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Synthesis and Characterization of Novel Titanium(III) and -(IV) Alkyls and Carbenes Supported by Amide Ligands. Crystal Structure of $[(Cy_2N)_2Ti(\mu\text{-}CH_2)]_2$

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Reaction of $(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (**1**) [TMEDA = *N,N,N′,N′*-tetramethylethylenediamine] with MeLi formed different complexes depending on the stoichiometric ratio of the reactants used. The novel Ti(III) complex $(Cy_2N)_2Ti(\mu\text{-}Me)_2Li(TMEDA)$ (**2**) was formed when 2 equiv of the organolithium reagent was used, while a tetravalent complex, $(Cy_2N)_2TiMe_2$ (**3**), was formed when a stiochiometric ratio of 1:1 was used. Complex **3** rapidly decomposed in toluene at 60 °C to form the bridging methylene complex $(Cy_2N)_2Ti(\mu\text{-}CH_2)_2Ti(NCy_2)_2$ (**5**). The structures of **2**, **3**, and **5** were elucidated by X-ray diffraction analysis. Crystal data are as follows. **2**: $C_{32}H_{66}N_4TiLi$, $M = 561.74$, monoclinic, $P2_1/n$, $a = 12.505(5)$ Å, $b = 19.333(9)$ Å, $c = 15.393(5)$ Å, $\beta = 109.10(2)°$, $V = 3517(3)$ Å^3, $Z = 4$, $T = -160$ °C, Mo Kα, $R = 0.066$, $R_w = 0.061$ for 3644 reflections and 343 parameters. Non-hydrogen atoms were refined anisotropically. **3**: $C_{26}H_{50}N_2Ti$, $M = 438.59$, monoclinic, $P2_1/n$, $a = 9.906(4)$ Å, $b = 18.520(6)$ Å, $c = 14.271(4)$ Å, $\beta = 96.87(3)°$, $V = 2599(3)$ Å^3, $Z = 4$, $T = -161$ °C, Mo Kα, $R = 0.053$, $R_w = 0.065$ for 3132 reflections and 263 parameters. Non-hydrogen atoms were refined anisotropically. **5**: $C_{50}H_{92}N_2Ti_2$, $M = 845.10$, monoclinic, $P2/n$, $a = 13.6190(9)$ Å, $b = 12.484(1)$ Å, $c = 14.811(1)$ Å, $\beta = 96.510(3)°$, V 2501.9(6) Å^3, $Z = 2$, $T = -160$ °C, Mo Kα, $R = 0.057$, $R_w = 0.065$ for 2637 reflections and 343 parameters. Non-hydrogen atoms were refined anisotropically.

Introduction

The discovery that highly reactive organic fragments, such as carbenes, may be trapped and stabilized by transition metals to form stable complexes[1] is one of the most significant discoveries in modern organometallic chemistry. In addition to the fundamental scientific interest stimulated by the chemical behavior of these highly reactive units, many important transformations[2] and industrially relevant processes have been developed[3] which are promoted or catalyzed by transition metal carbenes. As a result of the strong interest in this field, many examples of methylidene and methylidyne complexes have been reported for several metals.[1]

Titanium derivatives are among the most extensively studied examples in this class of compounds,[4] and a remarkable range of chemical reactivity has been documented.[5] They have been widely employed for ROMP,[6] olefin cyclization and cyclopropanation,[7] and metathesis and polymerization.[8] By contrast, stable Ti–methylene complexes have been obtained and fully characterized only for heterodimetallic complexes of titanocene with

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late transition metals[9] and aluminum alkyls (Tebbe's reagent).[10] In fact, the Ti=CH_2 moiety appears to be rather unstable and the transient formation of the monomeric $Cp_2Ti(=CH_2)PMe_3$ has been observed only by NMR spectroscopy.[11] The dinuclear homologue $[Cp_2Ti(\mu\text{-}CH_2)]_2$ has also been characterized on the basis of its spectroscopic data.[12]

One of the most common routes for the preparation of transition metal alkylidenes is via the C−H σ-bond metathesis of alkyl groups, which is typically achieved under thermal conditions. However, although this synthetic procedure is widely used for the preparation of group 5 and 6 carbenes,[13] it has never demonstrated to be a viable route for the preparation of the titanium homologues despite the availability of titanium alkyl precursors. This is likely to be ascribed to the fact that studies on group 4 metal alkyls have been almost exclusively carried out with ligands such as cyclopentadienyls which, under C−H σ-bond metathesis conditions, may be involved in the reactivity of the metal center.[14] Apart from this, the organometallic chemistry of titanium supported by other ligands remains otherwise in its infancy.[15]

Recently, low-valent early transition metal complexes of anionic organic amides have shown the unprecedented ability to eliminate hydrogen from their aliphatic groups to form olefin functions[16] and to transfer hydrogen to an organic substrate.[17] In addition, organic amides have been proven to be versatile supporting ligands for the stabilization of highly reactive moieties including metallacyclobutanes.[18] The reversibility of the reaction of titanium carbene with olefins to form a titanacyclobutane ring is a key feature of the catalytic ability of these species. Hence, we became interested in investigating the ability of alkylamido ligands to stabilize titanium alkyls, metallacycle, and carbene functions.

As a part of an ongoing project, this preliminary paper reports the synthesis, characterization, and properties of a novel series of titanium alkyls supported by amide ligands and the straightforward formation of the first crystallographically characterized titanium methylidene.

Experimental Part

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware on 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.[19,15h] Cy_2NH and TMEDA [TMEDA = *N,N,N',N'*-tetramethylethylenediamine] were distilled prior to use over Na and K metals, respectively. The preparation of Cy_2NLi was carried out by treating a hexane solution of Cy_2NH with a stoichiometric amount of *n*-BuLi. C_6D_6 was dried over Na/K alloy, vacuum-transferred into an ampule 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 the drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside a drybox. Magnetic susceptibility measurements were carried out on a Johnson Matthey balance at room temperature following standard methods.[20,21]

$(Cy_2N)_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (1). Lithium dicyclohexylamido, Cy_2NLi (15.7 g, 83.9 mmol), was added to a blue suspension of $TiCl_3THF_3$ (15.5 g, 41.9 mmol) in THF (170 mL) at −10 °C, followed by the addition of 1.5 equiv of TMEDA (9.5 mL, 62.9 mmol). The reaction mixture was allowed to warm to room temperature and stirring was continued for 2 h. The resulting emerald-green solution was evaporated to dryness and the foamy residue was redissolved in hexane (200 mL). The LiCl was removed by filtration and emerald-green crystals of **1** (14.6 g, 24.2 mmol, 57%) were obtained upon standing of the filtrate overnight at room temperature. Anal. Calcd (found) for $C_{30}H_{60}N_4Cl_2LiTi$: C, 59.80 (59.74); H, 10.04 (10.05); N, 9.30 (9.26). IR (KBr, Nujol mull, cm^{-1}): 1404(m), 1287(s), 1249(s), 1154(s), 1122(s), 1063(s), 1028(s), 982(s), 950(s), 888(s), 842(s), 803(m), 789(s), 777(m), 723(w), 690(s), 585(s), 489(s), 449(m), 419(m). $\mu_{eff} = 1.76\ \mu_B$.

$(Cy_2N)_2Ti(\mu\text{-}Me)_2LiTMEDA$ (2). A solution of MeLi (4.5 mL, 1.4 M, 6.3 mmol) was added to a stirred emerald-green solution of **1** (1.9 g, 3.1 mmol) in diethyl ether (70 mL) at −10 °C. The color changed to light-green and LiCl separated. The reaction mixture was allowed to warm to room temperature and the solvent was evaporated to dryness. The residual solid was dissolved in hexane (50 mL) and a small amount of insoluble residue was eliminated by filtration. Light-green crystals of **2** (0.6 g, 1.0 mmol, 34%) separated upon standing of the filtrate for ca. 30 min at room temperature. Anal. Calcd (found) for $C_{32}H_{66}N_4LiTi$: C, 68.42 (68.34); H, 11.84 (11.92); N, 9.97 (9.76). IR (KBr, Nujol mull, cm^{-1}): 1341(w), 1287(s), 1247(s), 1152(s), 1120(s), 1064(m), 1029(s), 982(m), 949(s), 887(s), 842(s), 800(m), 790(m), 723(w), 682(s), 583(s), 534(w), 496(w), 447(w). $\mu_{eff} = 1.77\ \mu_B$.

$(Cy_2N)_2TiMe_2$ (3). A reddish-orange suspension of **4** (1.8 g, 3.8 mmol) in diethyl ether (70 mL) was treated with a MeLi solution (5.5 mL, 1.4M, 7.6 mmol) at −10 °C under stirring. No apparent reaction occurred until the mixture reached near room temperature when a rapid color change to brown was observed. The stirring was continued further for about 1 h followed by evaporation of ether. The residual solid was redissolved in hexane (40 mL) and the small amount of insoluble residue was filtered out. Pale-green crystals of **3** (1.2 g, 2.9 mmol, 58%) separated upon cooling of the filtrate overnight at −30 °C. Anal. Calcd (found) for $C_{26}H_{50}N_2Ti$: C,

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Table 1. Crystal Data and Structural Analysis Results

complex	2	3	5
formula	$C_{32}H_{66}TiN_4Li$	$C_{26}H_{50}N_2Ti$	$C_{50}H_{92}N_2Ti_2$
formula weight	561.74	438.59	845.10
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2/n$
a (Å)	12.505(5)	9.906(4)	13.6190(9)
b (Å)	19.333(9)	18.520(6)	12.484(1)
c (Å)	15.393(5)	14.271(4)	14.811(1)
α (deg)			
β (deg)	109.10(2)	96.87(3)	96.510(3)
γ (deg)			
V (Å^3)	3517(3)	2599(3)	2501.9(6)
Z	4	4	2
Radiation (Mo Kα, Å)	0.71069	0.71069	0.71069
T (°C)	−160	−161	−160
D_{calcd} (g cm^{-3})	1.061	1.121	1.122
μ_{calcd} (cm^{-1})	2.62	3.38	3.49
no. of observations	3644	3132	2637
no. of parameters	343	263	343
R_F, R_w	0.066, 0.061	0.053, 0.065	0.057, 0.065
GoF	2.82	2.82	2.25

71.20 (71.05); H, 11.49 (11.37); N, 6.39 (6.44). IR (KBr, Nujol mull, cm^{-1}): 1410(w), 1340(m), 1300(w), 1250(m), 1160(s), 1145(m), 1115(m), 1100(s), 1065(w), 1020(s), 980(m), 950(s), 890(s), 840(s), 800(s), 775(s), 705(s), 685(m), 595(w), 580(m), 550(w), 520(s), 500(w), 490(w), 450(w), 420(w). ^{1}H NMR [200 MHz, C_6D_6, δ (ppm)]: 3.65 (m, 4H cyclohexyl), 2.1−1.0 (m, 40H cyclohexyl), 0.93 (s, 6H methyl). ^{13}C NMR [200 MHz, C_6D_6, δ(ppm)]: 57.6 (CH cyclohexyl), 36.4, 27.8, 26.1 (CH_2 cyclohexyl), 4.0 (CH_3).

$(Cy_2N)_2TiCl_2$ (4). Addition of 2 equiv of Cy_2NLi (2.4 g, 12.6 mmol) to a clear yellow solution of $TiCl_4$(TMEDA) (1.9 g, 6.3 mmol) in THF (50 mL) at −10 °C turned reddish-brown. The mixture was allowed to warm up to room temperature and then boiled for a few minutes. After evaporation of the solvent in vacuo, the residual solid was redissolved in hexane (60 mL) and the insoluble residue was eliminated by filtration. Dark-orange crystals of **4** (2.5 mmol, 40%) were obtained after standing of the filtrate overnight at room temperature. Anal. Calcd (found) for $C_{24}H_{44}N_2TiCl_2$: C, 60.13 (60.08); H, 9.25 (9.21); N, 5.84 (5.98). IR (KBr, Nujol mull, cm^{-1}): 1375(m), 1253(m), 1160(s), 1142(s), 1111(s), 1092(s), 1021(s), 978(m), 948(s), 890(s), 843(s), 806(m), 780(s), 723(w), 707(s), 601(m), 580(m), 522(s), 485(s), 432(s), 409(s). ^{1}H NMR [200 MHz, C_6D_6, δ (ppm)]: 3.7 (m, 4H cyclohexyl), 2.1−0.9 (m, 40H cyclohexyl).

$[(Cy_2N)_2Ti(\mu\text{-}CH_2)]_2$ (5). Addition of a MeLi solution (4.0 mL, 1.4 M, 5.6 mmol) to a solution of **1** (3.35g, 5.6 mmol) in diethyl ether at −10 °C immediately turned from emerald-green to pale-green. The stirring was continued for 30 min, followed by evaporation of the solvent to dryness. The residual foamy solid was redissolved in hexane (20 mL) and the insoluble residue was filtered out. The filtrate was allowed to stand at room temperature, upon which pale yellow crystals of **3** were formed. When the mixture was allowed to stand longer at room temperature, the yellow crystals redissolved t form red prisms of **5** (0.5 g, 1.2 mmol, 22%). Anal. Calcd (found) for $C_{50}H_{92}N_4Ti_2$: C, 70.89 (70.01); H, 11.18 (11.35); N, 6.61 (6.63). IR (KBr, Nujol mull, cm^{-1}): 2895(s), 1454(s), 1381(s), 1343(s), 1248(s), 1160(s), 1143(s), 1110(s), 1066(w), 1032(s), 982(m), 949(s), 888(s), 842(s0, 802(s), 777(s), 696(s), 649(s), 579(s), 502(s), 448(w), 419(w). ^{1}H NMR [500 MHz, C_6D_6, δ (ppm)]: 8.29 (s, μ-CH_2), 3.42 (m, 4H cyclohexyl), 2.23−1.17 (bd m, 40H cyclohexyl). ^{13}C [500 MHz, C_6D_6, δ (ppm)]: 224.7 (μ-CH_2), 56.5 (CH cyclohexyl), 37.6, 27.2, 26.4 (CH_2 cyclohexyl).

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. Redundant 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 and refined isotropically in the case of favorable observation/parameter ratio. 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 Fcalc. 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. The final atomic coordinates are given as supplementary material. Selected bond distances and angles are given in Table 2.

Description of the Crystal Structures. Complex 2. The heterodinuclear structure of the complex is composed of a tetrahedral $(R_2N_2)Ti(Me)_2$ unit with the two methyl groups bridged to a Li(TMEDA) moiety (Figure 1). The coordination geometry around the titanium atom is a distorted tetrahedron [N1−Ti1−N2 = 119.9(2)°, C25−Ti1−N1 = 105.6(2)°, C26−Ti1−N2 = 106.1(2)°] with the coordination polyhedron bounded by the two nitrogen atoms of the two amides and the carbon atoms [Ti−C26 = 2.229(3) Å, Ti1−C25 = 2.235(5) Å] of the

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

2	3	5
Ti1−N1 = 1.964(4)	Ti1−N1 = 1.888(3)	Ti1−N1 = 1.936(4)
Ti1−N2 = 1.941(4)	Ti1−N2 = 1.892(3)	Ti1−C1 = 2.020(5)
Ti1−C26 = 2.229(5)	Ti1−C25 = 2.111(4)	Ti2−C1 = 2.016(5)
Ti1−C25 = 2.235(5)	Ti1−C26 = 2.118(3)	Ti2−N2 = 1.939(4)
Li1−C25 = 2.24(1)	N1−Ti1−N2 = 118.4(1)	Ti1−Ti2 = 2.934(2)
Li1−C26 = 2.21(1)	N1−Ti1−C25 = 108.5(1)	N1−Ti1−N1a = 121.7(3)
Li1−H63 = 1.94	N1−Ti1−C26 = 106.5(1)	N1−Ti−C1 = 108.4(2)
Li1−H65 = 2.07	N2−Ti1−C25 = 109.2(1)	C1−Ti1−C1a = 86.6(3)
Ti1−Li1 = 2.784(9)	N2−Ti1−C26 = 107.3(1)	N2−Ti2−N2a = 123.9(3)
N1−Ti1−N2 = 119.9(2)	C25−Ti1−C26 = 105.9(1)	N2−Ti2−C1 = 11.8(2)
N1−Ti1−C25 = 105.6(2)		C1−Ti2−C2a = 86.8(3)
N1−Ti1−C26 = 112.3(2)		Ti1−C1−Ti2 = 93.3(2)
N2−Ti1−C25 = 109.3(2)		C1−Ti2−C1a = 86.8(3)
N2−Ti1−C26 = 106.1(2)		C2−N2−C8 = 116.0(4)
C25−Ti1−C26 = 102.3(2)		C2−N2−Ti2 = 106.8(3)
C25−Li1−C26 = 102.6(4)		C8−N2−Ti2 = 136.2(3)
Ti1−C25−Li1 = 77.0(3)		
Ti1−C26−Li1 = 77.6(3)		
C1−N1−Ti1 = 106.7(3)		
C7−N1−Ti1 = 137.0(3)		
C1−N1−C7 = 115.9(4)		

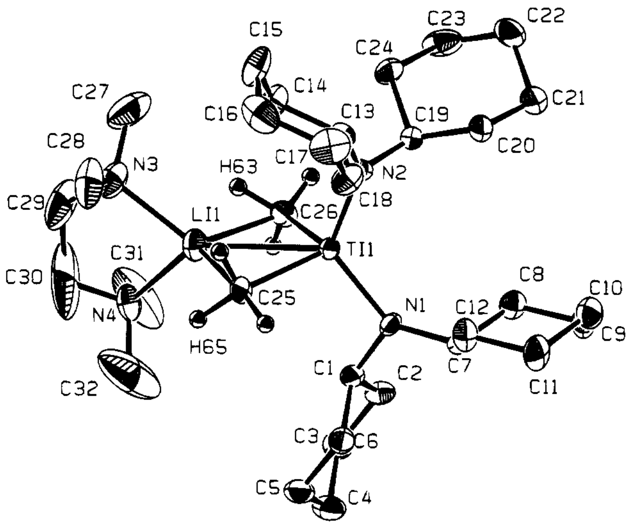


Figure 1. ORTEP plot of **2**. Thermal ellipsoids are drawn at the 50% probability level. Some of the hydrogen atoms have been omitted for clarity.

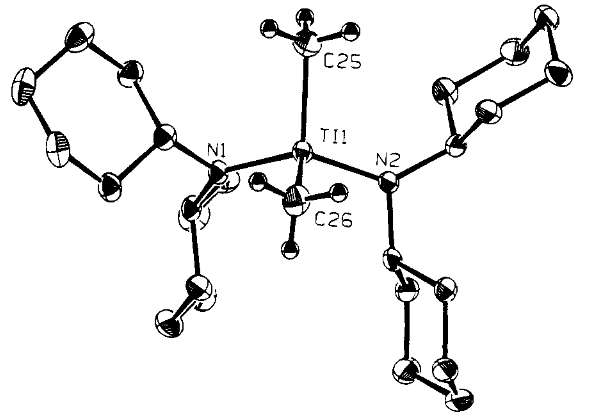


Figure 2. ORTEP plot of **3**. Thermal ellipsoids are drawn at the 50% probability level. Some of the hydrogen atoms have been omitted for clarity.

two methyl groups. The trigonal planar geometry of the nitrogen donor atoms [C1−N1−Ti1 = 106.7(3)°, Ti1−N1−C7 = 137.0(3)°, C1−N1−C7 = 115.9(4)°] together with the rather short titanium−nitrogen distances [Ti1−N1 = 1.964(4) Å, Ti1−N2 = 1.941(4) Å] indicate an sp^2 hybridization of the nitrogen atoms, and possibly some extent of a Ti−N π-bond. The TiMe$_2$-Li core [Li1−C26 = 2.21(1) Å, Li1−C25 = 2.24(1) Å, Li1−Ti1 = 2.784(9) Å] is almost planar [C25−Ti1−C26−Li1 = 5.7(3)°] with the angles subtended at the bridging carbon atoms significantly narrower than expected for sp^3 carbon atoms [Ti1−C25−Li1 = 77.0(3)°, Ti1−C26−Li1 = 77.6(3)°].

Complex 3. Complex **3** is monomeric and the structure consists of a titanium atom placed in the center of a distorted tetrahedron defined by the two nitrogen atoms of the two amido ligands and the two terminal methyl groups [N1−Ti1−C25 = 108.7(1)°, C25−Ti1−N2 = 109.2(1)°, N2−Ti1−C26 = 107.3(1)°, N1−Ti1−C26 = 106.5(1)°] (Figure 2). The geometry of the amido ligands is very similar to that of complex **2**, with comparable bond distances [Ti1−N1 = 1.888(3) Å, Ti1−N2 = 1.892(3) Å] and angles [Ti1−N1−C7 = 141.2(2)°, Ti1−N1−C20 = 103.4(2)°, Ti1−N2−C13 = 133.0(2)°, C1−N2−C13 = 115.2(2)°]. The slightly shorter Ti−N and Ti−C distances [Ti1−C25 = 2.111(4) Å, Ti1−C26 = 2.118(3) Å] with respect to complex **2** may be ascribed to the smaller atomic radius of the Ti(IV) atom.

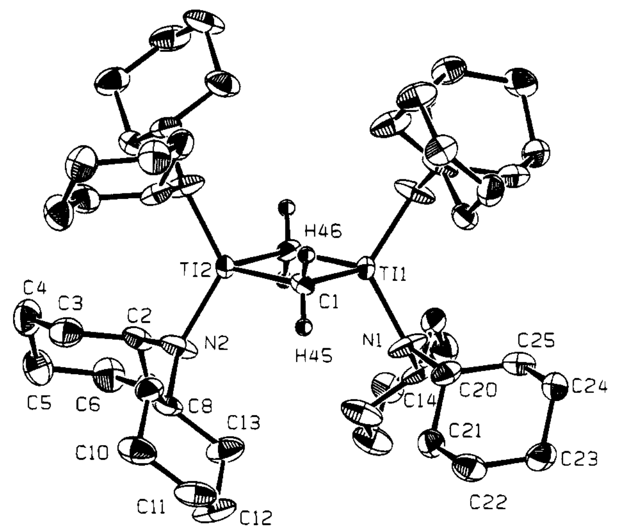
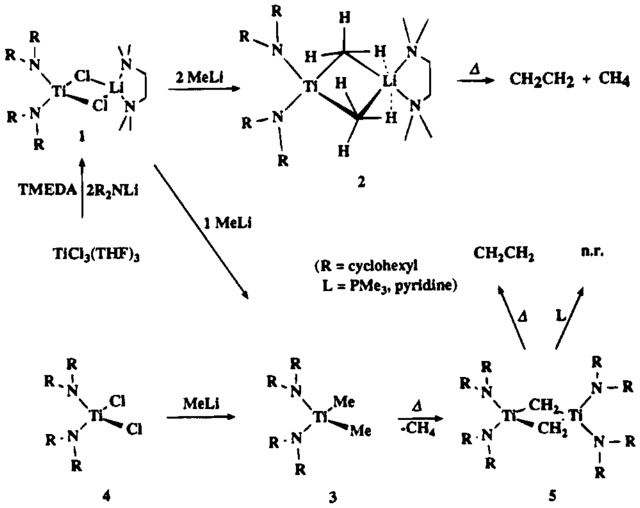


Figure 3. ORTEP plot of **5**. Thermal ellipsoids are drawn at the 50% probability level. Some of the hydrogen atoms have been omitted for clarity.

Scheme 1



Complex 5. The molecule is dimeric and consists of two identical (R$_2$N)$_2$Ti fragments connected by two bridging methylene groups (Figure 3). The coordination geometry around each titanium atom is distorted tetrahedral [N1−Ti1−N1a = 121.7(3)°, N2−Ti2−N2a = 123.9(3)°, C1−Ti1−N1 = 113.2(2)°, C1−Ti1−C1a = 86.6(3)°] and very similar to that of complexes **2** and **3**. Even in this case, the nitrogen atoms of the amido groups are trigonal planar, forming comparable Ti−N bond distances [Ti1−N1 = 1.936(4) Å, Ti2−N2 = 1.939(4) Å] and angles. The Ti$_2$(CH$_2$)$_2$ core is planar [C1−Ti1−C1a−Ti2 = 0.0°] forming rather short Ti⋯Ti contact [Ti1⋯Ti2 = 2.934(2) Å]. The Ti(μ-CH$_2$) distances [Ti1−C1 = 2.020(5) Å, Ti2−C1 = 2.016(5) Å] compare well with those of other heterodinuclear Ti−methylidene complexes.[9]

Results and Discussion

Addition of 2 equiv of R$_2$NLi [R = cyclohexyl] to a THF suspension of TiCl$_3$(THF)$_3$ containing 1.5 equiv of TMEDA resulted in the rapid formation of an emerald-green solution from which light-green crystals of the heterodinuclear (R$_2$N)$_2$Ti(μ-Cl)$_2$Li(TMEDA) (**1**) were isolated in good yield (Scheme 1). The ^{1}H-NMR spectrum was uninformative, only showing broad resonances, and therefore, the formulation had to be inferred from elemental analysis data. The chemical connectiv-

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(22) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol IV.

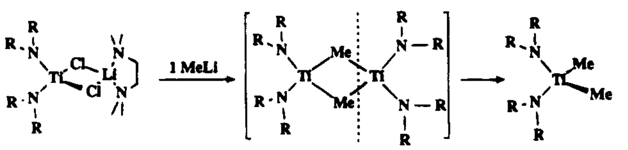
ity of **1** was further confirmed by an X-ray crystal structure.[23] The magnetic moment, measured at room temperature, was as expected for the d^1 electronic configuration of Ti(III) [$\mu_{\text{eff}} = 1.76\mu_B$].

As illustrated in Scheme 1, the reactions of **1** with MeLi gave two completely different products depending on the stoichiometry used. Reaction of **1** with 2 equiv of MeLi in diethyl ether at −10 °C afforded the isostructural $(R_2N)_2Ti(\mu\text{-Me})_2Li(TMEDA)$ (**2**), which was isolated upon crystallization from hexane as extremely air-sensitive and pyrophoric light-greenish crystals. As in the case of complex **1**, the ^{1}H-NMR spectrum of **2** did not offer any structural information while the magnetic moment, calculated on the basis of the formulation suggested by microanalysis, was in agreement with the d^1 electronic configuration expected for a Ti(III) complex. Crystals of **2** reacted violently with protic solvents, releasing methane which was almost quantitatively recovered (96%) during chemical degradation experiments carried out with HCl in a closed vessel connected to a Toepler pump.

The bonding of alkali cation in complex **2** is somewhat surprising. The lithium moiety is connected to the methyl group carbon atoms rather than to the two amido nitrogens which are expected to be better donor atoms. A possible explanation for this anomaly is provided by the crystal structure of **2**, which was of sufficient quality to locate all the H atom positions. The hydrogen atoms of each bridging methyl group define a slightly distorted tetrahedron centered on carbon with the fourth position occupied by titanium. The Li atom is placed side-on and almost perpendicular with respect to one of the three C−H bonds of each of the two bridging methyl groups [Li1−H63−C26 = 73.72°, Li1−H65−C25 = 66.57°], forming remarkably short lithium−hydrogen distances [Li1−H63 = 1.94 Å, Li1−H65 = 2.07 Å]. These geometrical features suggest, as long as we consider the H atom position as significant, that similar to the case of $Me_4CrLi_2(TMEDA)_2$,[24] two Li−H agostic interactions are responsible for holding together the heterodinuclear frame and are also responsible for the significantly short Ti−Li distance [Ti1−Li1 = 2.784(9) Å]. The crystal structure of **2** provides the first example of a non-cyclopentadienyl Ti(III)−alkyl complex.[14]

When the reaction of **1** with MeLi was carried out under similar conditions but with a 1:1 stoichiometric ratio, the pale-greenish very air-sensitive crystals of a new diamagnetic species (**3**) were obtained. The new complex tested negative for both Li and chloride while the analytical data were consistent for a $(R_2N)_2Ti(CH_3)_2$ formulation. The ^{1}H-NMR spectrum showed the characteristic resonances of the cyclohexyl rings as a sharp multiplet at 3.65 ppm for the methyne proton and a rather complicated feature in the region 2.1−1.0 ppm for the methylene protons of the cyclohexyl rings. A very sharp singlet was found at 0.90 ppm. This resonance was found coupled with a resonance at 4.10 ppm of the ^{13}C-NMR spectrum. A DEPT ^{13}C-NMR spectrum unequivocally identified the resonance to be due to a CH_3 group. The chemical degradation of **3** carried out with either 3 or 2 equiv of HCl gas released 2 equiv of methane, which was measured and identified with Toepler pump/GC combined experiments. Although the preparation of **3** following this route was not achieved in high yield, its formation is significant and reproducible. Complex **3** could be more conveniently prepared (78% yield) by treatment of the Ti(IV) $(R_2N)_2TiCl_2$ (**4**) starting material with 2 equiv of MeLi. The molecular structure was confirmed by a single crystal X-ray diffraction analysis.

Scheme 2



The oxidation of the metal center upon reaction of **1** with a potentially reducing agent such as MeLi is also surprising. The critical role of the reaction stoichiometry in the formation of the tetravalent **3** from the trivalent **1** provides a possible explanation. The reaction of **1** with 1 equiv of MeLi is expected to initially form $(R_2N)_2TiMe(LiCl)(TMEDA)$. Supposing that this species may eliminate 1 equiv of LiCl, the resulting $(R_2N)_2TiMe$ is expected to dimerize by sharing either the methyl or amide groups. We speculate that, as in the case of the dinuclear Zr(III) complexes, the resulting Ti(III) dimer might be unstable, forming the tetravalent **3** through a disproportionation reaction. In fact, simple cleavage of the intermediate $[(R_2N)_2Ti(Me)]_2$ may yield the tetravalent **3** and low-valent diamagnetic Ti species (Scheme 2). Unfortunately, attempts to isolate other species responsible for the dark brown color of the mother liquors have so far been unsuccessful.

Both complexes **2** and **3** display a moderate thermal stability. Complex **2** is completely decomposed in toluene at 60 °C within 24 h, forming a mixture of $CH_2\text{-}CH_2$ and CH_4 and a new diamagnetic complex which displays a very complicated and uninformative NMR spectrum. By contrast, thermolysis of **3** in toluene at 60 °C quantitatively and selectively formed a new species (**5**) in 30 min. The same decomposition was observed to occur, although much slower, at room temperature. The ^{1}H-NMR spectrum of this new complex showed a singlet at 8.29 ppm coupled to a methylene resonance at 224.7 ppm of the ^{13}C-NMR spectrum. These features suggest, in agreement with analytical data and with the fact that 1 equiv of CH_4 is released during its formation, that this complex might be the dimeric methylidene derivative $(R_2N)_2Ti(CH_2)$ (**5**). Red-orange crystals of **5** could also be isolated in moderate yield (22%) by allowing a hexane solution of **3** to stand at room temperature for several days. The thermal lability of **3** with respect to the formation of **5** was unexpected when compared to the thermal inertness of the isostructural $[(Me_3Si)_2N]_2TiMe_2$, which can be recovered unchanged after prolonged heating at 190 °C.[18b]

The dinuclear structure of **5** appears rather robust and, in contrast to the bis-cyclopentadienyl systems,[11,12] the complex could not be cleaved by treatment with coordinating ligands such as PMe_3 or pyridine. Complex **5** displays also a rather high thermal stability, but it decomposes within 42 h in toluene at 70 °C, to afford

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(23) Crystal Data for **1**: $C_{30}H_{60}N_4TiCl_2Li$, M = 602.58, monoclinic, $P2_1/n$, $a = 12.361(5)$ Å, $b = 19.616(4)$ Å, $c = 15.357(3)$ Å, $\beta = 109.39(2)°$, $V = 3512(2)$ Å^3, $Z = 4$, $T = -160$ °C, Mo Kα, $R = 0.077$, $R_w = 0.091$ for 4601 reflections and 519 parameters. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their idealized positions and not refined.

(24) Hao, S.; Gambarotta, S.; Bensimon, C. *J. Am. Chem. Soc.* **1992**, *114*, 3556.

quantitative yield of ethylene. Complex **5** is a highly reactive species and may be regarded as a dititanacyclobutane complex. The long H_2C–CH_2 nonbonding distance [C1–C1a = 2.771(1) Å] discourages the hypothesis that complex **5** might be a binuclear Ti(II) complex where two $(R_2N)_2Ti$ moieties are side-on ligated to an ethylene molecule. However, complex **5** is a potential catalysts for olefin methathesis and reacts with a number of olefins. It polymerizes ethylene and propylene at room temperature and atmospheric pressure through a very efficient albeit slow reaction. An extensive study on the reactivity of **5** will be reported elsewhere.

In summary, the results of this study show that a readily available organic amide is an effective ligand for the stabilization of a novel series of titanium(III) and -(IV) alkyls and methylidene compounds. The crystal structure of **5** is the first example of a homometallic and crystallographically characterized titanium methylene compound. Given that over the past few years a number of sources of the reactive fragment $Cp_2Ti{=}CH_2$ have been developed to characterize and to study this highly reactive moiety, we believe that the fact that organic amides may actually stabilize the $Ti{=}CH_2$ function may open new perspectives for studies of the structure and reactivity of this important class of compounds.

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

Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **2**, **3**, and **5** (53 pages). Ordering information is given on any current masthead page.

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