Tri- and Tetravalent Titanium Alkyls Supported by Organic Amides

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Received October 20, 1995[⊗]

The reactions of both trivalent [$(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$] (**1**) and tetravalent [$(Cy_2N)_2TiCl_2$] (**5**) with R′Li in THF or diethyl ether gave Ti(IV) complexes $(Cy_2N)_2TiR'_2$ [R′ = CH_2CMe_3 (**7**), CH_2CMe_2Ph (**8**), CH_2SiMe_3 (**9**)]. Conversely, the reactions of **1**, [$\{(i\text{-Pr})_2N\}_2TiCl_2$][$Li(TMEDA)_2$] (**2**), and [$\{(Me_3Si)_2N\}_2TiCl_2$][$Li(TMEDA)_2$] (**3**) with R′Li [R′ = Me, Ph, CH_2Ph] gave the corresponding trivalent derivatives [$(Cy_2N)_2Ti(\mu\text{-}Bz)_2Li(TMEDA)$] (**4a**), [$(Cy_2N)_2Ti(\mu\text{-}Me)_2Li(TMEDA)$] (**4b**), [$\{(i\text{-Pr})_2N\}_2TiPh_2$][$Li(TMEDA)_2$] (**11**), and [$\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2$][$Li(TMEDA)_2$] (**12**) *via* simple ligand replacement reactions. Oxidation of **12** with diphenylfulvene gave $\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2$ (**13**). All these compounds are thermally labile and yielded intractable materials upon thermolysis. Only in the case of the neophyl derivative $(Cy_2N)_2Ti(CH_2CMe_2C_6H_5)_2$ (**8**) a cyclometalated compound $(Cy_2N)_2Ti(CH_2CMe_2C_6H_4)$ (**10**) was isolated and crystallized from the thermolyzed solution. The reaction of **1** with styrene oxide provided the Ti−oxo complex [$(Cy_2N)_2TiCl]_2O$ (**14**) which gave, upon alkylation with MeLi, the corresponding dinuclear alkyl derivatives [$(Cy_2N)_2TiMe]_2O$ (**15**). The molecular structures of **1** and **10**−**14** were demonstrated by X-ray diffraction analysis.

Introduction

Transition metal alkyl complexes ($L_nM{-}R$) constitute a very important class of compounds because of the pivotal role played by these species in both synthesis and catalysis.[1] In particular, group IV organometallic derivatives have been the target of intense study since the initial discovery by Ziegler and Natta[2] that mixtures of $TiCl_3$ and aluminium alkyls act as catalysts for stereoselective olefin polymerization. As a result, interest in the synthesis, characterization, and reactivity of group IV organometallic species[3] has grown steady and titanium alkyls are today well-known[4] and widely employed in a number of important industrial processes (*e.g.* olefin cationic polymerization,[5] insertion reactions,[6] hydrogenation,[7] and metal-promoted organic synthesis[8]). A synthetically useful characteristic of titanium alkyls is their ability to act as precursors for the preparation of alkylidene[9] derivatives via C−H σ-bond

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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metathesis reactions. In this respect, sterically demanding alkyl groups lacking β-hydrogens (benzyl (Bz), neophyl (Nf), neopentyl (Np)) seem to be particularly versatile. In fact, by preventing β-H elimination reactions, it is possible to obtain an unusually high stability[10] and thus favor α-H abstraction during C−H σ-bond metathesis.[11] Tetravalent titanium alkylidene complexes have proven their potential use in important applications like ROMP[12] metathesis and polymerization.[13]

As a result of the great potential offered by Ti alkyl systems, their chemistry has been extensively studied even though the major effort was directed toward using cyclopentadienyl rings and related systems as supporting ligands.[4] Titanium alkyls containing other supporting ligands are somewhat less known, since these species are mainly generated in situ and usually not completely characterized. Nevertheless, a few complexes containing bulky phenoxides[9a,14] and amide[15] as ancillary ligands have been fully characterized including crystallographically. A large number of alkyltitanates with a variety of supporting ligands have been successfully used in metal-promoted organic synthesis.[16]

The employment of anionic organic amides as ancillary ligands has proven to be a viable alternative for the stabilization of a wide range of oxidation states of several transition elements. Such stability can be ascribed to both the reducing ability of these anions and the possibility of M−N π-bond formation, which obviously improves the stability of electron-rich complexes via an increased electronic delocalization. In addition, these ligands may function as bridging ligands, thus promoting multinuclear aggregation through bridging interactions of the nitrogen donor atom. The potential offered by amide-supported titanium alkyls is underlined by their well-documented ability to promote stereoselective organic reactions.[16] Recently, we have described the preparation and characterization of novel titanium methyl and methylidene complexes[9a,9c] stabilized by bulky organic amides. In this second paper, we further describe the synthesis, characterization, and thermal stability of other mono- and dinuclear Ti(III) and Ti(IV) alkyls along with a preliminary discussion of the factors influencing their stability.

Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware and a nitrogen−vacuum line. $TiCl_3$ and $TiCl_4$ were used as received (Aldrich) and transformed into the corresponding THF adducts by following literature procedures.[17,18] Cy_2NH, $i\text{-}Pr_2NH$, $(Me_3Si)_2NH$, and TMEDA were distilled prior to use over Na and K metals. The corresponding lithium salts (R_2NLi) were prepared by treating the hexane solutions of the amines with stoichiometric amounts of *n*-BuLi. NpLi, NfLi, and $LiCH_2SiMe_3$ were obtained according standard procedures. The complexes $[(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)]$ (**1**),[9a] $[\{(Me_3Si)_2N\}_2TiCl_2][Li(TMEDA)_2]$ (**3**),[19] $[(Cy_2N)_2Ti(\mu\text{-}Me)_2Li(TMEDA)]$ (**4b**),[9a] and $[(Cy_2N)_2TiCl_2]$ (**5**)[9a] were synthesized according to published procedures. C_6D_6 was dried over Na/K alloy, vacuum transferred into an impule, and stored under nitrogen. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer using vacuum-sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the drybox. Samples for magnetic susceptibility measurements were prepared inside the drybox, and the measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods[20] and corrections for underlying diamagnetism were applied to the data.[21] Combustion analyses were obtained with a Perkin-Elmer Series II CHN/O 2400 analyzer.

$[(i\text{-}Pr_2N)_2TiCl_2][Li(TMEDA)_2]$ (2). A solution of $i\text{-}Pr_2NLi$ (3.8 g, 35.5 mmol) in THF (50 mL) was added to a stirred suspension of $TiCl_3{\cdot}3THF$ (6.5 g, 17.6 mmol) in THF (150 mL) at −10 °C, followed by the addition of 2 equiv of TMEDA (5.0 mL, 33 mmol). The reaction was instantaneous, and the resulting green solution was warmed to room temperature. After the solution was stirred for an additional 30 min, the solvent was evaporated *in vacuo* and the residue was dissolved in hexane (150 mL). The LiCl was removed by filtration, and the resulting solution was allowed to stand overnight at −30 °C, upon which forest green crystals of **2** (4.2 g, 7.5 mmol, 43%) separated. Anal. Calcd (found) for $C_{24}H_{60}N_6TiLiCl_2$: C, 51.61 (51.56); H, 10.83 (10.04); N, 15.05 (14.64). IR (KBr, Nujol mull, cm^{-1}): 1461 (s), 1376 (m), 1292 (w), 1261 (w), 1168 (m), 1101 (m), 1035 (w), 931 (m), 811 (m), 792 (w), 723 (w), 605 (w), 493 (m). $\mu_{eff} = 1.81\ \mu_B$.

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[$(Cy_2N)_2Ti(\mu\text{-}CH_2Ph)_2Li(TMEDA)$] (4a). A solution of **1** (1.0 g, 1.7 mmol) in ether (80 mL) was treated with BzLi(TMEDA) (0.75 g, 3.5 mmol). The color of the solution changed immediately to the reddish brown, and stirring was continued for about 30 min. The white precipitate was eliminated by filtration and allowed to stand at room temperature for 2 h, upon which purple microcrystalline **4a** (0.4 g, 0.56 mmol, 33%) separated. Anal. Calcd (found) for $C_{44}H_{74}N_4TiLi$: C, 74.03 (73.85); H, 10.45 (10.41); N, 7.85 (7.79). IR (KBr, Nujol mull, cm^{-1}): 3056 (w), 1585 (m), 1288 (m), 1261 (m), 1213 (m), 1157 (m), 1143 (m), 1110 (s), 1097 (s), 1031 (s), 950 (s), 898 (s), 854 (m), 800 (s), 738 (s), 681 (s), 561 (m), 533 (m). $\mu_{eff} = 1.88\ \mu_B$.

$(Cy_2N)_2Ti(CH_2Ph)_2$ (6). Solid $PhCH_2Li\cdot TMEDA$ (1.75 g, 8.2 mmol) was added to an orange suspension of [$(Cy_2N)_2TiCl_2$] (**5**) (1.95 g, 4.0 mmol) in hexane (150 mL) yielding a dark orange solution over a period of 2 days. After removal of the small amount of white insoluble solid, the solvent was evaporated *in vacuo* to yield an orange oil. Anal. Calcd (found) for $C_{38}H_{58}N_2Ti$: C, 77.26 (77.01); H, 9.90 (9.76); N, 4.74 (4.64). ^1H NMR [C_6D_6, 200 MHz, δ (ppm)]: 7.25−6.85 (m, 5H, Ph), 3.7−3.52 (m, 2H, Cy), 2.7 (s, 2H, Bz), 1.88−0.82 (m, 20H, Cy). ^{13}C NMR [C_6D_6, 50 MHz, δ(ppm)]: 150.74 (C, Ph), 129.2, 127.6, 122.8 (CH, Ph), 80.9 (CH_2, Bz), 58.78 (CH, Cy), 36.8, 27.7, 26.6 (CH_2, Cy).

$(Cy_2N)_2Ti(CH_2CMe_3)_2$ (7). Method A. The addition of NpLi (Np = CH_2CMe_3, 0.8 g, 10.2 mmol) to an orange suspension of [$(Cy_2N)_2TiCl_2$] (**5**) (2.6 g, 5.4 mmol) in diethyl ether (150 mL) at −10 °C turned the color greenish-yellow. An insoluble light yellow-green solid separated, which was isolated and redissolved in hexane at room temperature. Yellow crystals of **7** were obtained after allowing the hexane solution to stand overnight at 0 °C (1.6 g, 2.9 mmol, 54%).

Method B. NpLi (0.4 g, 5.1 mmol) was added to a stirred emerald green solution of **1** (1.5 g, 2.5 mmol) in diethyl ether (60 mL) at −10 °C. The color turned brownish-orange, and the stirring was continued for about 3 h at room temperature. After the insoluble colorless material which had separated was filtered off, the resulting clear solution was allowed to stand overnight at −30 °C, upon which yellow microcrystalline **7** separated (0.5 g, 0.9 mmol, 36%). Anal. Calcd (found) for $C_{34}H_{66}N_2Ti$: C, 74.14 (74.57); H, 12.08 (12.27); N, 5.09 (5.11). IR (KBr, Nujol mull, cm^{-1}): 1455 (s), 1366 (s), 1252 (m), 1225 (m), 1158 (m), 1142 (m), 1107 (sh), 1091 (sh), 1025 (sh), 978 (m), 944 (sh), 887 (sh), 842 (sh), 803 (sh), 778 (sh), 750 (sh), 696 (sh), 680 (m), 589 (m), 579 (m), 546 (w), 506 (sh), 488 (sh), 453 (m). ^1H NMR [500 MHz, C_6D_6, δ (ppm)]: 3.75−3.69 (m, 2H, Cy), 2.02−1.11 (m, 20H, Cy), 1.65 (s, 2H, Np), 1.3 (s, 9H, Np). ^{13}C NMR [125.7 MHz, C_6D_6, δ (ppm)]: 98.7 (CH_2, Np), 58.2 (CH, Cy), 36.9 (C, Np), 34.8 (CH_3, Np), 36.3, 27.1, 26.2 (CH_2, Cy).

$(Cy_2N)_2Ti(CH_2CMe_2Ph)_2$ (8). Method A. Solid $LiCH_2CMe_2Ph$ (1.35 g, 9.6 mmol) was added to a stirred solution of [$(Cy_2N)_2TiCl_2$] (**5**) (2.3 g, 4.8 mmol) in diethyl ether (50 mL) at room temperature. The color turned instantaneously yellow, and stirring was continued for a few hours. The solvent was evaporated *in vacuo*, and the residual solid was redissolved in hexane (40 mL). Removal of LiCl followed by overnight standing at −30 °C afforded greenish-yellow crystals of **8** (1.7 g, 2.5 mmol, 52%). Anal. Calcd (found) for $C_{44}H_{70}N_2Ti$: C, 78.30 (77.88); H, 10.45 (10.46); N, 4.15 (4.02). IR (KBr, Nujol mull, cm^{-1}): 1600 (w), 1494 (sh) 1454 (bd), 1376 (m), 1249 (m), 1188 (w), 1172 (w), 1157 (m), 1093 (m), 1081 (sh), 1029 (m), 1020 (m), 975 (w), 944 (sh), 887 (sh), 842 (sh), 806 (m), 779 (m), 761 (sh), 698 (sh), 582 (w), 551 (m). ^1H NMR [500 MHz, C_6D_6, δ (ppm)]: 7.52−7.5 (m, 2H, Ph), 7.28−7.24 (m, 2H, Ph), 7.1−7.07 (m, 1H, Ph), 3.7−3.65 (m, 2H, Cy), 1.93−0.88 (m, 20H, Cy), 1.78 (s, 2H, CH_2, Nf), 1.54 (s, 6H, CH_3, Nf). ^{13}C NMR [125.7 MHz, C_6D_6, δ (ppm)]: 153.7 (C, Ph, Nf), 127.8 (CH, Ph, Nf), 126.0 (CH, Ph, Nf), 125.3 (CH, Ph, Nf), 97.5 (CH_2, Nf), 58.5 (CH, Cy), 43.6 (C, Nf), 34.3 (CH_3, Nf), 36.4, 27.0, 26.1 (CH_2, Cy).

Method B. A solution of **1** (1.16 g, 1.9 mmol) in ether (100 mL) was treated with freshly sublimed NfLi (0.52 g, 3.7 mmol). The color of the solution gradually changed to green and finally to brown. The mixture was stirred for another 2 h after which the white insoluble material was removed by filtration. The filtrate was concentrated to ca. 20 mL, and hexane (ca. 30 mL) was added until the solution became cloudy. The mixture was allowed to stand at −30 °C for 12 h, upon which brown microcrystalline **8** separated (0.75 g, 1.1 mmol, 58%).

$(Cy_2N)_2Ti(CH_2SiMe_3)_2$ (9). Method A. Addition of $LiCH_2SiMe_3$ (0.85 g, 10.5 mmol) to a stirred orange suspension of $(Cy_2N)_2TiCl_2$ (**5**) (2.5 g, 5.2 mmol) in THF (60 mL) at room temperature slowly turned the color brown. The stirring was continued overnight after which the small amount of white insoluble material was eliminated by filtration. The filtrate was cooled and allowed to stand overnight at −30 °C yielding yellow microcrystals of **9** (1.6 g, 2.7 mmol, 53%).

Method B. Addition of $LiCH_2SiMe_3$ (0.42 g, 5.2 mmol) to an emerald green solution of $(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (**1**) (1.6 g, 2.6 mmol) in hexane (40 mL) at −10 °C turned the color to brown. The solution was slowly warmed to room temperature, and the stirring was continued at room temperature for about 24 h. The resulting solution was filtered and allowed to stand overnight at −30 °C yielding bright yellow, microcrystalline **9** (0.9 g, 1.5 mmol, 58%). Anal. Calcd (found) for $C_{32}H_{66}N_2Si_2Ti$: C, 65.93 (65.76); H, 11.41 (11.48); N, 4.81 (4.62). IR (KBr, Nujol mull, cm^{-1}): 1452 (s), 1376 (s), 1344 (m), 1245 (s), 1159 (m), 1143 (w), 1103 (s), 1068 (w), 1027 (s), 980 (m), 952 (s), 897 (s), 836 (s), 779 (w), 747 (m), 718 (s), 682 (m), 614 (m), 591 (m), 580 (m), 510 (m), 493 (m), 427 (m). ^1H NMR [200 MHz, C_6D_6, δ (ppm)]: 3.5 (m, 2H, Cy), 2.1−1.1 (bd m, 20H, Cy), 1.3 (s, 2H, CH_2), 0.3 (s, 9H, $SiMe_3$). ^{13}C [50 MHz, C_6D_6, δ (ppm)]: 69.7 (CH_2, CH_2SiMe_3), 58.2 (CH, Cy), 37.1, 27.8, 26.3 (CH_2,Cy), 5.0 (CH_3, $SiMe_3$).

$(Cy_2N)_2Ti(CH_2CMe_2C_6H_4)$ (10). A solution of **8** (1.8 g, 2.7 mmol) in hexane (70 mL) was heated at 60 °C for 5 min. The resulting clear yellow solution yield yellow crystals of **10** (1.2 g, 2.2 mmol, 81%) upon standing at −30 °C for 2 days. Anal. Calcd (found) for $C_{34}H_{56}N_2Ti$: C, 75.52 (75.38); H, 10.44 (10.61); N, 5.18 (5.17). IR (KBr, Nujol mull, cm^{-1}): 1567 (w), 1421 (w), 1392 (w), 1376 (w), 1365 (w), 1348 (w), 1251 (m), 1230 (w), 1162 (m), 1143 (m), 1118 (br), 1089 (w), 1066 (w), 1031 (br), 981 (m), 966 (br), 890 (s), 840 (sh), 806 (sh), 781 (sh), 761 (sh), 723 (m), 709 (sh), 686 (w), 603 (s), 590 (m), 586 (m), 503 (sh), 488 (sh), 453 (sh). ^1H NMR [500 MHz, C_6D_6, δ (ppm)]: 7.27−7.16 (m, 2H, Ph), 7.12−7.0 (m, 2H, Ph), 3.85−3.79 (m, 4H, Cy), 2.02 (s, 2H, CH_2, Nf), 1.69 (s, 6H, CH_3, Nf), 1.99−0.87 (m, 4−H, CH_2, Cy). ^{13}C NMR [125.7 MHz, C_6D_6, δ (ppm)]: 193.5, 160.5 (C, Ph, Nf), 131.0, 128.6, 124.9, 123.8, (CH, Ph, Nf), 57.3 (CH, Cy), 41.8 (C, Nf), 37.02 (CH_2, Nf), 36.9 (CH_3, Nf), 27.09, 26.92, 26.06 (CH_2, Cy).

[$(i\text{-}Pr_2N)_2TiPh_2$][$Li(TMEDA)_2$] (11). The addition of $PhLi\cdot 1.5Et_2O$ (1.6 g, 8.2 mmol) to a forest green solution of [$(i\text{-}Pr_2N)_2TiCl_2$][$Li(TMEDA)_2$] (**2**) (2.4 g, 4.3 mmol) in Et_2O turned the color cherry red. The reaction mixture was stirred at room temperature for about 2 h and then filtered to remove LiCl. Dark red crystals of **11** (1.7 g, 2.6 mmol, 60%) were obtained upon allowing the resulting solution to stand overnight at room temperature. Anal. Calcd (found) for $C_{36}H_{20}N_6TiLi$: C, 67.37 (66.69); H, 10.99 (10.75); N, 13.09 (12.78). IR (KBr, Nujol mull, cm^{-1}): 1610 (w), 1549 (s), 1457 (s), 1407 (m), 1381 (s), 1346 (s), 1287 (s), 1245 (m), 1228 (m), 1169 (s), 1126 (m), 1099 (s), 1068 (s), 1043 (m), 1029 (s), 1009 (s), 978 (s), 946 (s), 921 (s), 848 (s) 806 (s), 788 (s), 714 (m), 705 (s), 633 (w). $\mu_{eff} = 1.77\ \mu_B$.

[$\{(Me_3Si)_2N\}_2Ti(CH_2Ph)_2$][$Li(TMEDA)_2$] (12). Neat TMEDA (4.0 mL) was added to a solution of [$\{(Me_3Si)_2N\}_2TiCl_2$][$Li(TMEDA)_2$] (**3**) (1.9 g, 2.8 mmol) in toluene (40 mL) at room temperature followed by the addition of *t*-BuLi (3.3 mL of 1.7 M, 5.6 mmol) at −78 °C. The reaction was instantaneous, and orange crystals of **12** (1.9 g, 2.4 mmol, 86%) separated from the resultant solution upon standing overnight at room tem-

Table 1. Crystal Data and Structural Analysis Results

	complex					
	1	**10**	**11**	**12**	**13**	**14**
formula	$C_{30}H_{60}TiCl_2LiN_4$	$C_{34}H_{56}N_2Ti$	$C_{36}H_{70}N_6TiLi$	$C_{38}H_{82}N_6Si_4TiLi$	$C_{26}H_{50}Si_4N_2Ti$	$C_{48}H_{88}N_4Ti_2Cl_2O$
fw	602.58	540.73	641.83	790.28	550.94	903.96
cryst color	green, prism	golden, cube	red, cube	yellow, block	red, prism	orange, cube
cryst system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
a (Å)	12.361(5)	10.318(1)	9.528(2)	13.757(2)	11.639(2)	16.205(4)
b (Å)	19.616(4)	15.5144(9)	21.675(5)	17.329(7)	17.188(2)	14.804(3)
c (Å)	15.357(3)	10.241(1)	19.867(9)	22.151(4)	8.935(2)	20.748(5)
α (deg)		98.909(9)			90.35(1)	
β (deg)	109.39(2)	99.40(1)	97.86(2)	104.31(1)	109.24(1)	96.11(2)
γ (deg)		86.106(9)			102.16(1)	
V (Å)^3	3512(2)	1596.2(5)	4065(4)	5117(2)	1644.2(4)	4949(4)
Z	4	2	4	4	2	4
radiation: λ(Mo Kα) (Å)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
T (°C)	−160	−144	−153	23	23	−161
D_{calcd} (g cm^{-3})	1.139	1.125	1.049	0.875	1.113	1.213
μ_{calcd} (cm^{-1})	4.16	2.86	2.35	2.76	4.15	4.64
F_{000}	1308	592	1412	1468	596	1960
no. of params	519	334	399	427	299	256
no. of observns	4601	3692	4232	3046	3970	2496
R, R_w, GoF	0.077, 0.091, 3.35	0.036, 0.047, 2.10	0.067, 0.081, 2.66	0.074, 0.065, 2.72	0.046, 0.067, 1.69	0.075, 0.087, 2.70

perature. Anal. Calcd (found) for $C_{38}H_{82}N_6Si_4TiLi$: C, 57.75 (57.45); H, 10.46 (10.12); N, 10.63 (10.52). IR (KBr, Nujol mull, cm^{-1}): 1589 (s), 1470 (br), 1376 (m), 1357 (m), 1288 (sh), 1249 (br), 1209 (m), 1182 (m), 1159 (m), 1128 (sh), 1097 (sh), 1068 (sh), 1029 (sh), 1014 (sh), 970−775 (v br), 746 (br), 698 (m), 665 (m), 624 (m), 588 (w), 559 (m), 512 (m), 493 (w), 439 (w). $\mu_{eff} = 1.73\ \mu_B$.

[{$(Me_3Si)_2N$}$_2$Ti(CH_2Ph)$_2$] (13). A solution of **12** (1.7 g, 2.1 mmol) in toluene (60 mL) was cooled to −10 °C and treated with diphenylfulvene (0.5 g, 2.2 mmol). The color immediately turned dark red, and the stirring was continued for 2 h at room temperature. After removal of the solvent, the residual solid was redissolved in Et_2O and the resulting solution allowed to stand at −30 °C overnight, upon which red cubes of **13** (0.7 g, 1.3 mmol, 62%) separated. Anal. Calcd (found) for $C_{26}H_{50}Si_4N_2Ti$: C, 56.68 (56.06); H, 9.15 (8.88); N, 5.08 (4.76). IR (KBr, Nujol mull, cm^{-1}): 1596 (sh), 1488 (m), 1465 (br), 1376 (m), 1249 (s, br), 1207 (m), 1027 (w), 1012 (w), 993 (w), 871−671 (br), 619 (w), 561 (m), 507 (m), 428 (m). ^{1}H NMR [200 MHz, C_6D_6, δ (ppm)]: 0.49 (s, 18H, Me_3Si), 3.32 (s, 2H, CH_2, Bz), 7.35−7.4 (m, 5H, Ph, Bz). ^{13}C NMR [50 MHz, C_6D_6, δ-(ppm)]: 148.7 (C, Ph, Bz), 128.3, 127.1, 123.5 (CH, Ph, Bz), 99.9 (CH_2, Bz), 5.9 (Me, $SiMe_3$).

[$(Cy_2N)_2TiCl$]$_2$O (14). The addition of styrene oxide to a green toluene solution of **1** (2.4 g, 4.0 mmol) at room temperature changed the color to orange. The solution was filtered to remove a small amount of white insoluble solid and allowed to stand at −30 °C overnight, upon which bright yellow-orange crystals of **14** separated (1.1 g, 2.4 mmol, 60%). Anal. Calcd (found) for $C_{48}H_{88}N_4Ti_2Cl_2O$: C, 63.78 (62.38); H, 9.81 (9.70); N, 6.20 (5.93). IR (KBr, Nujol mull, cm^{-1}): 1452 (sh, br), 1376 (sh), 1344 (w), 1251 (w), 1159 (m), 1143 (w), 1105 (s), 1079 (m), 1027 (br), 981 (m), 960 (sh), 892 (s), 842 (s), 808 (w), 786 (w), 746 (sh), 709 (w), 590 (w), 752 (m), 511 (m), 491 (w), 449 (m). ^{1}H NMR [500 MHz, C_6D_6, δ (ppm)]: 3.85 (m, 1H, Cy), 2.3−1.1 (br m, 10H, Cy). ^{13}C NMR [125.7 MHz, C_6D_6, δ (ppm)]: 60.3 (CH, Cy), 35.7, 26.7, 25.9 (CH_2, Cy).

(Cy_2N)$_2$TiMe]$_2$O (15). A solution of MeLi in ether (1.5 mL, 2.0 mmol of 1.4M) was added to a stirred suspension of **14** (0.9 g, 1.0 mmol) in THF (80 mL) at −70 °C. The solution was warmed to room temperature, and the stirring was continued for 24 h followed by removal of the solvent *in vacuo*. The residual solid was recrystallized from toluene (25 mL) yielding yellow microcrystalline **15** (80 mg, 0.09 mmol, 9%) upon cooling for 2 days at −30 °C. Anal. Calcd (found) for $C_{50}H_{94}N_4Ti_2O$: C, 69.58 (68.87); H, 10.98 (10.36); N, 6.49 (5.98), IR (KBr, Nujol mull, cm^{-1}): 1450 (sh), 1376 (s), 1344 (m), 1267 (w), 1249 (m), 1159 (m), 1143 (m), 1112 (sh), 1087 (sh), 1029 (br), 981 (m), 968 (sh), 890 (sh), 842 (sh), 771 (br), 707 (m), 588 (m), 576 (w), 530 (w), 501 (br). ^{1}H NMR [500 MHz, C_6D_6, δ (ppm)]: 3.66 (m, 4H, Cy), 2.1−1.13 (br, m, 40H, Cy), 0.94 (s, 3H, Me). ^{13}C NMR [125.7 MHz, C_6D_6, δ (PPM)]: 58.1 (CH, Cy), 38.4 (CH_3, Me), 36.4, 26.9, 26.8 (CH_2, Cy).

X-ray Crystallography. Data were collected at temperatures in the range −157 to −160 °C using the ω−2θ scan technique to a maximum 2θ value of 50.0°, for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Reducntant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $I > 2.5\sigma(I)$. Neutral atomic scattering factors were taken from Cromer and Waber.[22] Anomalous dispersion effects were included in F_c. All calculations were performed using the TEXSAN package on a Digital VAX station. Details on data collection and structure refinement are reported in Table 1. Final atomic coordinates for all the complexes are given as Supporting Information. Selected bond distances and angles are given in Table 2.

Results and Discussion

The reaction of $TiCl_3(THF)_3$ with 2 equiv of R_2NLi (R = Cy, *i*-Pr, Me_3Si) in THF and in the presence of TMEDA (Scheme 1) yielded the corresponding bis(amido) titanium halide derivatives which were isolated as air-sensitive green crystals. Depending upon the nature of the dialkylamide organic substituent, heterodinuclear $(R_2N)_2TiCl_2Li(TMEDA)$ [R = Cy (**1**)] or ionic [$(R_2N)_2TiCl_2$][Li(TMEDA)] [R = *i*-Pr (**2**); R = Me_3Si (**3**)] complexes were isolated. Combustion analyses were in agreement with the proposed formulation, while X-ray fluorescence data gave for all the complexes the

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[22] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974.

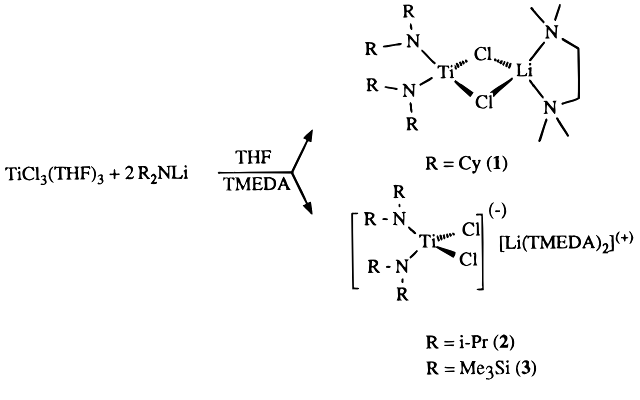
Table 2. Selected Bond Distances (Å) and Angles (deg)

1		**10**	
Ti1−Cl1	2.436(2)	Ti1−N1	1.896(2)
Ti1−Cl2	2.415(2)	Ti1−N2	1.879(2)
Ti1−N3	1.906(4)	Ti1−C25	2.121(2)
Ti1−N4	1.917(4)	Ti1−C30	2.089(2)
Cl1−Li1	2.35(1)	N1−Ti1−N2	120.93(8)
Cl2−Li1	2.31(1)	N1−Ti1−C25	111.98(8)
Cl1−Ti1−Cl2	93.18(5)	N1−Ti1−C30	110.26(8)
Cl1−Ti1−N3	107.5(1)	N2−Ti1−C25	110.81(8)
Cl1−Ti1−N4	107.6(1)	N2−Ti1−C30	112.26(8)
Cl2−Ti1−N3	107.4(1)	C25−Ti1−C30	84.92(9)
Cl2−Ti1−N4	116.9(1)	Ti1−N1−C1	141.3(1)
N3−Ti1−N4	120.5(2)	Ti1−N1−C7	103.2(1)
Ti1−Cl1−Li1	83.5(2)	C1−N1−C7	115.5(2)
Ti1−Cl2−Li1	84.8(2)		
Ti1−N4−C1	106.2(3)		
Ti1−N4−C7	138.4(3)		
C1−N4−C7	115.0(4)		

11		**12**	
Ti1−N3	1.962(4)	Ti1−N1	2.036(8)
Ti1−N4	1.965(4)	Ti1−N2	2.027(8)
Ti1−C1	2.173(5)	Ti1−C7	2.18(1)
Ti1−C7	2.210(5)	Ti1−C14	2.18(1)
Li2−N1	2.12(1)	N3−Li1	2.10(2)
Li2−N2	2.13(1)	N4−Li1	2.12(2)
Li2−N5	2.085(9)	N5−Li1	2.17(2)
Li2−N6	2.153(9)	N6−Li1	2.12(2)
N3−Ti1−N4	118.0(2)	N1−Ti1−N2	127.4(3)
N3−Ti1−C1	109.6(2)	N1−Ti1−C7	108.1(3)
N3−Ti1−C7	106.3(2)	N1−Ti1−C14	100.0(4)
N4−Ti1−C1	105.6(2)	N2−Ti1−C7	99.9(4)
C1−Ti1−C7	100.2(2)	N2−Ti1−C14	119.7(4)
Ti1−N3−C19	108.8(3)	Ti1−N1−Si1	116.5(4)
Ti1−N3−C22	135.7(3)	Ti1−N1−Si2	121.9(4)
C19−N3−C22	115.2(4)	Si1−N1−Si2	121.6(5)
		C7−Ti1−C14	97.4(4)

13		**14**	
Ti1−N1	1.931(3)	Ti1−C12	2.296(2)
Ti1−N2	1.939(3)	Ti1−O1	1.828(2)
Ti1−C13	2.092(5)	Ti1−N1	1.910(6)
Ti1−C20	2.109(4)	Ti1−N2	1.876(6)
N1−Ti1−N2	120.6(1)	C12−Ti1−O1	109.3(2)
N1−Ti1−C13	108.4(2)	C12−Ti1−N1	109.2(2)
N1−Ti1−C20	108.1(2)	Cl2−Ti1−N2	109.9(2)
N2−Ti1−C13	109.1(2)	O1−Ti1−N1	113.5(2)
N2−Ti1−C20	110.0(2)	O1−Ti1−N2	108.5(2)
C13−Ti1−C20	98.4(2)	N1−Ti1−N2	106.3(2)
Ti1−C13−C14	120.7(3)	Ti1−O1−Ti1a	154.9(4)
Ti1−C20−C21	119.2(3)	Ti1−N1−C1	120.6(5)
Ti1−N1−Si1	124.8(2)	Ti1−N1−C7	123.5(4)
Ti1−N1−Si2	117.5(2)	C1−N1−C7	115.7(5)
Si1−N1−Si2	117.5(2)		

Scheme 1



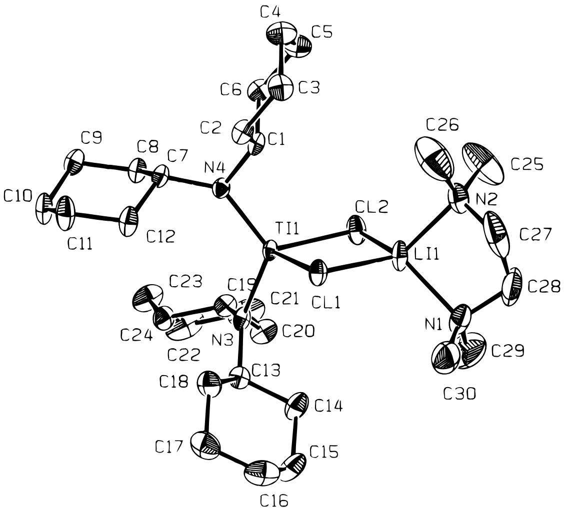


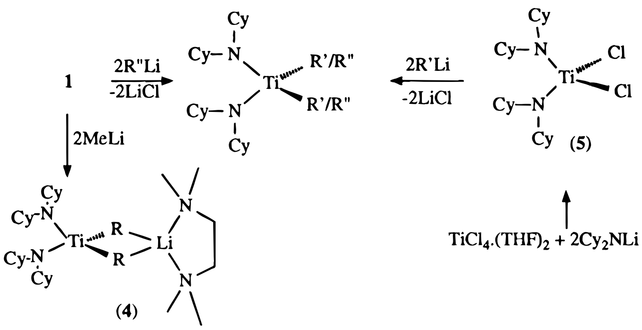
Figure 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level

expected 1:2 Ti:Cl ratios. Complexes **1**−**3** are paramagnetic, with magnetic moments ($\mu_{\text{eff}} = 1.7-1.8\ \mu_{\text{B}}$) as expected for the d^1 electronic configuration of Ti(III), and displayed uninformative NMR spectra. The molecular structures of complexes **1** and **3**[9a] were elucidated by X-ray crystal structures.

Complex **1** is heterodinuclear with the titanium and lithium atoms bridged by two chloride atoms (Figure 1). The distorted tetrahedral geometry of the titanium atom is defined [N4−Ti1−N3 = 120.5(2)°, N3−Ti1−Cl1 = 107.5(1)°, N3−Ti1−Cl2 = 107.4(1)°, Cl2−Ti1−Cl1 = 93.18(5)°] by two nitrogen atoms of two amides and two chlorides. The Ti−N and Ti−Cl bond distances are as expected [Ti1−N3 = 1.906(4) Å; Ti1−Cl1 = 2.436(2) Å]. The geometry of the two nitrogen atoms of the two amides slightly deviates from the regular trigonal planar [C1−N4−Ti1 = 106.2(3)°, Ti1−N4−C7 = 138.4(3)°, Cl−N4−C7 = 115.0(4)°] expected for the sp^2 hybridization of the nitrogen atom. The $TiCl_2Li$ core is almost planar [torsion angle Ti1−Cl1−Li1−C12 = 2.5(3)°]. One molecule of TMEDA completes the tetrahedral coordination geometry of the alkali cation.

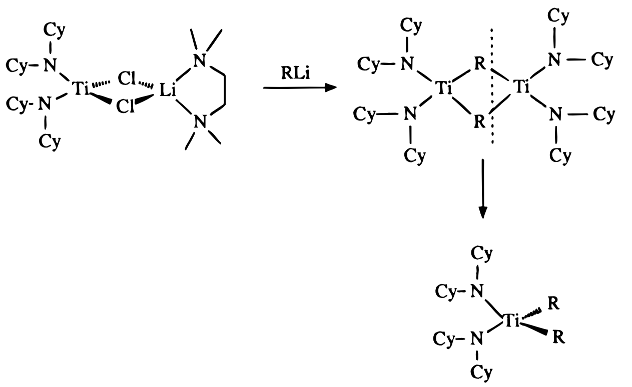
Alkylation of **1** carried out with alkyllithium reagents gave the corresponding tri- and tetravalent alkyl complexes depending on the nature of the alkylating agent employed. The reaction of **1** with either BzLi(TMEDA) or MeLi gave simple chloride subsitution forming the corresponding trivalent $[(Cy_2N)_2TiR_2Li(TMEDA)]$ [R = CH_2Ph (**4a**), Me (**4b**)], where both the oxidation state and the heterodinuclear frame were preserved.[9a] Conversely, in the case of bulkier alkylating agents, air-sensitive tetravalent neutral complexes, formulated as $(R_2N)_2TiR'_2$ [R″ = CH_2CMe_3(**7**), CH_2SiMe_3(**9**)] were formed (Scheme 2). The formulas were inferred from combustion analysis data. X-ray fluorescence data and qualitative analytical tests for Cl were also in agreement with the proposed formulation. Complexes **6**−**9** were conveniently synthesized in higher yield (50−55%) by using the tetravalent complex $(Cy_2N)_2TiCl_2$ (**5**) as starting material. All the complexes were yellow in color and have been isolated in crystalline form. The common feature in the ^1H NMR spectra of all these complexes is the presence of a broad multiplet in the range 2.1−1.0 ppm attributed to the methylene protons of the cyclohexyl rings and a pseudotriplet in the range 3.5−4.0 ppm due to the *ipso* protons of the cyclohexyl rings. Complex **6** shows a sharp singlet at 2.7 ppm for the

Scheme 2

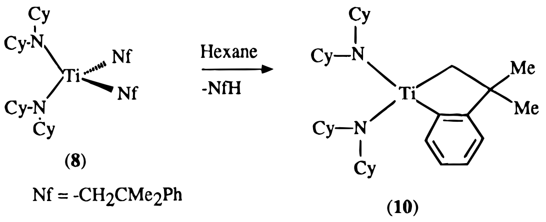


R = CH_2Ph (**4a**), CH_3 (**4b**)
R' = CH_2Ph(**6**), CH_2CMe_3(**7**), CH_2CMe_2Ph(**8**), CH_2SiMe_3(**9**)
R" = CH_2CMe_3 (**7**), CH_2SiMe_3 (**9**)

Scheme 3



Scheme 4



methylene protons of benzyl along with a multiplet in the aromatic region for the phenyl ring protons. $^{13}C\{^1H\}$ and HMQC spectra were also consistent with the proposed formulation showing the appropriate couplings. The ^1H NMR spectrum of complex **7** showed a sharp singlet at 1.65 ppm for the methylene protons of the alkyl group and another singlet at 1.3 ppm for the methyl protons of the neopentyl group in the ratio 2:9. Complex **8** showed three multiplets in the aromatic region (7.52−7.07 ppm) assigned to the phenyl groups. In addition, two singlets respectively at 1.78 ppm for the methylene protons and at 1.54 ppm for the methyl protons of the neophyl substituent were found in the correct ratio 1:3. The fact that only one methyne proton resonance was determined in the spectra of all these complexes indicates that the cyclohexyl rings are equivalent. Two singlets at 1.3 ppm for the methylene protons and at 0.3 ppm for the Me_3Si protons, respectively, in the ratio 2:9 are present in the ^1H NMR spectrum of complex **9**. The methylene groups of the alkyl directly connected to the titanium atom display chemical shifts at fields (2.7−1.3 ppm) which are considerably lower than those of the cyclopentadienyl analogues. This trend, which becomes even more pronounced in the ^{13}C NMR spectra, indicates that the amide groups significantly modify the nature of the Ti−C bond by introducing a higher degree of covalency.

In order to explain the oxidation of Ti(III) alkyls to the corresponding Ti(IV) derivatives, we tentatively suggest that the initially formed intermediate $(Cy_2N)_2TiR'$ species cannot be sufficiently stabilized by the formation of ionic structures such as in the case of complexes **1**−**4**. This is also indicated by the fact that the result of the reaction was not modified by a different stoichiometric ratio or by the use of excess of alkylating agent. We speculate that the coordinatively unsaturated $(Cy_2N)_2TiR'$ moiety probably forms a dinuclear complex where the two metal centers are bridged *via* ether amide or alkyl. Subsequent disproportionation (Scheme 3) forms both tetravalent and divalent species through a mechanism analogous to that previously described for **4** or Zr(III) dimers.[23] However, different from the case of Zr, attempts to isolate the corresponding Ti(II) species, formed as result of such a disproportionation, remained unsuccessful in the present work.

The Ti(IV) alkyl complexes **6**−**9** display a moderate thermal stability in the solid state. However, they were found to be rather unstable in solution where all these species showed a tendency to slowly decompose, even at room temperature. Complex **7** completely decomposes at room temperature in about 4−5 days forming neopentane together with intractable materials. However, complex **8** yielded the cyclometalated species **10** upon standing at room temperature for a period of 5−6 weeks (Scheme 4). As expected, the reaction was greatly accelerated when an hexane solution of **8** was heated for a few minutes at 50 °C. The ^1H NMR spectrum of complex **10** showed singlets attributed to methylene and methyl protons being considerably shifted to lower fields. For example, the methylene protons were found at 2.02 ppm while the methyl protons of neophyl were located at 1.69 ppm. The aromatic signals were also significantly modified with respect to those of complex **8**. The integration of the spectrum showed loss of one neophyl ligand. During a thermolysis in a sealed NMR tube, 1 equiv of $(CH_3)_3C(Ph)$ was formed thus indicating that deprotonation of the remaining neophyl molecule occurred, probably *via* metalation of the aromatic ring and consequent formation of a metallacycle.

The molecular structure of **10** was confirmed by single-crystal X-ray diffraction analysis. The molecule is monomeric with the Ti atom bonded to two NCy_2 groups and engaged into a five-membered metallacycle with an *ortho*-metalated neophyl group (Figure 2). The Ti atom possesses a slightly distorted tetrahedral geometry [N1−Ti1−N2 = 120.93(8)°, N1−Ti1−C25 = 111.98(8)°, N1−Ti1−C30 = 110.26(8)°, N2−Ti1−C25 = 110.81(8)°, C25−Ti1−C30 = 84.92(9)°], which is bound by two N atoms of the amide groups and two C atoms of one neophyl unit. The neophyl group chelates titanium through the methylene group and one *ortho* carbon atom of the phenyl group [Ti1−C25 = 2.121(2) Å, Ti1−C30 = 2.089(2) Å]. The Ti atom was found significantly elevated above the puckered plane [C30−C29−C26−C25 = −19.2(3)°] formed by the four C atoms which compose part of the five-membered ring. Conversely, the metallacycle is nearly coplanar with the

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[23] (a) Wielstra, Y.; Gambarotta, S.; Chiang, M. *Rec. Trav. Chim. Pay Bas* **1989**, *108*, 1. (b) Wielstra, Y.; Gambarotta, S.; Meetsma, A.; Spek, A. L. *Organometallics* **1989**, *8*, 2948.

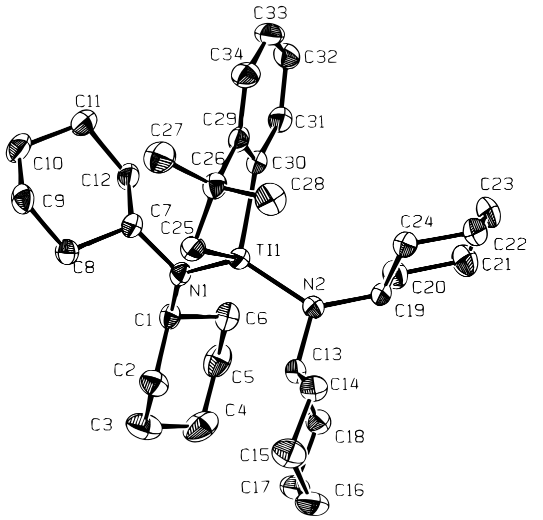
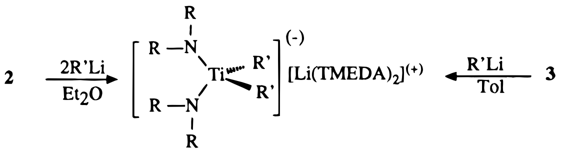


Figure 2. ORTEP plot of **10**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 5



R = i-Pr, R' = Ph (**11**)
R = Me3Si, R' = CH2Ph (**12**)

phenyl ring of the neophyl group. The distortion around Ti is predominantly caused by the bulky amide ligands, whose steric congestion is also indicated by the fact that the coordination of the nitrogen atoms significantly deviates from the regular trigonal planar geometry expected for the sp^2 hybridization [Ti1−N1−C7 = 103.2(1)°, Ti1−N1−C1 = 141.3(1)°, C1−N1−C7 = 115.5(2)°, Ti1−N2−C13 = 108.3(1)°, C13−N2−C19 = 117.2(2)°, Ti1−N2−C19 = 134.5(1)°].

The reaction of the isopropyl halide derivative [(*i*-$Pr_2N)_2TiCl_2$][Li(TMEDA)$_2$] (**2**) with a number of alkyllithium agents only yielded intractable materials. Only in the case of PhLi was a clean reaction obtained allowing the isolation of a new complex **11** in crystalline form (Scheme 5). The magnetic moment ($\mu_{\text{eff}} = 1.77\ \mu_B$), calculated on the basis of the formulation provided by analytical data, was in agreement with a d^1 electronic configuration of a Ti(III) metal center.

The molecular structure of **11** was elucidated by X-ray crystal structure. The complex is mononuclear and is composed of two distinct ionic moieties (Figure 3). The anion consists of a distorted tetrahedral titanium atom with a coordination geometry defined by two nitrogen atoms of two amides and two carbon atoms of two phenyl groups. Once again the distortion of the coordination geometry of Ti is caused by the steric bulk of the amide substituents which are slightly bent toward the phenyl groups [N3−Ti1−N4 = 118.0(2)°, N3−Ti1−C1 = 109.6(2)°, N4−Ti1−C7 = 115.6(2)°, C1−Ti1−C7 = 100.2(2)°]. The Ti−N [Ti1−N3 = 1.962(4) Å, Ti1−N4 = 1.965(4) Å] and the Ti−C bond distances [Ti1−C1 = 2.173(5) Å, Ti1−C7 = 2.210(5) Å] are in the expected range. The angles around the nitrogen atoms of the two amide ligands are severely distorted with respect to the expected sp^2 hybridization of the N atom. The cationic fragment consists of two molecules of TMEDA surrounding a slightly distorted tetrahedral Li atom [N1−Li2−N2 = 87.3(4)°, N1−Li2−N5 = 123.7(4)°, N1−Li2−N6 = 118.6(4)°, N2−Li2−N5 = 117.7(4)°, N5−Li2−N6 = 87.8(4)°] with Li−N distances in the expected range [Li2−N1 = 2.12(1) Å, Li2−N2 = 2.13(1) Å].

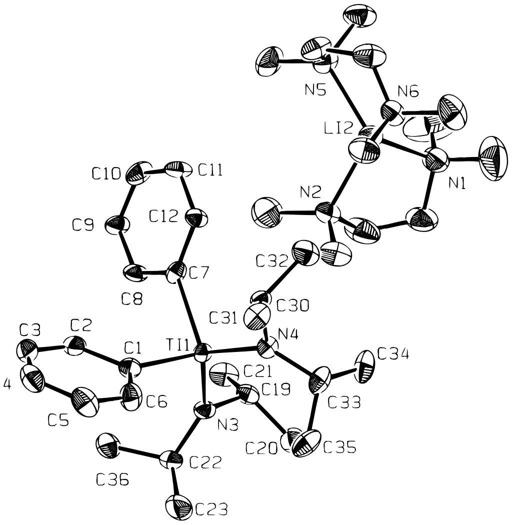


Figure 3. ORTEP plot of **11**. Thermal ellipsoids are drawn at the 50% probability level.

An anionic Ti(III) dibenzyl complex [{$(Me_3Si)_2N\}_2Ti(Bz)_2$][Li(TMEDA)$_2$] (**12**) was obtained upon treatment of the silylated amide derivative {[$(Me_3Si)_2N]_2TiCl_2$}{Li(TMEDA)$_2$} (**3**) with *t*-BuLi in toluene (Scheme 5). The complex was isolated as paramagnetic golden yellow-orange crystals. A mixture of isobutene and isobutane was found in both the gaseous mixture of the reaction vessel and in the mother liquor. The origin of the benzyl groups in complex **12** might be attributed to the formation of $PhCH_2Li$ generated *in situ* by the fast reaction of *t*-BuLi with toluene and subsequent reaction with the Ti substrate. However, we cannot exclude the possibility that **12** might also be originated by the reaction of an *in situ* generated {[$(Me_3Si)_2N]_2Ti(t\text{-}Bu)_2\}^-$[Li(TMEDA)$_2]^+$ complex with toluene. Reaction of **12** with *t*-BuLi in either hexane or ether gave only intractable materials.

Complex **12** is monomeric and also ionic with a Li(TMEDA)$_2$ cationic fragment very similar to that of complex **11** (Figure 4). The anion consists of a titanium atom with distorted tetrahedral geometry defined by two N atoms from the amide units and two C atoms of the two benzyl subsituents [N1−Ti1−N2 = 127.4(3)°, N1−Ti1−C7 = 108.1(3)°, N1−Ti1−C14 = 100.0(4)°, C7−Ti1−C14 = 97.4(4)°]. The nitrogen atoms of the amides show the usual trigonal planar geometry indicative of some extent of Ti−N π bonding [Ti1−N1−Si1 = 116.5(4)°, Ti1−N1−Si2 = 121.9(4)°, Si1−N1−Si2 = 121.6(5)°]. The Ti−N [Ti1−N1 = 2.036(8) Å, Ti1−N2 = 2.027(8) Å] and the Ti−C bond distances [Ti1−C7 = 2.18(1) Å, Ti1−C14 = 2.18 Å] are comparable with those of complex **11**.

Similar to the other Tl(III) and Ti(IV) alkyls reported in this work, complex **12** was also found to be thermally labile in both toluene and THF solutions, in which it decomposed forming intractable materials. Nevertheless, the reaction of **12** with diphenylfulvene resulted in the formation of a neutral Ti(IV) complex **13** which crystallized as red cubes from hexane in about 59% yield (Scheme 6). The complex was characterized by analyti-

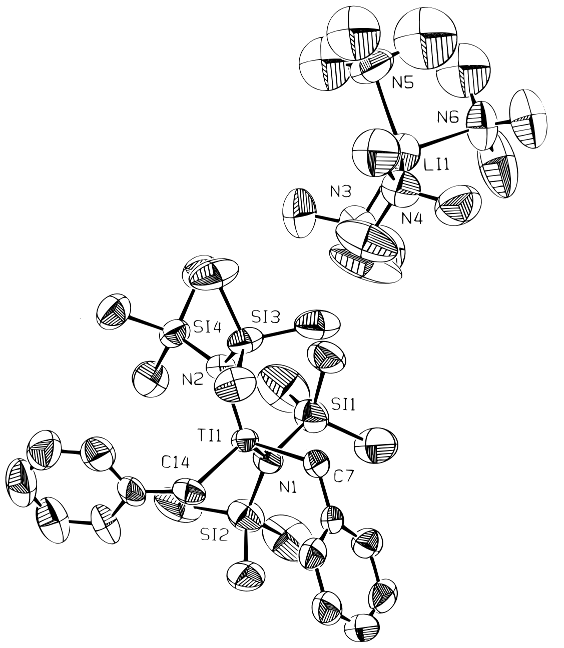
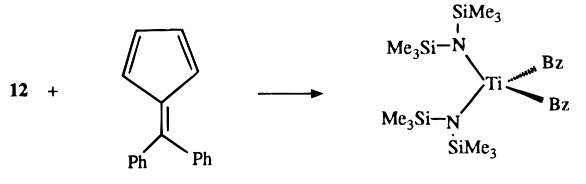


Figure 4. ORTEP plot of **12**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 6



(13)

cal and spectroscopic data. Complex **13** could not be synthesized by using the more straightforward synthetic pattern described for the other Ti(IV) alkyls reported above, since the starting {(Me$_3$Si)$_2$N}$_2$TiCl$_2$ could not be prepared. However, the reaction of **12** with diphenylfulvene provided the desired complex **13** in good yield *via* a simple electron transfer mechanism. Similar to the other Ti(IV) alkyl complexes reported in this work, the CH$_2$ benzilic resonance of complex **12** was found shifted to considerably low field in the ^{1}H NMR spectrum.

The crystal structure of **13** revealed the complex to be monomeric (Figure 5). Even in this case the steric bulk of the amide ligands is likely to be responsible for the significant distortion of the tetrahedral coordination geometry of the Tl atom [N1–Ti1–N2 = 120.6(1)°, N1–Ti1–C13 = 108.4(2)°, N1–Ti1–C20 = 108.1(2)°, C13–Ti1–C20 = 98.4(2)°]. The geometry of the two amide nitrogen atoms slightly deviates from the regular trigonal planar geometry [Ti1–N1–Si1 = 124.8(2)°, Ti1–N1–Si2 = 117.5(2)°, Si1–N1–Si2 = 117.5(2)°]. Conversely, the angles subtended at the benzylic carbon, C13 and C20 [Ti1–C13–C14 = 120.7(3)°, Ti1–C20–C21 = 119.2(3)°], deviate severely from the normal tetrahedral angle. The Ti–N [Ti1–N1 = 1.931(3) Å, Ti1–N2 = 1.939(3) Å] and Ti–C [Ti1–C13 = 2.092(5) Å, Ti1–C20 = 2.109(4) Å] bond distances are slightly shorter with respect to complex **12** as a probable result of the smaller atomic *radius* of the Ti(IV) atom.

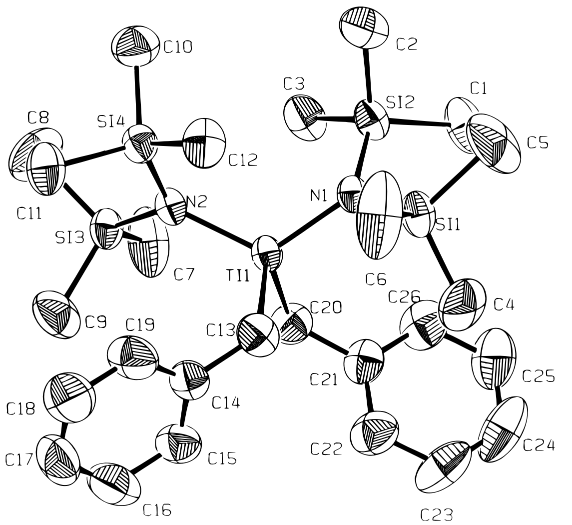
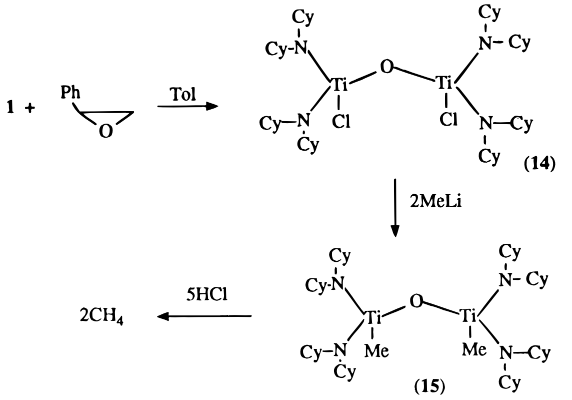


Figure 5. ORTEP plot of **13**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 7



Complex **1** reacted with styrene oxide in toluene at room temperature to form a new complex [(Cy$_2$N)$_2$TiCl]$_2$(μ-O) (**14**) (Scheme 7), which was isolated as orange crystals. The IR spectrum showed the Ti–O stretching as a broad intense band at 746 cm^{-1}. The ^{1}H NMR spectrum of the complex showed only one type of cyclohexyl group, with a multiplet at 3.85 ppm and the characteristic series of multiplets in the range 1.1–2.3 ppm.

The X-ray crystal structure determination has proven the molecule to be dimeric consisting of two identical (Cy$_2$N)$_2$TiCl fragments bridged by an oxygen atom (Figure 6). Each titanium atom possesses a tetrahedral geometry [Cl2–Ti1–N2 = 109.9(2)°, Cl2–Ti1–N1 = 109.2(2)°, Cl2–Ti1–O1 = 109.3(2)°, O1–Ti1–N1 = 113.5(2)°, O1–Ti1–N2 = 108.5(2)°, N1–Ti1–N2 = 106.3(2)°] defined by two nitrogen atoms from two amides, one chloride, and the oxygen atom. The nitrogen atoms have a slightly distorted trigonal planar geometry [Ti1–N1–C1 = 120.6(5)°, Ti1–N1–C7 = 123.5(4)°, C1–N1–C7 = 115.7(5)°]. The short Ti–N distances [Ti1–N1 = 1.910(6) Å, Ti1–N2 = 1.876(6) Å] are as expected. The Ti–O distances are remarkably short [Ti1–O1 = 1.828(2) Å] while the Ti–O–Ti frame is bent. The angle subtended at the oxygen atom [Ti1–O1–Ti1a = 154.9(4)°] is rather similar to that of other μ-oxo-bridged titanium complexes.[4d,5k]

Attempts to alkylate complex **14** were successful only in the case of MeLi. The reaction yielded the corresponding dimethyl complex [(Cy$_2$N)$_2$TiMe]$_2$(μ-O) (**15**), which was characterized on the basis of analytical and

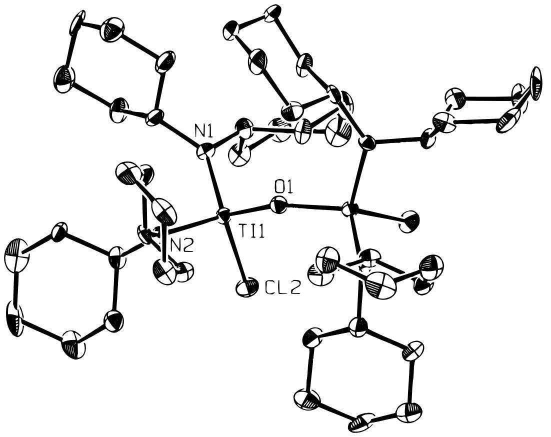


Figure 6. ORTEP plot of **14**. Thermal ellipsoids are drawn at the 50% probability level.

spectroscopic data. In addition to the resonances of the cyclohexyl groups shifted to slightly higher field, a new sharp singlet at 0.94 ppm corresponding to the methyl group was observed in the ^{1}H NMR spectrum. $^{13}C\{^1H\}$ and HMQC spectra also confirmed the formulation. The IR spectrum showed a Ti–O resonance at 771 cm^{-1}, which is slightly shifted with respect to that of the starting material **14**. Unfortunately, numerous attempts to prepare X-ray-quality crystals remained unsuccessful. However, chemical degradation experiments with gaseous HCl carried out in a closed vessel connected to a Toepler pump yielded the expected amount of methane.

In conclusion, in this work we have shown that anionic organic amides are versatile supporting ligands for the stabilization of a full series of reactive Ti alkyl derivatives. A broad study on the chemical reactivity of these new species will be described elsewhere.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating and strategic grants).

Supporting Information Available: ORTEP drawings and tables giving details on structure determinations, atomic positional and thermal parameters, anisotropic thermal parameters, and bond distances and angles (123 pages). Ordering information is given on any current masthead page.

OM9508288