1470 *Organometallics* **1996,** *15,* 1470−1476

Synthesis of Titanium Complexes That Contain Triamido−Amine Ligands

Richard R. Schrock,* Christopher C. Cummins, Thomas Wilhelm, Shirley Lin,
Steven M. Reid, Moshe Kol, and William M. Davis

*Department of Chemistry, Room 6-331, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

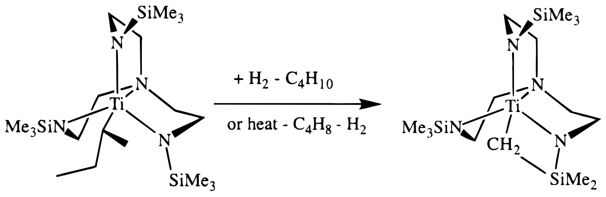
Received October 23, 1995⊗

We report the synthesis of a variety of titanium complexes that contain $(Et_3SiNCH_2CH_2)_3N$, $(C_6F_5NCH_2CH_2)_3N$, or $(Me_3SiNCH_2CH_2CH_2)_3N$ ligands. Complexes in the first category include $[(Et_3SiNCH_2CH_2)_3N]TiCl$, $[(Et_3SiNCH_2CH_2)_3N]Ti(OTf)$, and $[(Et_3SiNCH_2CH_2)_3N]Ti$(*t*-Bu). Complexes in the second category include $[(C_6F_5NCH_2CH_2)_3N]TiX$ (X = Cl, Br, I, OTf) and $[(C_6F_5NCH_2CH_2)_3N]TiR$ (R = Me, Et). Complexes in the third category include $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ and $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCH_3$. In an X-ray study $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ was shown to contain a coordinated amino nitrogen and TiN_2C_3 rings that were puckered in a pseudocyclohexane chair form. The TiN_2C_3 rings are proposed to "flip" via dissociation of the amino nitrogen donor in the methyl complex, but the flipping rate is slow on the NMR time scale in $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ as a consequence of the greater electrophilicity of the metal.

Introduction

A variety of compounds that contain ligands of the type $[(RNCH_2CH_2)_3N]^{3-}$ (R = alkyl, trialkylsilyl, C_6F_5) have been reported in the last few years.[1−14] These trianionic ligands give rise to relatively rigid trigonal bipyramidal transition metal complexes when they behave as tetradentate ligands (i.e., when the amino nitrogen binds in an apical position) in which chemistry can be restricted to one apical site. When R is a sterically bulky group, then rarely observed types of complexes can be prepared, e.g., a tantalum phosphinidene,[6] a tungsten alkylidene hydride complex,[15] or tungsten or molybdenum terminal phosphido complexes.[16] Complexes that do not have a ligand in the other apical site, so-called trigonal monopyramidal species,[4] have also been prepared for first-row metals (Ti−Fe).

A transition metal that is useful in initial studies involving multidentate amido ligands is titanium. For example, we reported the synthesis of $[(Me_3SiNCH_2CH_2)_3N]TiCl$ and some of its alkyl derivatives,[2] as well as trigonal monopyramidal Ti[(*t*-$BuMe_2SiNCH_2CH_2)_3N]$,[4] while others have reported ethyl- and isopropyl-substituted titanium derivatives.[9] We found that the reaction between $[(Me_3SiNCH_2CH_2)_3N]TiCl$ and lithium reagents yielded highly soluble titanium *n*-Bu and *s*-Bu complexes and that the *s*-Bu titanium complex cleanly eliminates butenes and dihydrogen upon heating to give a metallacycle (eq 1) that we presume to be related to others that are known for titanium.[17] The metallacycle is also formed upon treating the *s*-Bu complex with dihydrogen (25 °C, 12 h, 3 atm). (Only butane is produced in this reaction.) A resonance that appears at δ 8.29 in the proton NMR spectrum during the reaction with dihydrogen in a sealed NMR tube was tentatively assigned to a titanium(IV) monohydride intermediate. Therefore it was proposed that the reaction with dihydrogen proceeds via hydrogenolysis of the *sec*-butyl ligand to give unstable $[(Me_3SiNCH_2CH_2)_3N]TiH$, which loses dihydrogen to give the cyclometalated product. This reaction is analogous to the cyclometalation observed in complexes of the type $HM[N(SiMe_3)_2]_3$ (M = Th, U).[18]



(1)

We became interested in preparing other types of $[(RNCH_2CH_2)_3N]Ti$ complexes in order to determine if

---

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1996.

[1] Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009.

[2] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.

[3] Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.

[4] Cummins, C. C.; Lee, J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.

[5] Plass, W.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 3762.

[6] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756.

[7] Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.

[8] Shih, K.-Y.; Totland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103.

[9] Schubart, M.; O'Dwyer, L.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Inorg. Chem.* **1994**, *33*, 3893.

[10] Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

[11] Freundlich, J.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

[12] Cummins, C. C.; Schrock, R. R. *Inorg. Chem.* **1994**, *33*, 395.

[13] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.

[14] Duan, Z.; Verkade, J. G. *Inorg. Chem.* **1995**, *34*, 1576.

[15] Schrock, R. R.; Shih, K.-Y.; Dobbs, D.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 6609.

[16] Zanetti, N. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2044.

[17] Simpson, S. J.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3627.

[18] Simpson, S. J.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.

0276-7333/96/2315-1470$12.00/0

cyclometalation could be prevented and a rare[19−21] monomeric Ti(IV) hydride isolated. In this paper we report the synthesis of a variety of titanium complexes that contain triethylsilyl- or pentafluorophenyl-substituted triamido−amine ligands, along with examples of compounds that contain the new $(Me_3SiNCH_2CH_2CH_2)_3N$ ligand. Complete synthetic procedures for the $(Me_3SiNCH_2CH_2)_3N$ complexes that were reported in a preliminary fashion[2] are also included here, as no further studies were carried out.

Results

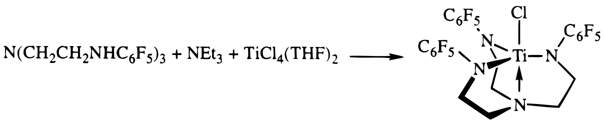
Synthesis of $[(Et_3SiNCH_2CH_2)_3N]Ti$ Complexes. Crystalline $[(Et_3SiNCH_2CH_2)_3N]TiCl$ can be prepared readily from $Li_3[(Et_3SiNCH_2CH_2)_3N]$ and $TiCl_4(THF)_2$ in pentane in a manner analogous to the synthesis of $[(Me_3SiNCH_2CH_2)_3N]TiCl$. $Li_3[(Et_3SiNCH_2CH_2)_3N]$ had to be prepared in situ from $(Et_3SiNHCH_2CH_2)_3N$, as it could not be crystallized. Orange, crystalline $[(Et_3SiNCH_2CH_2)_3N]TiCl$, which was obtained in 30% yield overall, had ^1H and ^{13}C NMR spectra consistent with the expected trigonal bipyramidal, 3-fold symmetric structure.

Addition of *t*-BuLi to $[(Et_3SiNCH_2CH_2)_3N]TiCl$ in pentane yielded a yellow-green reaction mixture, but NMR spectra of aliquots revealed only resonances for unreacted starting materials. However, when the reaction mixture was stored at −35 °C for 1 to 10 days, orange-red needles were deposited along with a white precipitate of LiCl. Proton and carbon NMR spectra of the orange-red crystalline product were consistent with its formulation as $[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$. The *tert*-butyl proton resonance is found at 1.59 ppm while the quaternary carbon resonance is found at 70.3 ppm in the carbon NMR spectrum. $[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$ is not likely to form via nucleophilic substitution at Ti in view of severe steric constraints. A possible explanation is that $[(Et_3SiNCH_2CH_2)_3N]TiCl$ is slowly reduced by *t*-BuLi to $[(Et_3SiNCH_2CH_2)_3N]Ti$ (see below) and LiCl and that $[(Et_3SiNCH_2CH_2)_3N]Ti$ subsequently traps a *tert*-butyl radical to give $[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$. Yields for this reaction therefore are understandably low (15−30%) and appear to decrease upon scaling up the reaction. In our hands the reaction is reproducible only on a scale of ~200 mg of $[(Et_3SiNCH_2CH_2)_3N]TiCl$.

$[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$ decomposes slowly and smoothly at 25 °C in C_6D_6 to give isobutylene and what we propose to be $[(Et_3SiNCH_2CH_2)_3N]TiH$, according to NMR studies. The hydride resonance in $[(Et_3SiNCH_2CH_2)_3N]TiH$ appears at 8.21 ppm in C_6D_6. This chemical shift should be compared with the resonance at 8.29 ppm in $[(Me_3SiNCH_2CH_2)_3N]TiH$ above and at 8.5 ppm in $Ta(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(H)(PMe_3)$.[21] Loss of isobutylene from $[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$ follows first-order kinetics in $CDCl_3$ (k (40 °C) $= 1.2 \times 10^{-4}\ s^{-1}$ and k (50 °C) $= 2.9 \times 10^{-4}\ s^{-1}$, as determined by proton NMR); under these conditions as soon as $[(Et_3SiNCH_2CH_2)_3N]TiH$ is formed it is converted into $[(Et_3SiNCH_2CH_2)_3N]TiCl$, which is thermally stable in $CDCl_3$ (28 h at 85 °C). When $[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$ is allowed to decompose in C_6D_6 in the absence of any trapping agent, resonances attributable to a cyclometalated complex are observed before formation of $[(Et_3SiNCH_2CH_2)_3N]TiH$ is complete. Therefore loss of isobutylene from $[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$ is too slow for this reaction to serve as a synthetic route to $[(Et_3SiNCH_2CH_2)_3N]TiH$. When $[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$ is allowed to decompose in the presence of ethylene (~10 equiv), resonances consistent with the formation of $[(Et_3SiNCH_2CH_2)_3N]Ti(Et)$ also can be observed in the proton NMR spectrum, although $[(Et_3SiNCH_2CH_2)_3N]TiH$ can be observed during the course of the reaction. We conclude from these experiments that $[(Et_3SiNCH_2CH_2)_3N]TiH$ resists cyclometalation to a much greater degree than does $[(Me_3SiNCH_2CH_2)_3N]TiH$ and that it might be isolable, at least at low temperatures, if a route to it can be devised. Unfortunately no route has yet been found.

Triflate complexes are potentially useful in chemistry involving triamido−amine complexes.[7] The triflate complex, $[(Et_3SiNCH_2CH_2)_3N]Ti(OTf)$, could be prepared via a two-step route. $[(Et_3SiNCH_2CH_2)_3N]TiCl$ could be reduced by sodium amalgam to an oily blue complex that by analogy with isolated $[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Ti$[4] we believe to be $[(Et_3SiNCH_2CH_2)_3N]Ti$. Subsequent oxidation of $[(Et_3SiNCH_2CH_2)_3N]Ti$ by ferrocenium triflate yields crystalline, yellow-orange $[(Et_3SiNCH_2CH_2)_3N]Ti(OTf)$ in an overall yield of ~80%. Attempts to prepare $[(Et_3SiNCH_2CH_2)_3N]Ti(OTf)$ by treating $[(Et_3SiNCH_2CH_2)_3N]TiCl$ with silver triflate were not successful.

Synthesis of $[(C_6F_5NCH_2CH_2)_3N]Ti$ Complexes. A ligand that is potentially more resistent to metalation reactions of the type observed for titanium silyl derivatives is $[(C_6F_5NCH_2CH_2)_3N]^{3-}$.[7] Since $Li_3[(C_6F_5NCH_2CH_2)_3N]$ does not appear to be a stable isolable species, the parent ligand was employed in the presence of a base. Addition of a mixture of $(C_6F_5NHCH_2CH_2)_3N$ and Et_3N in THF to $TiCl_4(THF)_2$[22] in THF yielded the chloride derivative shown in eq 2 in a >90% yield. The bromo and iodo derivatives could be prepared in analogous reactions involving TiX_4 (X = Br, I) in dichloromethane. Highly insoluble, dark red $[(C_6F_5NCH_2CH_2)_3N]Ti(OTf)$ could be prepared by treating $[(C_6F_5NCH_2CH_2)_3N]TiCl$ with TMSOTf in DME. All $[(C_6F_5NCH_2CH_2)_3N]TiX$ species are highly colored crystalline compounds (the iodo derivative is dark purple) with proton NMR spectra consistent with their expected 3-fold symmetry on the NMR time scale, i.e., structures analogous to that of $[(C_6F_5NCH_2CH_2)_3N]MoCl$[7] in which the donor nitrogen atom is bound to the metal, as shown in eq 2.



(2)

$[(C_6F_5NCH_2CH_2)_3N]TiMe$ could be prepared in ~80% yield as red-orange crystals by treating $[(C_6F_5NCH_2CH_2)_3N]TiI$ or $[(C_6F_5NCH_2CH_2)_3N]TiBr$ with MeMgCl. Reactions involving $LiCH_3$ or $ZnMe_2$ in several different solvents gave low to moderate yields. $[(C_6F_5NCH_2$-

---

[19] Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

[20] Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179.

[21] Nöth, H.; Schmidt, M. *Organometallics* **1995**, *14*, 4601.

[22] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

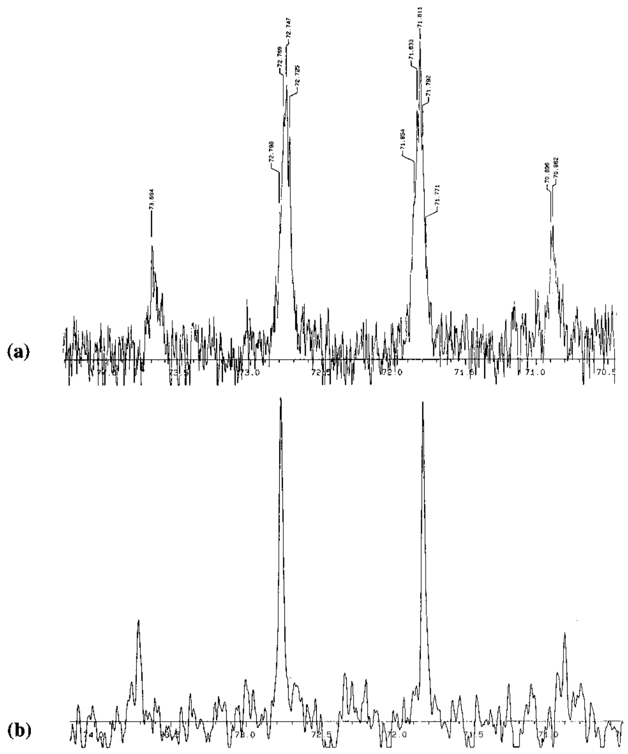


Figure 1. (a) TiMe resonance in the proton- and fluorine-coupled ^{13}C NMR NMR spectrum of $[(C_6F_5NCH_2CH_2)_3N]TiMe$. (b) TiMe resonance in the proton-coupled, fluorine-decoupled ^{13}C NMR NMR spectrum of $[(C_6F_5NCH_2CH_2)_3N]TiMe$.

$CH_2)_3N]TiCl$ reacted relatively slowly with CH_3MgCl to give a mixture of ~85% $[(C_6F_5NCH_2CH_2)_3N]TiMe$ and ~15% $[(C_6F_5NCH_2CH_2)_3N]TiCl$ (by proton NMR). Use of excess CH_3MgCl led to more complex mixtures from which $[(C_6F_5NCH_2CH_2)_3N]TiMe$ could not be isolated readily. The proton and fluorine NMR spectra of $[(C_6F_5NCH_2CH_2)_3N]TiMe$ are characteristic of complexes of this general type, with one exception. The methyl resonance in the proton NMR spectrum is relatively broad and shows fine structure consistent with it being a septet ($J \approx 1.5$ Hz). The proton-decoupled carbon NMR spectrum showed a methyl resonance at 72.26 ppm which was split into a septet ($J_{CF} \approx 1.9$ Hz). The proton and fluorine coupled carbon NMR spectrum shows a methyl quartet ($^1J_{CH} = 118$ Hz) with additional coupling to six nuclei of spin 1/2 ($J \approx 2$ Hz; Figure 1a). When the methyl carbon is decoupled from fluorine each of the quartet lines narrows as shown in Figure 1b. Therefore, we conclude that the methyl group's protons and carbon are coupled to six fluorines in the three C_6F_5 groups in $[(C_6F_5NCH_2CH_2)_3N]TiMe$, presumably the six *ortho* fluorines. Coupling of the ortho fluorines to the methyl protons was not observable by ^{19}F NMR.

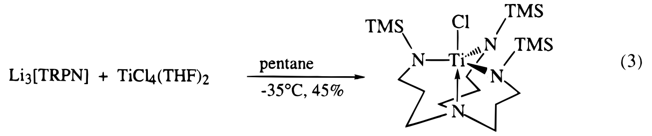
$[(C_6F_5NCH_2CH_2)_3N]TiEt$ could be prepared by treating $[(C_6F_5NCH_2CH_2)_3N]TiBr$ with $MgEt_2$(dioxane). Addition of EtMgCl to $[(C_6F_5NCH_2CH_2)_3N]TiBr$ or $[(C_6F_5NCH_2CH_2)_3N]TiI$ resulted in halogen exchange to give a mixture containing $[(C_6F_5NCH_2CH_2)_3N]TiCl$ rather than pure $[(C_6F_5NCH_2CH_2)_3N]TiEt$. Evidently halogen exchange is faster relative to displacement of halogen by the alkyl group for steric reasons in reactions involving EtMgCl but not in reactions involving MeMgCl.

Attempts to synthesize *n*-Bu, *i*-Bu, *s*-Bu, and neopentyl complexes using a variety of alkylating agents did not yield complexes that we can say unambiguously are analogous $[(C_6F_5NCH_2CH_2)_3N]TiR$ species. We suspect that nucleophilic replacement of Cl, Br, or I is simply too slow if the alkyl is larger than ethyl, and other reaction pathways (attack on the C_6F_5 rings or reduction via electron transfer) begin to dominate.

Reactions between $[(C_6F_5NCH_2CH_2)_3N]TiMe$ or $[(C_6F_5NCH_2CH_2)_3N]TiEt$ and hydrogen (1 atm) so far have been inconclusive. It does not appear that hydrogenolysis of the Ti−C bond is facile and that hypothetical $[(C_6F_5NCH_2CH_2)_3N]TiH$ is accessible in this manner.

Synthesis of $[(Me_3SiNCH_2CH_2CH_2)_3N]Ti$ Complexes. We felt that a potentially useful variation of a trisubstituted TREN ligand would be a trisubstituted tris(3-aminopropyl)amine (TRPN) ligand.[23,24] A ligand that contains one more methylene unit per backbone arm might allow transition metals (especially larger second- or third-row metals, actinides, or early lanthanides) to reside deeper inside the steric "pocket", quite possibly in the plane defined by the three equatorial nitrogens. A potential disadvantage is that the apical nitrogen donor might be more prone to dissociation than in analogous TREN derivatives.

Deprotonation of TRPN with 3.3 equiv of BuLi in THF at −70 °C followed by quenching with 3.3 equiv of TMSCl gave $(Me_3SiNHCH_2CH_2CH_2)_3N$, which was deprotonated once more with 3.3 equiv of BuLi in pentane at −70 °C to give microcrystalline $Li_3[(Me_3SiNCH_2CH_2CH_2)_3N]$. Addition of $Li_3[(Me_3SiNCH_2CH_2CH_2)_3N]$ to $TiCl_4(THF)_2$[22] in pentane at −35 °C gave amber $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ in high yield (eq 3). Isolated yields were limited to ~50% as a consequence of the high solubility of $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ in hydrocarbon solvents. The room-temperature proton NMR spectrum of $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ in C_6D_6 shows the expected TMS resonance at 0.52 ppm but *six* complex methylene resonances in the 1.25−4.30 ppm range. Heating a sample of $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ in toluene-d_8 to 90 °C did not induce any change in line shapes. Carbon NMR spectra confirmed the presence of three unique methylene carbons, each of which has two diastereotopic protons bonded to it. These data suggest that the ligand framework is "rigid" on the NMR time scale in $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$, i.e., that methylene protons on a given carbon atom cannot interconvert readily by "flipping" of the six-membered TiN_2C_3 ring.



(3)

The structure of $[(Me_3SiNCH_2CH_2CH_2)_3N]TiCl$ was determined by X-ray crystallography (Table 1). Two views of the structure are shown in Figure 2, while selected distances and angles are shown in Table 2. The Ti atom is nearly coplanar with the equatorial nitrogens (average $Ti-N_{eq} = 1.90$ Å), and the $Ti-N_{ax}$ distance ($Ti-N_{ax} = 2.360(6)$ Å) is somewhat longer compared to the $V-N_{ax}$ bond distance in $[(Me_3SiNCH_2CH_2)_3N]VCl$

---

(23) vanWinkle, J. L.; McClure, J. D.; Williams, P. H. *J. Org. Chem.* **1966**, *31*, 3300.

(24) Chin, J.; Banaszczyk, M.; Jubian, V.; Zou, X. *J. Am. Chem. Soc.* **1989**, *111*, 186.

Table 1. Experimental Details for the X-ray Structure of [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl

A. Crystal Data	
empirical formula	C$_{18}$H$_{45}$N$_4$Si$_3$TiCl
fw	485.19
cryst color, habit	orange, prismatic
cryst dimens	0.280 × 0.320 × 0.180 mm
cryst system	monoclinic
no. reflcns used for unit	tot. 7971; unique 7685 (R_{int} = 0.050)
cell determination (2θ range)	25 (13.0−22.0°)
ω scan peak width at half-height	0.27
lattice params	a = 17.900(2) Å b = 17.134(2) Å c = 20.116(3) Å β = 113.60(2)° V = 5653(3) Å
space group	$P2_1/n$ (No. 14)
Z value	8
D_{calc}	1.140 g/cm^3
F_{000}	2096
μ(Mo Kα)	5.30 cm^{-1}
B. Intensity Measurements	
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα (λ = 0.710 69 Å)
temp	25 ± 1 °C
attenuator	Zr foil (factor = 17.9)
take-off angle	2.8°
detector aperture	2.0 × 2.5 × 2.0 mm
cryst to detector dist	21 cm
scan type	$\omega-2\theta$
scan rate	(1.9−16.5°)/min (in ω)
scan width	(0.80 + 0.35 tan θ)°
2θ_{max}	44.9°
no. of reflcns measd	tot. 7971 unique: 7685 (R_{int} = 0.050)
corrs	Lorentz−polarization abs (transm factors: 0.74−1.11) secondary extinction (coeff: 0.53392 × 10^{-7})
C. Structure Solution and Refinement	
struct solution	direct methods
refinement	full-matrix least-squares
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/s^2(F_o^2)$
p-factor	0.03
anomalous dispersion	all non-H atoms
no. observns ($I > 3.00\sigma(I)$)	3619
no. variables	488
reflcns/param ratio	7.42
residuals: R; R_w	0.052; 0.051
goodness of fit indicator	1.40
max shift/error in final cycle	0.03
max peak in final diff map	0.22 e/Å^3
min peak in final diff map	−0.23 e/Å^3

(V−N$_{ax}$ = 2.238 Å).[2] The Ti atom is displaced from the equatorial NNN plane by 0.203 Å in [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl compared to 0.310 Å in [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]VCl. The Ti−Cl bond distance (2.353(2) Å) is also longer than that reported in [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]TiCl (2.259(6) Å).[25] An important structural feature that must be a consequence of the longer "arms" in [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl is the formation of three "chair form" TiN$_2$C$_3$ rings. The resulting "propeller" orientation of the trimethylsilyl groups can be measured by the dihedral angle N$_{ax}$−Ti−N$_{eq}$−Si. In [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl the average dihedral angle is 138°. This value should be compared to analogous dihedral angles in [(Me$_2$(t-Bu)SiNCH$_2$CH$_2$)$_3$N]V (average 168°), [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]V=NH (average 177°), and [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]VCl (average 147°).[13] One could speculate that the silyl groups are "tilted" to a greater degree in [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl as a consequence of the chair form of each TiN$_2$C$_3$ ring. The Ti−N$_{eq}$−Si angle in [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl (120°) is slightly less than what it is the vanadium complexes noted above (ca. 126°).

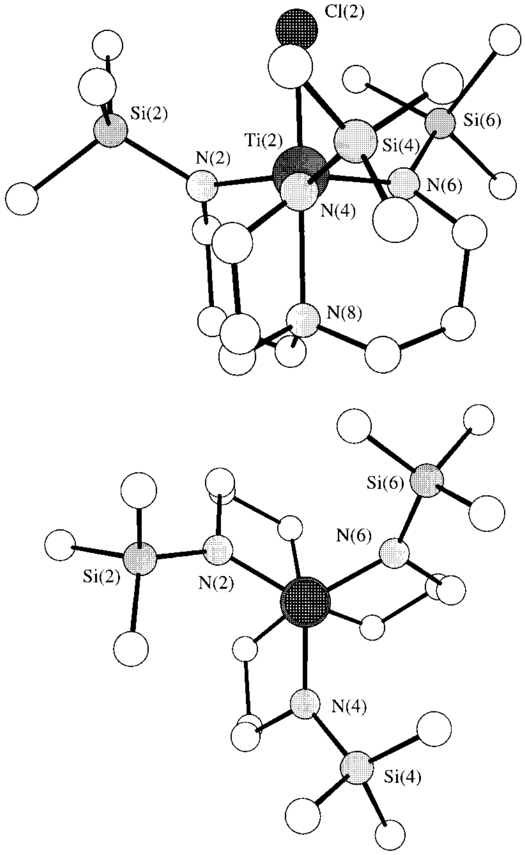
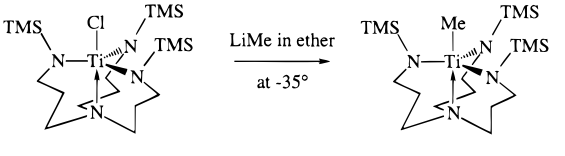


Figure 2. Two Chem 3D views of the structure of [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl.

Table 2. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl

Bond Lengths			
Ti(2)−N(2)	1.910 (5)	Ti(2)−Cl(2)	2.352 (2)
Ti(2)−N(4)	1.905 (6)	Ti(2)−N(8)	2.360 (6)
Ti(2)−N(6)	1.897 (5)		
Bond Angles			
Ti(2)−N(2)−Si(2)	129.7 (3)	N(2)−Ti(2)−N(6)	117.2 (2)
Ti(2)−N(4)−Si(4)	130.0 (3)	N(4)−Ti(2)−N(6)	119.6 (4)
Ti(2)−N(6)−Si(6)	129.7 (4)	N(8)−Ti(2)−N(2)−Si(2)	136.8 (4)
N(8)−Ti(2)−Cl(2)	179.0 (2)	N(8)−Ti(2)−N(4)−Si(4)	142.4 (4)
N(2)−Ti(2)−N(4)	120.6 (4)	N(8)−Ti(2)−N(6)−Si(6)	137.5 (4)

[(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl is alkylated cleanly by 1.1 equiv of LiMe in cold ether to furnish the expected methyl complex (eq 4). Its high solubility limited



(4)

isolated yields, however. Proton and carbon NMR spectra of the methyl complex show broad ligand backbone (methylene) resonances consistent with a

---

[25] Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

more rapid "flipping" of the TiN_2C_3 rings and consequent equilibration of the diastereotopic methylene protons, in contrast to the behavior observed in the chloride derivative. We speculate that the more electron-rich metal center in the methyl derivative allows more facile dissociation of the axial amine donor nitrogen, a process that should facilitate equilibration of methylene protons on a given backbone carbon atom.

Conclusions

We have shown that titanium halide and some alkyl complexes can be prepared that contain the triamido−amine ligand $[(Et_3SiNCH_2CH_2)_3N]^{3-}$, $[(C_6F_5NCH_2CH_2)_3N]^{3-}$, or $[(Me_3SiNCH_2CH_2CH_2)_3N]^{3-}$. However, so far such ligands have not proven to have any significant advantages as far as stabilization of a Ti(IV) monohydride complex is concerned. TRPN derivatives, of which the last is an example, might prove useful in chemistry of larger second- or third-row metals, actinides, or early lanthanides, especially if substituents larger than TMS (e.g., Et_3Si or *i*-Pr_3Si) are employed.

Experimental Section

General Methods. All experiments were carried out in purified, dry solvents under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques, unless otherwise specified. $TiBr_4$, TiI_4, and $N(CH_2CH_2CH_2NH_2)_3$ were purchased from Strem Chemicals and used as received. $TiCl_4(THF)_2$,[22] $Li_3(Me_3SiNCH_2CH_2)_3N$,[13,26,27] and $(C_6F_5NHCH_2CH_2)_3N$[7] were prepared by literature methods. NMR coupling constants normally are not noted unless they are unusual or informative. Within the TREN backbond J_{HH} = 5−6 Hz and $J_{CH} \approx 135$ Hz for the methylene groups.

Preparation of Compounds. $[(Me_3SiNCH_2CH_2)_3N]TiCl$. A 100 mL round bottom flask was charged with $TiCl_4(THF)_2$ (2.64 g, 7.91 mmol) and $Li_3(Me_3SiNCH_2CH_2)_3N$ (3.01 g, 7.91 mmol). Pentane (60 mL) was added, and the mixture was stirred for 26 h at 25 °C. The off-white LiCl precipitate was removed by filtration through a bed of Celite, and the deep orange filtrate was concentrated in vacuo. The crude yield of orange crystalline solid was 3.02 g (6.82 mmol, 86%). A solution of the crude material in a minimum of pentane was chilled to −35 °C to provide pure $[(Me_3SiNCH_2CH_2)_3N]TiCl$ as orange crystals (1.99 g, 4.49 mmol, 57%): ^1H NMR (C_6D_6) δ 3.36 (t, CH_2), 2.276 (t, CH_2), 0.35 (s, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 63.17 (CH_2), 50.81 (CH_2), 1.61 ($SiMe_3$). Anal. Calcd for $C_{15}H_{39}ClN_4Si_3Ti$: C, 40.66; H, 8.87; N, 12.64; Cl, 8.00. Found: C, 40.36; H, 8.64; N, 12.53; Cl, 8.05.

$[(Me_3SiNCH_2CH_2)_3N]Ti(n\text{-}Bu)$. A 20 mL vial containing $[(Me_3SiNCH_2CH_2)_3N]TiCl$ (0.81 g, 1.82 mmol) in 12 mL of pentane was treated with a 1.6 M solution of *n*-BuLi in hexanes (1.1 equiv, 800 μL) at −35 °C. After the mixture was warmed to 25 °C and stirred for 2 h, it was filtered through a plug of alumina (height, 2 cm; diameter, 2 cm). The yellow-gold filtrate was concentrated in vacuo to give a yellow crystalline solid (581 mg, 1.26 mmol, 69%). A pentane solution of this material was chilled to −35 °C to provide $[(Me_3SiNCH_2CH_2)_3N]Ti(n\text{-}Bu)$ (480 mg, 57%) as lemon yellow crystals: ^1H NMR (C_6D_6) δ 3.35 (t, NCH_2), 2.15 (t, NCH_2), 2.15 (m, CH_2), 1.48 (m, CH_2), 1.39 (m, CH_2), 1.03 (t, CH_3), 0.33 (s, $SiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 72.90 ($TiCH_2$), 61.99 (NCH_2), 50.39 (NCH_2), 35.32 (CH_2), 29.40 (CH_2), 13.90 (CH_2), 1.68 ($SiMe_3$). Anal. Calcd for $C_{19}H_{48}N_4Si_3Ti$: C, 49.10; H, 10.41; N, 12.05. Found: C, 48.92; H, 10.10; N, 12.40.

$[(Me_3SiNCH_2CH_2)_3N]Ti(s\text{-}Bu)$. A 20 mL vial containing $[(Me_3SiNCH_2CH_2)_3N]TiCl$ (0.846 g, 1.91 mmol) in 15 mL of pentane was treated with a 1.3 M solution of *s*-BuLi in cyclohexane (1.1 equiv, 800 μL) at −35 °C. An immediate color change to green was observed, but after 2−3 min a white LiCl precipitate was observed and the color of the reaction mixture had become yellow-orange. After being warmed to 25 °C and stirred for 1.5 h, the reaction mixture was filtered through a plug of alumina (height, 2 cm; diameter, 2 cm). The yellow-orange filtrate was concentrated in vacuo to give orange crystalline solid (657 mg, 1.42 mmol, 75%). A pentane solution of this material was chilled to −35 °C for 3 days to provide $[(Me_3SiNCH_2CH_2)_3N]Ti(s\text{-}Bu)$ (397 mg, 45%) as an orange crystalline solid that was pure by proton NMR except for a trace of $[(Me_3SiNCH_2CH_2)_3N]Ti(n\text{-}Bu)$: ^1H NMR (C_6D_6) δ 3.40 (ddd, 3, NCH_2), 3.31 (ddd, 3, NCH_2), 2.65 (ddq, 1, CH_2), 2.17 (t, 6, NCH_2), 1.77 (ddq, 1, CH_2), 1.75 (d, CH_3), 1.06 (t, CH_3), 0.85 (ddq, TiCH), 0.33(s, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 82.88 (d, TiCH), 62.51 (t, NCH_2), 50.52 (t, NCH_2), 32.91 (t, CH_2), 22.22 (q, CH_3), 15.03 (q, CH_3), 1.97 (q, $SiMe_3$). Anal. Calcd for $C_{19}H_{48}N_4Si_3Ti$: C, 49.10; H, 10.41; N, 12.05. Found: C, 48.69; H, 10.14; N, 12.06.

$Ti[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]$. A 50 mL pressure vessel containing $[(Me_3SiNCH_2CH_2)_3N]Ti(s\text{-}Bu)$ (0.771 g, 1.67 mmol) in 12 mL of benzene was freeze−pump−thaw degassed three times prior to admission of H_2 (1 atm), with the vessel at −196 °C. The reaction mixture was warmed to 25 °C with the vessel closed, giving approximately 3 atm of H_2. The orange-red solution turned yellow over a 48 h period. Removal of the benzene in vacuo gave a yellow-brown oil (667 mg, 1.64 mmol, 98%). The oil was transferred to a sublimation vessel. Sublimation (50−60 °C, 0.05 Torr, probe temperature = −78 °C) provided $Ti(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSi(CH_2)Me_2$ (571 mg, 1.40 mmol, 84%) as a waxy yellow solid: ^1H NMR (C_6D_6) δ 3.72 (t, NCH_2), 3.23 (ddd, 2, NCH_2), 3.12 (ddd, 2, NCH_2), 2.34 (t, NCH_2), 2.27 (dd, 2, NCH_2), 2.25 (dd, 2, NCH_2), 1.31 (s, $TiCH_2Si$), 0.37 (s, $SiMe_2$), 0.32 (s, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 58.47 (t, NCH_2), 56.91 (t, NCH_2), 55.87 (t, $TiCH_2Si$), 53.66 (t, NCH_2), 48.84 (t, NCH_2), 1.87 (q, $SiMe_2$), 1.48 (q, $SiMe_3$).

$(Et_3SiNHCH_2CH_2)_3N$. This ligand was prepared from TREN and Et_3SiCl in a manner analogous to that used to prepare $(Me_3SiNHCH_2CH_2)_3N$.[13] It was isolated without purification and treated with 3 equiv of Li−*n*-butyl in order to form $Li_3(Me_3SiNCH_2CH_2)_3N$ in situ.

$[(Et_3SiNCH_2CH_2)_3N]TiCl$. $TiCl_4(THF)_2$ (14.29 g, 42.80 mmol) was added to 250 mL of pentane at −35 °C, and then a solution of crude $Li_3[(Et_3SiNCH_2CH_2)_3N]$ (42.80 mmol, 0.25 M in pentane) was added. The reaction mixture was allowed to warm to 25 °C and was stirred for 24 h and then was filtered through a bed of Celite. The pentane was removed in vacuo to give an oily residue which was dissolved in 50 mL of pentane. The pentane solution was chilled to −35 °C for 72 h. Orange crystals were collected by filtration, washed quickly with 10 mL of cold pentane, and dried in vacuo (7.33 g, 12.90 mmol, 30%): ^1H NMR (C_6D_6) δ 3.48 (t, NCH_2), 2.41 (t, NCH_2), 1.10 (t, CH_3), 0.94 (q, $SiCH_2$); ^{13}C NMR (C_6D_6) δ 63.48 (NCH_2), 51.45 (NCH_2), 8.01 ($SiEt_3$), 6.18 ($SiEt_3$). Anal. Calcd for $C_{24}H_{57}ClN_4Si_3Ti$: C, 50.63; H, 10.09; N, 9.84. Found: C, 50.72; H, 10.36; N, 9.45.

$[(Et_3SiNCH_2CH_2)_3N]Ti(t\text{-}Bu)$. A solution of $[(Et_3SiNCH_2CH_2)_3N]TiCl$ (276 mg, 490 μmol) in pentane (40 mL) was chilled to −35 °C and treated with *t*-BuLi (530 μmol, 315 μL, 1.7 M in pentane). After the mixture was stirred for 25 min at 25 °C, the volume was reduced to 5 mL under reduced pressure, and the turbid green reaction mixture was chilled to −35 °C. After 48 h a crop (ca. 50 mg) of large orange crystals had formed mixed with LiCl. The LiCl was slurried in the cold supernatant and removed via pipet: ^1H NMR (C_6D_6) δ 3.53 (br, NCH_2), 2.26 (br, NCH_2), 1.59 (s, CMe_3), 1.14 (t,

---

(26) Duan, Z.; Yound, V. G.; Verkade, J. G. *Inorg. Chem.* **1995**, *34*, 2179.

(27) Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.

$SiCH_2CH_3$), 0.97 (q, $SiCH_2$); ^{13}C NMR (C_6D_6) δ 70.27 (Ti*C*Me$_3$), 63.73 (NCH_2), 51.80 (NCH_2), 35.73 (TiC*Me*$_3$), 8.48 ($SiEt_3$), 7.18 ($SiEt_3$).

[($Et_3SiNCH_2CH_2$)$_3$N]Ti(OTf). A solution of [(Et_3Si)$_3N_4$]TiCl (1.02 g, 1.78 mmol) in pentane (30 mL) was treated with fresh sodium amalgam (2.67 mmol Na, 62 mg Na, 12.24 g Hg), and the reaction mixture was stirred vigorously for 48 h. The solids were allowed to settle, and the bright blue solution was decanted and filtered through a bed of Celite. The pentane was removed from the filtrate in vacuo to give a viscous blue liquid. This liquid was dissolved in ether (40 mL), and the solution was chilled to −35 °C. [$FeCp_2$][O_3SCF_3] (1.78 mmol, 598 mg) was added to the stirred solution in solid portions over a period of 1 to 2 min to produce a golden reaction mixture. After 40 min at 25 °C the solution was filtered and the ether was removed in vacuo. Ferrocene was removed by sublimation (45 °C, 0.05 Torr, probe temperature −78 °C) over 3 to 4 h and the residue was recrystallized from pentane (45 mL) to provide yellow-orange crystals (966 mg, 1.41 mmol, 79%): ^1H NMR (C_6D_6) δ 3.47 (t, NCH_2), 2.40 (t, NCH_2), 1.07 (t, CH_3), 0.88 (q, $SiCH_2$); ^{13}C NMR (C_6D_6) δ 65.51 (NCH_2), 51.59 (NCH_2), 7.96 ($SiEt_3$), 5.68 ($SiEt_3$); ^{19}F NMR (C_6D_6) δ −75 (CF_3). Anal. Calcd for $C_{25}H_{57}N_4Si_3O_3SF_3Ti$: C, 43.97; H, 8.41; N, 8.20. Found: C, 44.20; H, 8.71; N, 7.80.

[($C_6F_5NCH_2CH_2$)$_3$N]TiCl. A solution of ($C_6F_5NHCH_2CH_2$)$_3$N (3.86 g, 5.99 mmol) and triethylamine (1.88 g, 3.1 equiv) in THF (−35 °C) was added dropwise to a solution of $TiCl_4(THF)_2$ (2.0 g, 5.99 mmol) in THF at −35 °C. The reaction mixture was allowed to warm to room temperature and stirred for 6 h. The red reaction mixture was then filtered through Celite. The filtrate was taken to dryness in vacuo, and the residue was dissolved in minimal methylene chloride. Chilling the solution to −40 °C produced red microcrystals (2.60 g, 3.59 mmol, 60%): ^1H NMR (C_6D_6) δ 3.30 (t, 6), 2.33 (t, 6); ^{19}F NMR δ −149.46 (d, 6, J_{FF} = 20), −149.46 (d, 6, J_{FF} = 20), −164.52 (t, 6, J_{FF} = 21). Anal. Calcd for $TiC_{24}H_{12}N_4F_{15}Cl$: C, 39.78; H, 1.67; N, 7.73; Cl, 4.89. Found: C, 39.81; H, 1.97; N, 7.49; Cl, 5.40.

[($C_6F_5NCH_2CH_2$)$_3$N]TiBr. $TiBr_4$ (1.00 g, 2.72 mmol) was dissolved in dichloromethane, and the solution was cooled to −40 °C. A solution containing ($C_6F_5NHCH_2CH_2$)$_3$N (1.75 g, 2.72 mmol) and NEt_3 (0.866 g, 8.54 mmol, 3.04 equiv) in CH_2Cl_2 was also cooled to −40 °C and then added slowly over a period of several minutes to the $TiBr_4$. The reaction mixture darkened from light orange-yellow to deep red. After the mixture was stirred for 3 h, it was reduced to dryness in vacuo and the residue was dissolved in toluene. The extract was filtered, and the toluene was removed from the filtrate in vacuo. The product was recrystallized from a minimum of dichloromethane at −35 °C to give nearly black crystals (1.64 g, 2.13 mmol, 78%): ^1H NMR (C_6D_6) δ 3.31 (t, 6, CH_2), 2.32 (t, 6, CH_2); ^{19}F NMR δ −148.95 (d, 6, J_{FF} = 19), −160.81 (t, 3, J_{FF} = 22), −164.35 (t, 6, J_{FF} = 20). Anal. Calcd for $TiC_{24}H_{12}N_4F_{15}Br$: C, 37.48; H 1.57; N, 7.28. Found: C, 37.55; H, 1.63; N 7.10.

[($C_6F_5NCH_2CH_2$)$_3$N]TiI. A solution containing ($C_6F_5NHCH_2CH_2$)$_3$N (1.16 g, 1.82 mmol) and triethylamine (570 mg, 3.1 equiv) in methylene chloride (−35 °C) was added dropwise to a solution of TiI_4 (1.0 g, 1.80 mmol) in methylene chloride at −35 °C. The reaction mixture was allowed to warm to room temperature and was stirred for more than 3 h. The dark purple reaction mixture was filtered through Celite to remove the ammonium salts. The filtrate was taken to dryness in vacuo, and the residue was extracted with 1,2-dimethoxymethane (dme). The solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The residue was dissolved in a small amount of dichloromethane and the solution was chilled to −35 °C to give dark purple microcrystals (1.175 g, 1.44 mmol, 80%): ^1H NMR (C_6D_6) δ 3.32 (t, 6, CH_2), 2.27 (t, 6, CH_2); ^{19}F NMR δ −148.32 (d, 6, J_{FF} = 19), −160.50 (t, 3, J_{FF} = 22), −164.16 (t, 6, J_{FF} = 20). Anal. Calcd for $TiC_{24}H_{12}N_4F_{15}I$: C, 35.32; H, 1.48; N, 6.86; I, 15.55. Found: C, 35.28; H, 1.44; N, 7.02; I, 15.72.

[($C_6F_5NCH_2CH_2$)$_3$N]Ti(OTf). A solution of [($C_6F_5NCH_2CH_2$)$_3$N]TiCl (1.00 g, 1.38 mmol) in 70 mL of dimethoxyethane was added to a precooled (−30 °C) solution containing trimethylsilyl triflate (350 μL, 1.38 mmol). The reaction mixture was stirred at room temperature overnight, and the insoluble red product was collected on a glass frit and washed with dimethoxyethane and pentane (990 mg, 1.18 mmol, 86%). The product is too insoluble to obtain NMR spectra. Anal. Calcd for $C_{25}H_{12}N_4F_{18}SO_3Ti$: C, 35.82; H, 1.44; N, 6.68. Found: C, 36.03; H, 1.62; N, 6.45.

[($C_6F_5NCH_2CH_2$)$_3$N]Ti(CH_3). MeMgCl (3.0M in THF, 314 μL, 1.22 equiv) was added dropwise over 10 min to a −40 °C methylene chloride solution of [($C_6F_5NCH_2CH_2$)$_3$N]TiI (628 mg, 0.769 mmol). The reaction appeared to be virtually instantaneous, but the reaction mixture was allowed to stir for 4 h at room temperature before placing it in the −40 °C freezer. After 16 h the orange-red crystalline product was filtered off (435 mg, 0.62 mmol, 80%): ^1H NMR (CD_2Cl_2) δ 3.92 (t, 6, CH_2), 3.07 (t, 6, CH_2), 0.43 (m, 3, CH_3); ^1H NMR (C_6D_6) δ 3.32 (t, 6, CH_2), 2.27 (t, 6, CH_2); ^{19}F NMR δ −150.10 (d, 6, J_{FF} = 21), −163.27 (t, 3, J_{FF} = 22) −164.47 (t, 6, J_{FF} = 22); $^{13}C\{^1H\}$ (CD_2Cl_2) δ 142.7−130.7 (C_6F_5), 72.3 (q, CH_3, J_{CH} = 118, J_{CF} = 2), 57.28−53.37 (NCH_2CH_2N). Anal. Calcd for $TiC_{25}H_{15}N_4F_{15}$: C, 42.63; H, 1.72; N, 7.99. Found: C, 42.39; H, 2.03; N 8.18.

Alternatively CH_3MgCl (0.780 mmol, 1.2 equiv) in ether was slowly added to [($C_6F_5NCH_2CH_2$)$_3$N]TiBr (0.500 g, 0.650 mmol) dissolved in toluene. The solution turned from dark red to a bright orange, and salt precipitated from solution. The reaction mixture was stirred for 1 h and filtered. The filtrate was reduced to dryness in vacuo, and the residue was recrystallized from dichloromethane at −40 °C.

[($C_6F_5NCH_2CH_2$)$_3$N]Ti(CH_2CH_3). [($C_6F_5NCH_2CH_2$)$_3$N]TiBr (0.500 g, 0.650 mmol) was dissolved in toluene, and Mg(CH_2CH_3)$_2$(dioxane) (0.066 g, 0.390 mmol, 1.2 equiv) in ether was added slowly. The solution turned from dark red to a lighter orange-red and then darkened again. After 2 h, the solution was filtered and the filtrate was taken to dryness in vacuo. The residue was recrystallized from a mixture of toluene and pentane at −40 °C: ^1H NMR (C_6D_6) δ 3.31 (t, 6, CH_2), 2.08 (t, 6, CH_2), 1.19 (q, 2, CH_2CH$_3$), 0.32 (t, 3, CH$_2$CH_3); ^{19}F NMR δ −149.74 (d, 6, J_{FF} = 19), −163.37 (t, 3, J_{FF} = 22), −164.35 (t, 6, J_{FF} = 21). Anal. Calcd for $TiC_{26}H_{17}N_4F_{15}$: C, 43.48; H, 2.39; N, 7.80. Found: C, 43.06; H, 2.60; N, 7.52.

Li_3[($Me_3SiNCH_2CH_2CH_2$)$_3$N]. A 1 L Schlenk flask was charged with N($CH_2CH_2CH_2NH_2$) (18.00 g, 0.096 mol) in 350 mL of THF. The solution was stirred magnetically and cooled to −65 °C. Butyllithium (0.296 mol, 2.5 M in hexane) was syringed in; a white precipitate formed immediately. The mixture was allowed to warm to room temperature over 7 h, cooled again to −65 °C, and treated with TMSCl (32.16 g, 0.296 mol). The white mixture was allowed to warm to room temperature overnight. Solvents were removed *in vacuo*, and the residue was extracted three times with 150 mL of pentane and filtered through a bed of Celite. The solvents were removed from an aliquot of the filtrate to give a pale yellow oil: ^1H NMR ($CDCl_3$) δ 2.68 (q, 6, NCH$_2$CH$_2$CH_2), 2.37 (t, 6, NCH_2CH$_2$CH$_2$), 1.49 (m, 6, NCH$_2$CH_2CH$_2$), 0.01 (s, 27, $SiMe_3$).

The pentane extracts were combined, cooled to −65 °C, and treated with butyllithium (0.30 mmol, 2.5M in hexane). The mixture containing a thick white precipitate was allowed to warm to room temperature overnight and then was chilled to −35 °C overnight. The white microcrystalline powder was filtered off, washed quickly with cold pentane, and dried *in vacuo* to give pure product (30.52 g, 72.2 mmol, 75%).

[($Me_3SiNCH_2CH_2CH_2$)$_3$N]TiCl. Li_3[($Me_3SiNCH_2CH_2CH_2$)$_3$N] (2.30 g, 5.44 mmol) was added in one portion to a stirred suspension of $TiCl_4(THF)_2$ (2.00 g, 5.99 mmol) in 50 mL of pentane at −35 °C. The canary yellow mixture darkened slightly and was allowed to stir at room temperature overnight. LiCl and excess $TiCl_4(THF)_2$ were removed via filtration through Celite. The yellow filtrate was concentrated and chilled to −35 °C to give amber plates of [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl (1.19 g, 2.45 mmol, 45%): ^{1}H NMR (C$_6$D$_6$) δ 4.24 (td, 3), 3.36 (td, 3), 3.24 (m, 3), 1.64 (m, 6), 1.25 (m, 3), 0.52 (s, 27, SiMe$_3$); ^{13}C{H} NMR (C$_6$D$_6$) δ 59.24, 51.18, 27.66, 1.38. Anal. Calcd for C$_{18}$H$_{45}$N$_4$ClSi$_3$Ti: C, 44.56; H, 9.35; N, 11.55. Found: C, 44.44; H, 9.21; N, 11.38.

[(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCH$_3$. Methyllithium (0.79 mmol, 1.4 M in ether) was added dropwise to a stirred solution of [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl (350 mg, 0.72 mmol) in 25 mL of ether at −35 °C. The yellow mixture was stirred overnight, and ether was removed *in vacuo*. The yellow residue was taken up in pentane, and the solution was filtered through a bed of Celite. The filtrate was concentrated in vacuo and chilled to −35 °C to give yellow crystals of the product (67 mg, 20%): ^{1}H NMR (C$_6$D$_6$) δ 4.26 (m, 3), 3.20 (m, 6), 1.60 (m, 6), 1.18 (m, 3), 0.89 (s, 3, TiCH$_3$), 0.35 (s, 27, SiMe$_3$); ^{13}C{H} NMR (C$_6$D$_6$) δ 58.01, 50.12, 44.18, 28.72 (TiCH$_3$), 1.44. Anal. Calcd for C$_{19}$H$_{48}$N$_4$Si$_3$Ti: C, 49.10; H, 10.41; N, 12.05. Found: C, 49.23; H, 10.02; N, 11.94.

X-ray Structure of [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl. An orange prismatic crystal of C$_{18}$H$_{45}$N$_4$Si$_3$TiCl was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection, were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $13.00 < 2\theta < 22.00°$.

Of the 7971 reflections collected, 7685 were unique ($R_{\text{int}} = 0.050$); equivalent reflections were merged. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3619 observed reflections ($I > 3.00\sigma(I)$) and 488 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of $R = 0.052$ and $R_w = 0.051$. See the Supporting Information and Table 2 for further details.

Acknowledgment. R.R.S. thanks the National Science Foundation (Grant CHE 91 22827) for research support. S.L. thanks the MIT Undergraduate Research Opportunities Program (UROP) for funding, A. LaPointe for experimental advice, and K. Totland for NMR spectra. T.W. thanks the MIT Undergraduate Research Opportunities Program (UROP) for funding and M. K. for experimental advice. M. K. thanks the Rothschild Foundation for a postdoctoral fellowship.

Supporting Information Available: Text describing experimental details of the X-ray study of [(Me$_3$SiNCH$_2$CH$_2$CH$_2$)$_3$N]TiCl, an ORTEP drawing of the structure, and tables of final positional parameters, final thermal parameters, and data collection parameters (13 pages). Ordering information is given on any current masthead page.

OM9508389