm, $^2J_{HH}$ = 10.1 Hz, 1 H, SCH_2), 2.58 (dm, $^2J_{HH}$ = 10.1 Hz, 1 H, SCH_2), 2.18 (d, $^2J_{HH}$ = 10.1 Hz, 2 H, SCH_2), 1.97 [s, 9 H, C(CH_3)$_3$], 1.80 [s, 9 H, C(CH_3)$_3$], 1.33 [s, 9 H, C(CH_3)$_3$], 1.23 [s, 9 H, C(CH_3)$_3$], 1.20 [s, 9 H, NC(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 168.86 (Ph-*C*1), 167.23 (Ph-*C*1′), 150.01 (NC_5H_5-*o*-*C*), 139.73 (Ph-*C*6), 138.36 (Ph-*C*6′), 138.27 (NC_5H_5-*p*-*C*), 138.08 (Ph-*C*4), 137.03 (Ph-*C*4′), 128.43 (Ph-*C*5), 128.31 (Ph-*C*5′), 126.02 (Ph-*C*3), 126.01 (Ph-*C*3′), 124.10 (NC_5H_5-*m*-*C*), 117.20 (Ph-*C*2), 116.11 (Ph-*C*2′), 68.28 [N*C*(CH_3)$_3$], 37.84 (S*C*H$_2$), 36.16 [*C*(CH_3)$_3$], 35.69 [*C*(CH_3)$_3$], 34.53 [*C*(CH_3)$_3$], 34.29 (S*C*H$_2$), 34.23 [*C*(CH_3)$_3$], 32.04 [NC(*C*H_3)$_3$], 31.85 [C(*C*H_3)$_3$], 31.73 [C(*C*H_3)$_3$], 29.87 [C(*C*H_3)$_3$], 29.76 [C(*C*H_3)$_3$] ppm. $C_{39}H_{58}N_2O_2S_2Ti$ (698.89): calcd. C 67.02, H 8.36, N 4.01; found C 67.86, H 8.43, N 3.87.

[Ti(edtbp)(NC_6H_3*i*Pr_2-2,6)(NC_5H_5)] (2): To a solution of [Ti(N-C_6H_3*i*Pr_2-2,6)Cl_2(NC_5H_5)$_3$] (1.55 g, 2.92 mmol) in THF (20 mL) was slowly added at –35 °C a solution of Li_2(edtbp) in 30 mL of toluene, generated in situ from edtbpH_2 (1.47 g, 2.92 mmol) and *n*BuLi (2.34 mL, 2.5 M in hexane, 5.85 mmol). The reaction mixture was warmed to room temperature and further stirred 6 h. After evaporation of volatile under vacuum, the residue was recrystallized with toluene/pentane to give [Ti(edtbp)(NC_6H_3*i*Pr_2-2,6)(NC_5H_5)] (**2**) as brown crystals (1.87 g, 80%). ^{1}H NMR ([D$_6$]-benzene): δ = 9.16 (dt, $^3J_{HH}$ = 4.6, $^4J_{HH}$ = 1.7 Hz, 2 H, *o*-H, NC_5H_5), 7.64 (d, ^4J = 2.4 Hz, 1 H, Ph-5-*H*), 7.58 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5′-*H*), 7.29 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.22 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 7.03 (d, $^3J_{HH}$ = 7.9 Hz, 2 H, NAr-3-*H*), 6.85 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, NAr-4-*H*), 6.66 (tt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.7 Hz, 1 H, *p*-H, NC_5H_5), 6.40 (tm, $^3J_{HH}$ = 6.4 Hz, 2 H, *m*-H, NC_5H_5), 4.49 [sept, $^3J_{HH}$ = 6.8 Hz, 2 H, $(CH_3)_2$C*H*], 2.60 (dm, $^2J_{HH}$ = 10.1 Hz, 1 H, SCH_2), 2.48 (dm, $^2J_{HH}$ = 10.1 Hz, 1 H, SCH_2), 2.24 (td, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1 H, SCH_2), 2.13 (td, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1 H, SCH_2), 1.89 [s, 9 H, C(CH_3)$_3$], 1.71 [s, 9 H, C(CH_3)$_3$], 1.32 [s, 9 H, C(CH_3)$_3$], 1.23 [d, $^3J_{HH}$ = 6.8 Hz, 6 H, (CH_3)$_2$CH], 1.22 [s, 9 H, C(CH_3)$_3$], 1.04 [d, $^3J_{HH}$ = 6.8 Hz, 6 H, (CH_3)$_2$CH] ppm. ^{13}C{^{1}H} NMR ([D$_6$]benzene): δ = 168.68 (Ph-*C*1), 166.89 (Ph-*C*1′), 156.92 (NAr-*C*1), 149.33 (NC_5H_5-*o*-*C*), 143.31 (NAr-*C*2), 140.92 (Ph-*C*6), 139.01 (Ph-*C*6′), 138.24 (NC_5H_5-*p*-*C*), 138.17 (Ph-*C*4), 136.95 (Ph-*C*4′), 127.62 (Ph-*C*5), 127.46 (Ph-*C*5′), 126.11 (Ph-*C*3), 125.85 (Ph-*C*3′), 124.22 (NC_5H_5-*m*-*C*), 121.92 (NAr-*C*3), 120.78 (NAr-*C*4), 117.47 (Ph-*C*2), 117.00 (Ph-*C*2′), 37.74 (S*C*H$_2$), 35.07 (S*C*H$_2$), 35.62 [*C*(CH_3)$_3$], 35.25 [*C*(CH_3)$_3$], 33.82 [*C*(CH_3)$_3$], 33.70 [*C*(CH_3)$_3$], 31.47 [C-(*C*H_3)$_3$], 31.31 [C(*C*H_3)$_3$], 29.56 [C(*C*H_3)$_3$], 29.41 [C(*C*H_3)$_3$], 27.41 [*C*H(CH_3)$_2$], 24.47 [CH(*C*H_3)$_2$], 24.06 [CH(*C*H_3)$_2$] ppm. $C_{47}H_{66}N_2O_2S_2Ti$ (803.04): calcd. C 70.30, H 8.28, N 3.49; found C 69.63, H 8.58, N 3.42.

[Ti{*rac*-(cydtbp)}(N*t*Bu)(NC_5H_5)] (3): To a solution of [Ti(N*t*Bu)-Cl_2(NC_5H_5)$_3$] (0.75 g, 1.76 mmol) in THF (20 mL) was slowly added at –35 °C a solution of Li_2{*rac*-(cydtbp)} in 30 mL of toluene, generated in situ from *rac*-(cydtbp)H_2 (0.98 g, 1.76 mmol) and *n*BuLi (1.40 mL, 2.5 M in hexane, 3.52 mmol). The reaction mixture was warmed to room temperature and further stirred overnight. After removal of all volatiles under vacuum, the residue was recrystallized from pentane to give [Ti{*rac*-(cydtbp)}(N*t*Bu)(NC_5H_5)] (**3**) as yellow crystals (1.15 g, 87%). ^{1}H NMR ([D$_6$]benzene): δ = 9.34 (dt, $^3J_{HH}$ = 4.6, $^4J_{HH}$ = 1.7 Hz, 2 H, *o*-H, NC_5H_5), 7.67 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-5-*H*), 7.65 (d, ^4J = 2.4 Hz, 1 H, Ph-5′-*H*), 7.48 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3-*H*), 7.30 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, Ph-3′-*H*), 6.68 (tt, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.7 Hz, 1 H, *p*-H, NC_5H_5), 6.47 (tm, $^3J_{HH}$ = 6.4 Hz, 2 H, *m*-H, NC_5H_5), 2.47 (td, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1 H, SC*H*), 2.34 (td, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 3.2 Hz, 1 H, SC*H*), 2.03 (m, 2 H, cyclohexyl), 2.01 [s, 9 H, C(CH_3)$_3$], 1.83 [s, 9 H, C(CH_3)$_3$], 1.68 (m, 2 H, cyclohexyl), 1.38 [s, 9 H, C(CH_3)$_3$], 1.28 [s, 9 H, NC(CH_3)$_3$], 1.22 [s, 9 H, C(CH_3)$_3$], 1.14 (m, 2 H, cyclo-

hexyl), 0.43 (m, 2 H, cyclohexyl) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): δ = 169.11 (Ph-*C*1), 167.47 (Ph-*C*1′), 150.13 (NC_5H_5-*o*-*C*), 138.24 (NC_5H_5-*p*-*C*), 137.92 (Ph-*C*6), 137.08 (Ph-*C*6′), 130.65 (Ph-*C*4), 130.61 (Ph-*C*4′), 128.44 (Ph-*C*5), 128.32 (Ph-*C*5′), 126.27 (Ph-*C*3), 126.18 (Ph-*C*3′), 124.04 (NC_5H_5-*m*-*C*), 114.89 (Ph-*C*2), 114.30 (Ph-*C*2′), 68.07 [N*C*(CH$_3$)$_3$], 52.68 (S*C*H), 50.71 (S*C*H), 36.21 [*C*(CH$_3$)$_3$], 35.75 [*C*(CH$_3$)$_3$], 34.08 [*C*(CH$_3$)$_3$], 34.05 [*C*(CH$_3$)$_3$], 32.03 [NC(*C*H$_3$)$_3$], 31.85 [C(*C*H$_3$)$_3$], 31.74 [C(*C*H$_3$)$_3$], 30.01 (cyclohexyl), 29.94 [C(*C*H$_3$)$_3$], 29.85 [C(*C*H$_3$)$_3$], 29.48 (cyclohexyl), 25.56 (cyclohexyl), 25.44 (cyclohexyl) ppm. $C_{43}H_{64}N_2O_2S_2Ti$ (752.98): calcd. C 68.59, H 8.57, N 3.72; found C 67.92, H 8.60, N 3.41.

[Ti(edtbp)(NMe$_2$)$_2$] (4): [Ti(NMe$_2$)$_4$] (0.45 g, 1.99 mmol) and 15 mL toluene were charged in a 100 mL Schlenk tube and a solution of edtbpH$_2$ (1.0 g, 1.99 mmol) in 50 mL of toluene was added dropwise at –50 °C. The reaction mixture was warmed to room temperature and further stirred overnight. After removal of all volatiles under vacuum, the residue was recrystallized from pentane to give [Ti(edtbp)(NMe$_2$)$_2$] (**4**) as red crystals (1.08 g, 85%). ^1H NMR ([D$_6$]benzene): δ = 7.55 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, Ph-5-*H*), 7.25 (d, $^4J_{HH}$ = 2.4 Hz, 2 H, Ph-3-*H*), 3.53 [s, 12 H, N(C*H*$_3$)$_2$], 2.56 (d, $^2J_{HH}$ = 12.0 Hz, 2 H, SC*H*$_2$), 2.16 (d, $^2J_{HH}$ = 12.0 Hz, 2 H, SC*H*$_2$), 1.77 [s, 18 H, C(C*H*$_3$)$_3$], 1.22 [s, 18 H, C(C*H*$_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): δ = 166.91 (Ph-*C*1), 140.94 (Ph-*C*6), 137.17 (Ph-*C*4), 127.37 (Ph-*C*5), 125.91 (Ph-*C*3), 117.01 (Ph-*C*2), 47.70 [N(*C*H$_3$)$_3$], 37.12 (S*C*H$_2$), 35.38 [*C*(CH$_3$)$_3$], 33.83 [*C*(CH$_3$)$_3$], 31.32 [C(*C*H$_3$)$_3$], 29.61 [C(*C*H$_3$)$_3$] ppm. $C_{34}H_{56}N_2O_2S_2Ti$ (636.82): calcd. C 64.13, H 8.86, N 4.40; found C 64.54, H 8.70, N 4.08.

[Ti(edtbp)(NMe$_2$)Cl] (5): [Ti(NMe$_2$)Cl$_3$] (0.40 g, 2.02 mmol) and 15 mL toluene were charged in a 100 mL Schlenk, and a solution of Li$_2$(edtbp) in 50 mL of toluene, generated in situ from edtbpH$_2$ (1.02 g, 2.02 mmol) and *n*BuLi (1.61 mL, 2.5 M in hexane, 4.04 mmol), was added dropwise at –50 °C. The reaction mixture was warmed to room temperature and further stirred overnight. After evaporation of volatile under vacuum, the residue was recrystallized from pentane to give [Ti(edtbp)(NMe$_2$)Cl] (**5**) as red crystals (1.03 g, 81%). ^1H NMR ([D$_6$]benzene): δ = 7.52 (d, $^4J_{HH}$ = 2.2 Hz, 2 H, Ph-5-*H*), 7.22 (d, $^4J_{HH}$ = 2.2 Hz, 1 H, Ph-3-*H*), 7.08 (d, $^4J_{HH}$ = 2.2 Hz, 1 H, Ph-3′-*H*), 3.68 [s, 6 H, N(C*H*$_3$)$_2$], 2.52 (dt, $^2J_{HH}$ = 10.2, $^3J_{HH}$ = 3.0 Hz, 1 H, SC*H*$_2$), 2.38 (dt, $^2J_{HH}$ = 10.2, $^3J_{HH}$ = 3.0 Hz, 1 H, SC*H*$_2$), 2.22 (td, $^2J_{HH}$ = 10.2, $^3J_{HH}$ = 3.0 Hz, 1 H, SC*H*$_2$), 1.97 (td, $^2J_{HH}$ = 10.2, $^3J_{HH}$ = 3.0 Hz, 1 H, SC*H*$_2$), 1.72 [s, 9 H, C(C*H*$_3$)$_3$], 1.66 [s, 9 H, C(C*H*$_3$)$_3$], 1.20 [s, 9 H, C(C*H*$_3$)$_3$], 1.19 [s, 9 H, C(C*H*$_3$)$_3$] ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene): δ = 166.55 (Ph-*C*1), 166.50 (Ph-*C*1′), 143.60 (Ph-*C*6), 143.15 (Ph-*C*6′), 138.05 (Ph-*C*4), 136.20 (Ph-*C*4′), 128.50 (Ph-*C*5), 128.13 (Ph-*C*5′), 126.33 (Ph-*C*3), 126.14 (Ph-*C*3′), 120.03 (Ph-*C*2), 118.93 (Ph-*C*2′), 50.50 [N(*C*H$_3$)$_2$], 37.87 (S*C*H$_2$), 37.80 (S*C*H$_2$), 35.75 [*C*(CH$_3$)$_3$], 35.64 [*C*(CH$_3$)$_3$], 34.58 [*C*(CH$_3$)$_3$], 34.48 [*C*(CH$_3$)$_3$], 31.62 [C(*C*H$_3$)$_3$], 31.60 [C(*C*H$_3$)$_3$], 29.85 [C(*C*H$_3$)$_3$], 29.80 [C(*C*H$_3$)$_3$] ppm. $C_{32}H_{50}ClNO_2S_2Ti$ (628.19): calcd. C 61.18, H 8.02, N 2.23; found C 61.63, H 7.73, N 2.22.

Typical Hydroamination Reaction Procedure: In the glovebox, a Teflon-valved NMR tube was charged with 5 mol-% or 10 mol-% of the imidotitanium complex (0.01 mmol or 0.02 mmol). Deuterated toluene (ca. 0.5 mL) was added via syringe. Then, 0.2 mmol of the substrate was added and the reaction mixture was shaken for a moment. The reaction was carried out at 150 °C and NMR spectra were recorded periodically.

Crystal Structure Determination of Complexes 1 and 5: X-ray diffraction measurements were performed on a Bruker AXS diffractometer with Mo-K_α radiation using ω-scans. Crystal parameters and result of the structure refinement are given in Table 3. Absorption corrections were carried out with the multi-scan method using SADABS.[11] The structures were solved by direct and Fourier difference methods (SIR-92)[12a] and refined (SHELXS-97)[12b] against all F^2 data. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included into calculated positions. For the graphical representation, the program ORTEP was used as implemented in the program system WinGX.[13]

Table 3. Crystallographic and data collection parameters for **1** and **5**.

Compound	**1**	**5**
Empirical formula	$C_{39}H_{58}N_2O_2S_2Ti{\cdot}C_5H_{12}$	2 $C_{32}H_{50}ClNO_2S_2Ti{\cdot}C_5H_{12}$
M_r	771.04	1328.55
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$\bar{P}1$
a [Å]	18.237(3)	15.5137(11)
b [Å]	28.490(5)	15.9150(11)
c [Å]	9.4719(18)	17.9791(13)
α [°]		113.213(1)
β [°]	100.459(4)	96.392(1)
γ [°]		108.034(1)
V [Å^3]	4849.1(15)	3738.4(5)
Z	4	2
$D_{calcd.}$ [g·cm^{-3}]	1.056	1.180
T [K]	130(2)	110(2)
μ(Mo-K_α) [mm^{-1}]	0.295	0.441
F(000)	1672	1428
θ Range [°]	2.27–28.34	2.31–25.54
Number of reflections collected	66138	42238
Number of reflections observed [$I > 2\sigma(I)$]	8736	10962
Number of independent reflections (R_{int})	12100 (0.0575)	13971 (0.0464)
Data / restraints / parameters	12100 / 0 / 474	13971 / 0 / 778
Goodness-of-fit on F^2	1.054	1.033
R_1, wR_2 [$I > 2\sigma(I)$]	0.0725, 0.1995	0.0549, 0.1373
R_1, wR_2 (all data)	0.1009, 0.2191	0.0720, 0.1486
Largest difference in peak and hole [e·Å^{-3}]	1.757 and –0.431	1.463 and –1.009

CCDC-704368 (for **1**) and -704369 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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