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Li, Ti(III), and Ti(IV) Trisamidotriazacyclononane Complexes. Syntheses, Reactivity, and Structures

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The preparations of 1,4,7-$(NHPhSiMe_2)_3$-1,4,7-triazacyclononane (H_3N_3-tacn) and its lithium and sodium derivatives are described. The X-ray structure of the THF adduct of the lithium derivative, Li_3N_3-tacn$(THF)_2$, shows that one of the macrocycle pendant arms is bent to allow the coordination of the its lithium ion to two tacn amines. In solution, a fluxional process makes all the pending arms magnetically equivalent. The reactions of Li_3N_3-tacn or Na_3N_3-tacn with either $TiCl_4$ and $TiCl_3(THF)_3$ led to the formation of [Ti(N_3-tacn)], **5**. The oxidation of **5** with various oxidizing reagents gave cationic complexes [Ti(N_3-tacn)]X, **6** (X = I, Cl, SCN, PF_6, BPh_4), that exist as a pair of enantiomers, $\Lambda(\lambda\lambda\lambda)/\Delta(\delta\delta\delta)$, which interconvert in solution. The molecular structures of **5** and **6** (X = I, BPh_4) show the coordination of the six nitrogen donor set to the titanium. Due to the short length of the tacn pendant arms, the hexadentate bonding mode of the ligand is mainly achieved through the sharpening of the N–Si–N angles. The reaction of [Ti(N_3-tacn)]I, **6a**, with $W(CO)_6$ led to the synthesis of [Ti(N_3-tacn)][$W(CO)_5I$], **7**.

Introduction

The search for new ligand frameworks able to promote new reactivity pathways is a current topic in transition metal organometallic chemistry. In this context, nitrogen donor ligands proved to be a versatile approach since they are readily prepared and allow suitable combinations of electronic and stereochemical properties. New catalysts for olefin polymerization,[1,2] the activation of the N_2 and P_4 bonds,[3−5] and the stabilization of reactive unsupported early−late bonds[6] are relevant examples of new reactivity patterns supported by such ligands. Several types of polyfunctional ligands where at least one bonding moiety is an amido fragment have been reported in the last 10 years.[7,8] However, examples of functionalized 1,4,7-triazacyclononane (tacn) and other saturated nitrogen macrocycles with anionic nitrogen moieties (amido or imido) are scarce. Despite the extensive study of transition metal complexes of polyaza macrocyclic ligands bearing functionalized pendant arms,[9−11] [M{1,4,7-(o-NH-benzyl)$_3$tacn}] (M = Fe, Co, Mn) are the sole reported examples of trisamido-tacn metal derivatives.[12] On the other hand, suitable synthetic methods for monosubstituted tacn ligands have only recently been optimized, and therefore, the study of metal derivatives of such compounds is still in its infancy.[13−16] Aiming to synthesize a ligand able to protect and direct the reactivity of metal centers through

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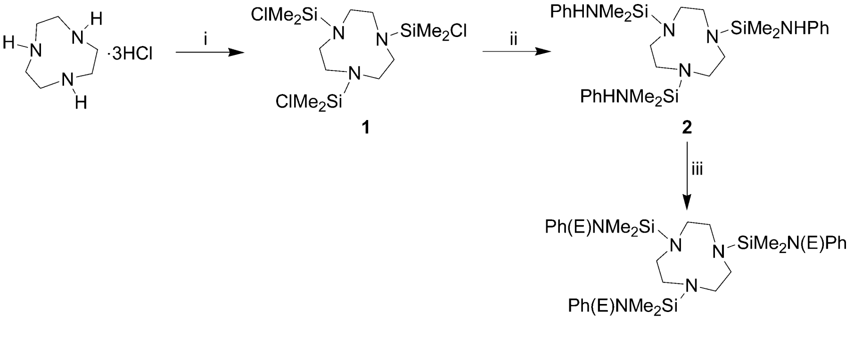
Scheme 1 [a]



[a] (i) $SiMe_2Cl_2$, NEt_3, CH_2Cl_2, 0 °C; (ii) NaN(H)Ph, THF, toluene, −40 °C; (iii) **3**, n-LiBu, hexane, −78 °C; **4**, NaH, THF, −40 °C, then 12 h at 50 °C.

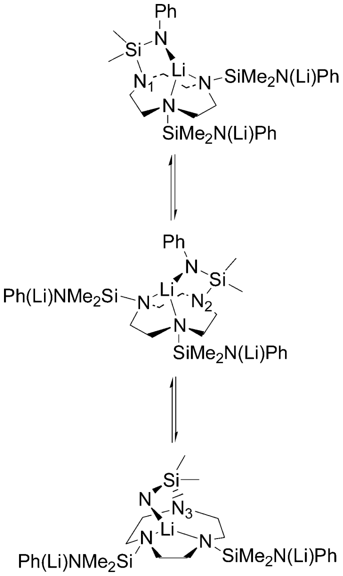
a new balance of bonding features, we designed a trisamido-triamine ligand precursor by introducing three $Si(Me)_2N(H)Ph$ pendant arms on the nitrogen atoms of tacn. We became interested in the reactivity of “encapsulated” metals where structural features and oxidation states may be dictated by the metal/ligand match and report here the syntheses of the ligand precursors and their titanium derivatives.

Results and Discussion

The ligand precursors Li_3N_3-tacn, **3**, and Na_3N_3-tacn$(THF)_2$, **4**, were prepared according to the reaction sequence presented in Scheme 1. The addition of an excess of $SiMe_2Cl_2$ and NEt_3 to a CH_2Cl_2 suspension of tacn·3HCl at 0 °C led to the quantitative formation of 1,4,7-$(ClSiMe_2)_3$-tacn, **1**, which was isolated as an off-white solid. Treatment of **1** with NaN(H)Ph, prepared in situ by reacting $PhNH_2$ and NaH, gave 1,4,7-$[\{N(H)Ph\}SiMe_2]_3$-tacn (H_3N_3-tacn, **2**). The characterization data for **1** and **2** are consistent with their formulation as 1,4,7-tris-substituted tacn derivatives. The ^1H and ^{13}C NMR spectra show singlets for the macrocyclic protons and carbons and three equivalent $SiMe_2$ and N(H)Ph groups consistent with C_{3v} symmetry. The reactions of **2** with n-LiBu or NaH gave the corresponding lithium and sodium anions, Li_3N_3-tacn, **3**, and Na_3N_3-tacn$(THF)_2$, **4**, respectively, in quantitative yields.

The ^1H NMR spectra of **3**, its THF adduct (**3**·THF), and **4** show two resonances for the macrocyclic protons that NOE experiments identified as H_{syn} and H_{anti}, respectively. As observed for **2**, the three pendant arms and the macrocyclic carbon atoms of Li_3N_3-tacn, Li_3N_3-tacn$(THF)_2$, and Na_3N_3-tacn$(THF)_2$ are magnetically equivalent. The interpretation of the NMR data requires the assumption of a fluxional process that renders the three pendant arms equivalent and simultaneously differentiates the H_{syn} and H_{anti} macrocyclic protons. Attempts to study by VT ^1H NMR the exchange process in a d_8-toluene solution of **3** and **3**·THF were unsuccessful until −90 °C.[17] However, taking in account the solid state structure of Li_3N_3-tacn$(THF)_2$ (Figure 2) where one of the lithium centers is bonded to two macrocyclic amines, we tentatively suggest the exchange process represented in Scheme 2, where the sequential coordination of the lithium ions to the tacn amines would be responsible for the apparent C_3 symmetry observed in the NMR spectrum.

Scheme 2



Treatment, at room temperature, of a toluene solution of $TiCl_4$ with a solution of **3** in the same solvent led to the synthesis of $[Ti\{N(Ph)SiMe_2\}_3$-tacn] ([Ti(N_3-tacn)], **5**), in variable yields (25−45%). The reduction of the metal, frequently reported in transition metal halide metathesis reactions, hampers the reproducibility of the substitution reaction. In the present case, the homolytic cleavage of a titanium−chloride bond at a trisamido-chloro intermediate is most likely occurring, as has been claimed in the reaction of $[TiCl\{(Et_3SiNCH_2CH_2)_3N\}]$ with Li^tBu.[18]

The solution EPR of **5** consists of a symmetrical line with line width of 0.9 mT and g_{av} of 1.958. Anisotropy was shown by the powder spectrum, of tetragonal symmetry, with $g_{\|}$= 1.986 and $g_{\perp}$=1.940.[19]

The oxidation of **5** is readily accomplished with a wide range of oxidants leading to the synthesis of [Ti{N(Ph)-

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Scheme 3

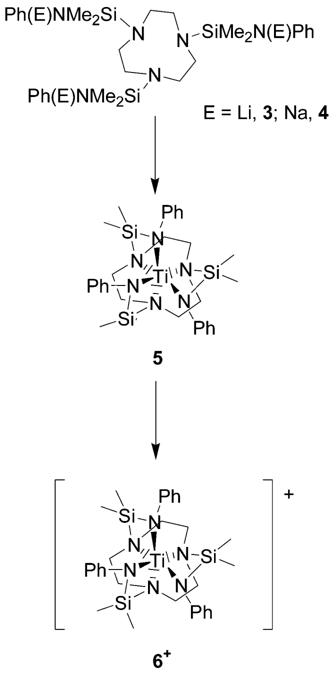

Table 1. Selected ^{1}H NMR Data for **6**

	CD_2Cl_2	C_6D_5Br	CD_3CN
6a	3.55−3.65, m, br, $6H_{syn}$ 3.90−4.00, m, br, $6H_{anti}$	3.75−3.95, $6H_{syn}$ 4.50−4.70, $6H_{anti}$	3.57, s, $12H_{syn+anti}$
6b	3.50−3.60, m, br, $6H_{syn}$ 4.00−4.10, m, br, $6H_{anti}$	3.80−4.00, $6H_{syn}$ 4.78−4.96, $6H_{anti}$	3.59, s, $12H_{syn+anti}$
6c		4.02−4.20, $6H_{syn}$ 4.30−4.58, $6H_{anti}$	
6d	3.61, s, $12H_{syn + anti}$	3.60−3.72, $6H_{syn}$ 3.73−3.86, $6H_{anti}$	3.44−3.62, m, $12H_{syn+anti}$
6e	2.24−3.36, m, $6H_{syn}$ 2.96−3.08, m, $6H_{anti}$	2.78−2.93, $6H_{syn}$ 3.02−3.20, $6H_{anti}$	3.42−3.61, m, $12H_{syn+anti}$

$SiMe_2\}_3$-tacn]X ([Ti(N_3-tacn)]X), **6**, (X = I, **6a**, Cl, **6b**, SCN, **6c**, PF_6, **6d**, BPh_4, **6e**) (Scheme 3). The NMR spectra of **6** show that ^{1}H tacn resonances are strongly dependent on the solvent and on the counterion X (Table 1), and VT NMR studies of **6a**, **6b**, and **6d** in CD_2Cl_2 have shown that a fluxional process occurs in solution (Figure 1). The exchange process makes the two methyl silyl groups (c and d in Scheme 4) as well as the two macrocyclic methylene carbons (a and b in Scheme 4) equivalent. Static spectra, obtained at −70 °C for **6d** in CD_2Cl_2, show two singlets for the methyl silyl protons and carbons and two separate resonances for the macrocyclic carbons. Accordingly, the macrocyclic methylene protons appear as four different resonances at δ 3.68 (Ha_{ax-syn}), 3.56 ($Ha_{eq-anti}$), 3.42 (Hb_{eq-syn}), and 3.28 ($Hb_{ax-anti}$). These protons give rise to an ABCD spectrum with proton coupling constants obtained from simulation of the experimental spectrum J_{HaxHeq} (geminal) −14 Hz, J_{HaxHax} 14 Hz, J_{HeqHeq} 0 Hz, and J_{HaxHeq} (vicinal) 3 and 4.8 Hz. The two vicinal coupling constants correspond respectively to the $H_{ax-syn}H_{eq-syn}$ and $H_{ax-anti}H_{eq-anti}$ pairs that arise from the two possible conformations of the five member metallocycles $M(NCH_2CH_2N)$.

The fluxional process observed in solution by NMR is readily understood as the intramolecular conversion of the $\Lambda(\lambda\lambda\lambda)/\Delta(\delta\delta\delta)$ enantiomorphic pair resulting, respectively, from the clockwise or anticlockwise shift of the amido nitrogen plane by an angle θ in relation to the trigonal plane defined by the amine nitrogens[20] that, in turn, determines the conformation of the Ti−NCH_2CH_2N five member metallocycles,[21] as shown in Scheme 4.

Complete line shape analysis of the coalescence process involving the methyl silyl protons of **6a**, performed with a modified version of DNMR5 Program,[22] yielded the following activation parameters: $\Delta H^{\ddagger}$ 39.3 ± 2.6 kJ·mol^{-1}; ΔS −35.7 ± 11.3 J·mol^{-1}K^{-1}; $\Delta G^{\ddagger}_{298}$ 49.9 ± 0.8 kJ·mol^{-1}. These values are of the same order of magnitude as those calculated for other metal tacn derivatives.[23]

At room temperature, the NMR spectra of cations **6** discussed in preceding paragraphs differ considerably from that of a comparable hexadentate tacn titanium(IV) cation ([Ti(O_3-tacn)]PF_6 = titanium 1,4,7-tris(5-*tert*-butyl-2-oxybenzyl)-1,4,7-triazacyclononane hexafluorophosphate) for which static proton and carbon spectra were registered.[24] The different solution behavior between cations [Ti(N_3-tacn)]$^+$ and [Ti(O_3-tacn)]$^+$ is most probably associated with different Ti−O and Ti−N bond features. Being better π donors, the amido moieties may release higher electron density to the metal center turning weaker the opposite titanium−amine bonds. Although relations between the metal−macrocycle bond strengths and the activation energies associated with metallocycle configuration exchanges of azamacrocycles have not been established, the comparison of NMR spectral data for [Ti(N_3-tacn)]$^+$ and [Ti(O_3-tacn)]$^+$ suggests this kind of dependence. A related interpretation was claimed to drive the different flipping rates of the TiN_2C_3 rings of [Ti(tren)X] (X = Cl, Me; tren = $(Me_3SiNCH_2CH_2)_3N$).[18]

Attempts to create a vacant coordination site at the metal by cleavage of a titanium−amine bond, in order to allow the synthesis of neutral [Ti(X)N_3-tacn], were unsuccessful. Despite the steric demands of the anions X, only cationic [TiN_3-tacn]X complexes have been obtained. The NMR spectral data confirm that the denticity of the trisamidotacn ligand does not change in solution, regardless of the solvent.[25] In addition, the bulkiness of the phenylamido moieties, which effectively shield the metal center, circumvents the syntheses of the neutral, seven coordinate compounds. A similar observation has been reported for aminopyridinato titanium derivatives [(R-Apy)$_3$TiCl] (R-Apy = 2-N(R)-C_6H_5N, R = Me, $SiMe_3$, Ph) for whom the synthesis of seven coordinated titanium aminopyridinato complexes depends on the steric bulk of the R groups and correlates to the ligand "cone angles".[24]

Attempts to use the amido nitrogen set of complexes **6** as a facial ligand to other metal centers, aiming the synthesis

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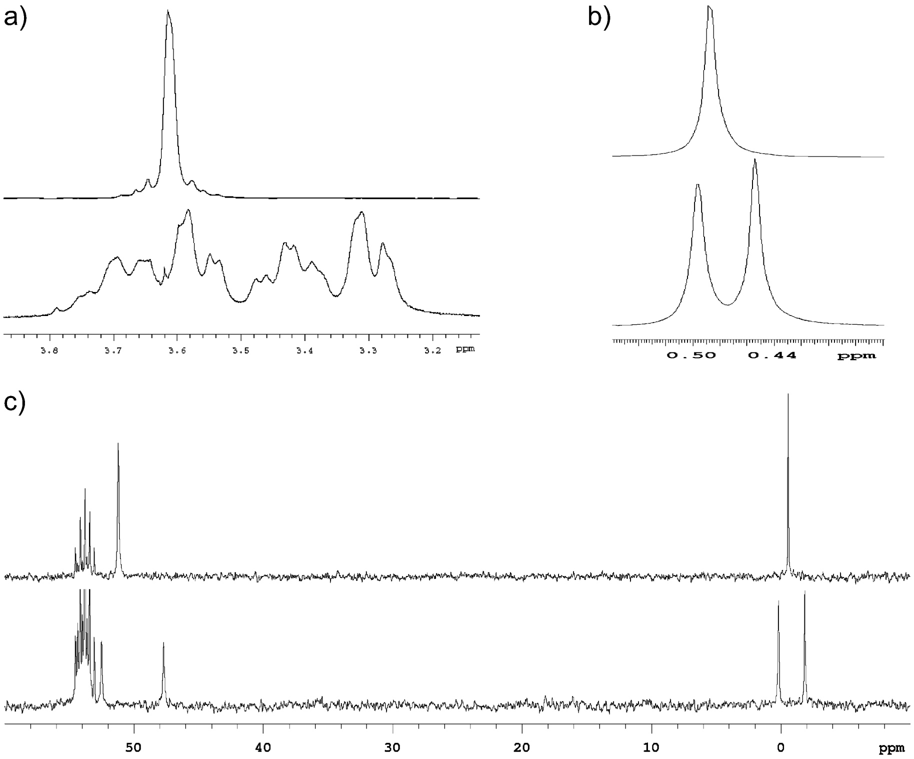


Figure 1. Selected NMR spectra of **6d** at 23 °C (top) and −70 °C (bottom): (a) macrocyclic methylenic ^{1}H resonances; (b) pendant arm $Si(CH_3)_2$ proton resonances; (c) macrocyclic methylenic and $Si(CH_3)_2$ pendant arm ^{13}C resonances.

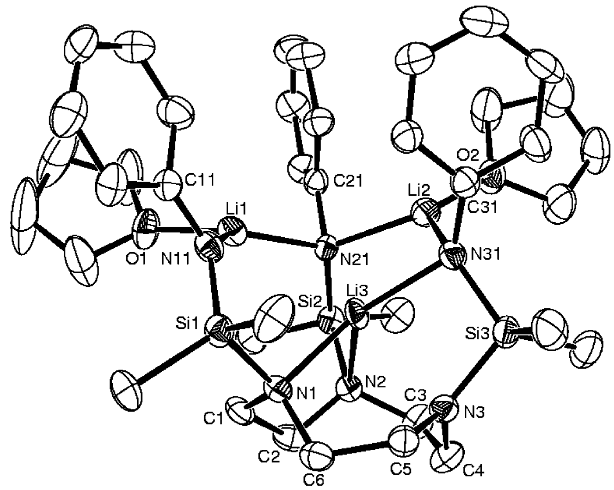
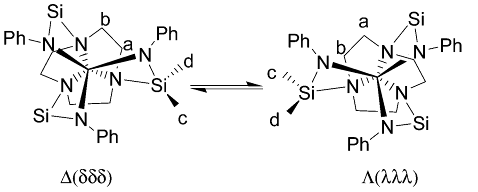


Figure 2. ORTEP perspective of one of the molecules of **3**. H atoms were omitted for clarity as well as THF solvent molecules not coordinated to the Li atoms. Ellipsoids were drawn at 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles [deg] for Compound **3**

N(21)−Li(2)	2.082(7)	N(21)−Li(1)	2.113(7)
N(31)−Li(2)	2.020(7)	N(31)−Li(3)	2.053(7)
N(1)−Li(3	2.124(7)	N(2)−Li(3)	2.276(7)
O(1)−Li(2)	1.923(7)	N(11)−Li(1)	1.979(7)
O(2)−Li(1)	1.928(7)		
N(21)−Si(2)−N(2)	102.73(15)	N(31)−Si(3)−N(3)	104.71(15)
N(11)−Si(1)−N(1)	106.01(15)	C(6)−N(1)−C(1)	111.5(3)
C(3)−N(2)−C(2)	113.4(3)	C(4)−N(3)−C(5)	115.5(3)
Si(1)−N(11)−Li(1)	127.6(3)	O(2)−Li(1)−N(11)	110.2(3)
O(2)−Li(1)−N(21)	117.6(3)	N(11)−Li(1)−N(21)	129.4(3)
O(1)−Li(2)−N(31)	125.3(4)	O(1)−Li(2)−N(21)	122.7(4)
N(31)−Li(2)−N(21)	109.2(3)	N(31)−Li(3)−N(1)	138.1(3)
N(31)−Li(3)−N(2)	124.9(3)	N(1)−Li(3)−N(2)	84.7(2)
N(31)−Li(3)−N(3)	75.7(2)	N(1)−Li(3)−N(3)	82.3(2)
N(2)−Li(3)−N(3)	80.2(2)		

Scheme 4



of bimetallic compounds, were unsuccessful.[26] In the majority of cases, we did not observe reactions when compounds **6** were treated with $M(CO)_6$ or $M(CO)_3(CH_3CN)_3$ (M = Mo, W). The exception to this disappointing situation was the synthesis of $[Ti(N_3\text{-tacn})][W(CO)_5I]$, **7**, obtained from the reaction of $[Ti(N_3\text{-tacn})]I$, **6a**, with $[W(CO)_6]$. The patterns characteristic of the titanium cation are observable in the ^{1}H and ^{13}C NMR spectra of **7**, and in addition, the ^{13}C NMR shows two resonances, at δ 202.4 and 197.7 ppm, attributed to the carbonyl ligands of the anion. The IR spectrum of **7** shows four CO bands at 2060.8 (w), 1920.6 (sh), 1906.8 (s), and 1844.4 (m), characteristic of $[M(CO)_5X]$ structures.

Crystals of $[Li_3N_3\text{-tacn}(THF)_2]$, **3·THF**, were grown from a THF solution of **3** at −4 °C. The molecular structure is presented in Figure 2, and selected bond lengths and angles are listed in Table 2. The molecule has three differently coordinated lithium centers. Li(1) and Li(2) are bonded to two amido nitrogens (N(11), N(21) and N(21), N(31), respectively) and to the oxygen atom of a THF molecule, but they do differ from the fact that N(11) is planar while

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(26) Beissel, T.; Glaser, T.; Kesting, F.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 3936.

N(31) is tetrahedral. These two Li centers also differ in respect to the lithium−nitrogen bond lengths. The coordination of Li(1) is asymmetric, with a Li(1)−N(11) bonding distance that is much shorter than Li(1)−N(21) (1.979(7) vs 2.113(7) Å) while Li(2) is more symmetrically bonded to N(21) and N(31) with distances of 2.082(7) and 2.020(7) Å, respectively. Li(3) has a different coordination as it is bonded to the amido nitrogen atom N(31) and to two tacn amines, N(1) and N(2). As expected, the Li(3)−N(31) bond length (2.053(7) Å) is much shorter than Li(3)−N(1) and Li(3)−N(2) for which bond lengths of 2.124(7) and 2.276(7) Å have been determined. The similarity between Li(1)−N(21), Li(3)−N(1), and Li(3)−N(2) distances is remarkable and might suggest that the Li(1)−N(21) bond would have a mainly covalent dative character. The detailed analysis of the coordination environments of both lithium and nitrogen show that, as previously noted by other authors,[27] the Li−N bond lengths in **3·THF** are dependent not only on the nitrogen formal charge (amido vs amine) but also on the nitrogen coordination numbers. (The coordination numbers (CNs) of all the lithium cations are three while those of the nitrogens are three, for N(11) and N(3), and four, for N(21), N(31), N(1), and N(2).) Indeed, the shortest lithium−nitrogen bond length is between N(CN3)−Li(CN3), namely, N(11)−Li(1).

Due to its implications in reactivity, structural arrangements of lithium amides have been extensively studied either in solution or in the solid state, and a great diversity of structures has been found. For simple monoamides, complex structure/solvation relationships in solution were related with steric and electronic parameters intrinsic to R_2NLi and to the solvent and also with other features as the solvent (or L donor ligand) concentration, the solvation degree, and the correlated solvation.[28] This concept, which attests from the fact that the presence of different L donors (or solvents) affects the relative stabilities of homo- and heterosolvates owing to cooperative solvation effects, plays a role in determining the structures of polyfunctional lithium amides as **3·THF** due to the competition between the intramolecular available L donors and the solvent. So, despite the fact that the basic principles underlying ring stacking and ring laddering structures are well characterized and, to the authors' best knowledge, $(N-Li)_n$ rings have always been found in all lithium amides solid structures,[29−31] the structural arrangement of the lithium atoms in **3·THF** is unique due to the lack of $(N-Li)_n$ rings. Also remarkable is the fact that the two planes defined by N(11)−N(21)−N(31) and N(1)−N(2)−N(3) are almost parallel (5.5(1)°), due to the array imposed by the coordination of the three lithium cations. The angles around the $Si(Me)_2$ bridges and inside the macrocyclic backbone are not far from the normal values.

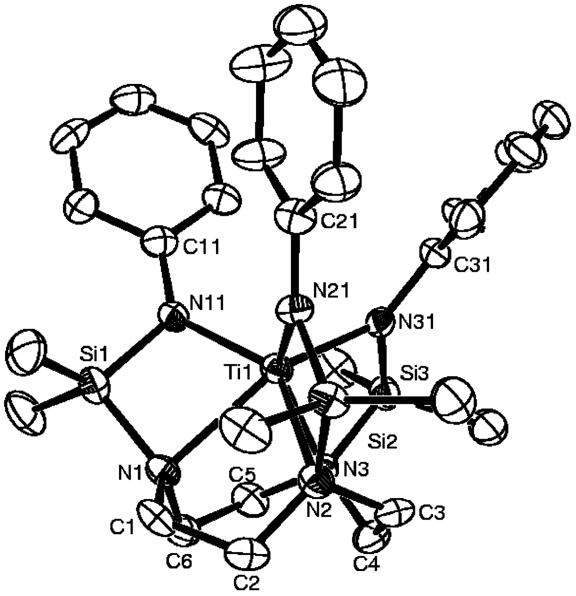

Figure 3. ORTEP perspective of compound **5**. H atoms were omitted for clarity. Ellipsoids were drawn at 30% probability level.

Table 3. Bond Distances and Angles for **5**, **6a**$^+$, and **6e**$^+$

	5	**6a**$^+$	**6e**$^+$
Ti(1)−N(21)	2.050(5)	1.936(7)	1.994(19)
Ti(1)−N(11)	2.052(5)	1.930(7)	1.922(18)
Ti(1)−N(31)	2.059(5)	1.940(7)	1.924(17)
Ti(1)−N(3)	2.285(4)	2.295(7)	2.29(2)
Ti(1)−N(2)	2.314(5)	2.270(7)	2.33(2)
Ti(1)−N(1)	2.376(5)	2.283(7)	2.30(2)
N(11)−Ti(1)−N(1)	70.81(18)	72.7(3)	75.3(7)
N(21)−Ti(1)−N(2)	72.38(18)	73.8(3)	73.9(7)
N(31)−Ti(1)−N(3)	72.29(17)	73.5(3)	72.0(7)
N(11)−Si(1)−N(1)	95.5(2)	92.4(4)	93.0(9)
N(21)−Si(2)−N(2)	96.0(2)	92.5(3)	96.5(9)
N(31)−Si(3)−N(3)	95.2(2)	92.9(4)	91.7(9)
C(31)−N(31)−Si(3)	122.3(4)	122.6(5)	123.2(14)
C(31)−N(31)−Ti(1)	138.2(4)	134.5(5)	131.5(13)
Si(3)−N(31)−Ti(1)	99.4(2)	103.0(4)	105.3(10)
C(11)−N(11)−Si(1)	124.0(4)	122.8(6)	122.1(16)
C(11)−N(11)−Ti(1)	134.3(4)	133.8(6)	135.1(16)
Si(1)−N(11)−Ti(1)	100.5(2)	103.2(4)	102.7(9)
C(21)−N(21)−Si(2)	125.3(4)	123.5(6)	128.0(18)
C(21)−N(21)−Ti(1)	132.2(4)	133.1(6)	130.1(17)
Si(2)−N(21)−Ti(1)	101.9(2)	103.3(3)	101.9(10)

Crystals of **5** suitable for X-ray diffraction were obtained from toluene, at −20 °C. The molecular structure of the complex is presented in Figure 3 while selected distances and angles are displayed in Table 3. The triazacyclononane ring and the three pendant arms are coordinated to the metal through the six nitrogen atoms of the ligand in a distorted trigonal prismatic geometry with twist angles θ of 25.4(6)°, 26.0(6)°, and 21.0(6)°. (θ values are the dihedral angles N_{amino}−cent1−cent2−N_{amido} with N_{amino} and N_{amido} of the respective pending arms. Cent1 and cent2 are the dummy centroid atoms defined, respectively, by the three N_{amino} (N(1), N(2), N(3)) and the three N_{amido} atoms (N(11), N(21), N(31)).) The angle cent1−Ti−cent2 is 178.4(5)°, and the two planes defined by the macrocyclic nitrogen atoms (N(1), N(2), and N(3)) and the three amido nitrogens (N(11), N(21), and N(31)) are nearly parallel with an angle of 2.8(1)° between them. The distances between the metal and each of these planes are 1.632(6) and 0.820(6) Å, respectively.

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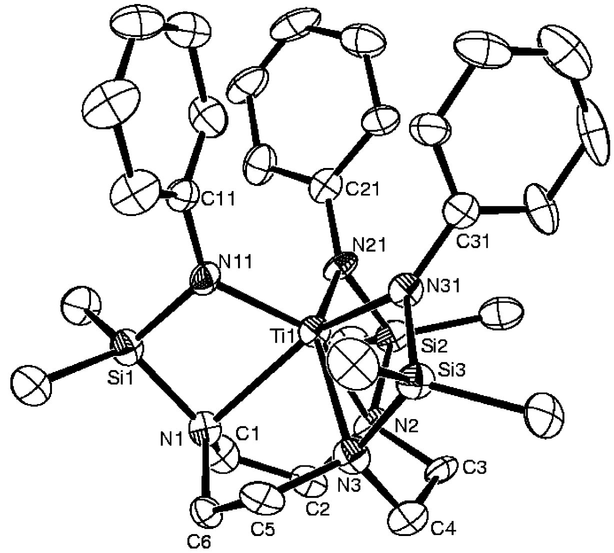

Figure 4. ORTEP perspective of one of the cations of **6e**$^+$. H atoms were omitted for clarity. Ellipsoids were drawn at 30% probability level.

Accordingly, two sets of Ti−N bond lengths are observed. The titanium−amido distances fall in the range 2.050(5)−2.059(5) Å, and the titanium−amine bond lengths are, as expected, longer (2.285(4)−2.376(4) Å). The amido nitrogen atoms are planar as reflected by the sum of angles around them (358.7° for N(11), 359.3° for N(21), and 359.9° for N(31)).

The titanium−N$_{amine}$ and titanium−N$_{amido}$ bond lengths in **5** are slightly longer than the values reported for [$TiCl_3$(1,4,7-Me_3-tacn)][33] and [Ti{N($SiMe_3$)$_2$}$_3$],[32] respectively. The Ti−N$_{amido}$ distances are comparable to the ones reported for anionic Ti(III) complexes as [Ti{N($SiMe_3$)$_2$}$_2${N($SiMe_3$)-$SiMe_2C(CH_2)N(C_6H_{11})$}]$^{-22}$ and evidence that the trisamido-tacn framework leads to a electron rich metal center. The coordination of the six nitrogen atoms constrains the angles inside the four member metallocycles. Particularly acute are the N−Si−N angles that reflect the aptitude of the NSi-(Me_2)N bridges to fit the metal binding requirements.

The solid state structure of the **6**$^+$ cation, obtained from crystals of **6a** and **6e**, is shown in Figure 4. Selected bond lengths and angles for the two cations are listed in Table 3. The crystals of **6a** were grown in a C_6H_5Br solution, at −20 °C, and those of **6e** were obtained from CH_3CN, at the same temperature. The structural features of [TiN_3-tacn]$^+$ are similar to those described for the parent complex, **5**, independently of the counterion used. The titanium is coordinated by the six nitrogen atoms of the ligand donor set in a distorted trigonal prismatic geometry. The dihedral angles N$_{amino}$−cent1−cent2−N$_{amido}$ are 24.7(6)°, 24.2(6)°, and 25.2(6)° for **6a** and 26.6(7)°, 25.1(7)°, and 24.6(7)° for **6e**, and the angles between the planes defined by the macrocyclic nitrogen atoms (N(1), N(2), and N(3)) and the amido nitrogens (N(11), N(21), and N(31)) are 0.5(2)° and 2.1(3)°, respectively. The metal distances to the mean planes are 1.605(6), 0.819(6) Å and 1.615(9), 0.809(9) Å while the cent1−Ti−cent2 angles are 178.5(6)° and 179.8(8)° for **6a** and **6e**, respectively. As for the parent complex **5**, the sum of angles around the amido nitrogen atoms is close to 360° and displays similar values in both molecules (see Table 3). As remarked for **5**, the metal−amido and metal−amine distances in **6a**$^+$ are slightly longer than observed in other Ti(IV) compounds (see Table 3).[33,34] Particularly noteworthy is the difference between the structures of [Ti(N_3-tacn)]$^+$ and [Ti(O_3-tacn)]$^+$ for which an octahedral metal environment and shorter metal−amine distances have been reported.[24]

As already mentioned, two centers of chirality exist in complexes **5** and **6**. Although there is similarity in their structural parameters, the enantiomorphic pairs identified in the solid state structures are different. Complex **5** exhibits the $\Delta(\lambda\lambda\lambda)/\Lambda(\delta\delta\delta)$ pair whereas the $\Lambda(\lambda\lambda\lambda)/\Delta(\delta\delta\delta)$ pair is observed in **6a**$^+$.

Experimental Section

General Procedures and Starting Materials. All reactions were conducted under a nitrogen atmosphere. Solvents were predried using 4 Å molecular sieves and refluxed over sodium-benzophenone (diethyl ether, tetrahydrofuran and toluene) or calcium hydride (dichloromethane and *n*-hexane) under an atmosphere of nitrogen, and collected by distillation. Deuterated solvents were dried with molecular sieves and freeze−pump−thaw degassed prior to use. Proton (300 MHz) and carbon (75.419 MHz) NMR spectra were recorded in a Varian Unity 300, at 298 K unless stated otherwise, referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (δ 0). Assignments were supported by NOE experiments and by $^{13}C-^1H$ heterocorrelations, as appropriate. EPR spectra were recorded at 23 °C with a Bruker 300E spectrometer at X-band frequency ($\nu \approx$ 9.5 GHz). Two samples were run: a 10^{-2} M solution in toluene and a powder sample. Mass spectra were performed at IST, Lisbon, Portugal, and Laboratoire de Spectrométrie de Masse, Université de Rouen, Rouen, France. Elemental analyses were obtained from Laboratório de Análises do IST, Lisbon, Portugal.

Triethylamine, aniline, $SiMe_2Cl_2$, n-LiBu (1.6 M in hexanes), $TiCl_4$, $TiCl_3$, and NaH (60% dispersion in mineral oil) were purchased from Aldrich. NEt_3 and NH_2Ph were predried with molecular sieves, refluxed over calcium hydride, and collected by distillation. $SiMe_2Cl_2$ was purified by removal of residual HCl and then distilled trap-to-trap. The n-LiBu solution was titrated by usual methods before use. $TiCl_4$ was freeze−pump−thaw degassed and then distilled trap-to-trap. NaH was washed with THF prior to use. [$TiCl_3(THF)_3$],[35] $PhICl_2$,[36] $AgBPh_4$,[37] and tacn·3HCl[38] were prepared according to described procedures.

1,4,7-($ClSiMe_2$)$_3$-tacn (1). A suspension of tacn·3HCl (0.91 g, 3.81 mmol) in CH_2Cl_2 was cooled at 0 °C, and NEt_3 (5.3 mL, 38.1 mmol) and $SiMe_2Cl_2$ (2.8 mL, 23 mmol) were added. The mixture was allowed to warm to room temperature while being stirred over 17 h. The volatiles were removed in a vacuum, and the residue was extracted in hexane and filtered. The solution was evaporated

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to dryness. An off-white solid formed in quantitative yield based on tacn·3HCl (1.55 g). ^{1}H NMR (C_6D_6): δ 2.79 (s, 12H, CH_2), 0.30 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 50.15 (CH_2), 2.10 (CH_3). Anal. Calcd for $C_{12}H_{30}N_3Cl_3Si_3$: C, 35.39; H, 7.43; N, 10.33. Found: C, 35.64; H, 7.40; N, 10.14. IR (KBr): 2963 (m), 1592 (s), 1446 (s), 1415 (s), 1377 (ms), 1348 (m), 1262 (s), 1085 (s), 1040 (s), 933 (m), 864 (s), 803 (s), 700 (ms), 660 (m), 482 (m) cm^{-1}. MS (EI) *m/z*: 407 (15, $[M]^{+\cdot}$), 371 (100, $[M - Cl]^{+}$).

1,4,7-[{N(H)Ph}SiMe$_2$]$_3$-tacn (2). Aniline (2.0 mL, 21.9 mmol) was added to a suspension of NaH (0.95 g, 39.6 mmol) in THF. The mixture was heated at 60 °C for 12 h. The excess of NaH was filtered off and then washed with 20 mL of THF, at room temperature. The filtrates were added dropwise to a solution of 1,4,7-($ClSiMe_2$)$_3$-tacn (2.74 g, 6.74 mmol) in toluene (80 mL), cooled at −40 °C. The mixture was warmed to room temperature and stirred for 12 h. The solvents were evaporated, and the product was extracted in hexane and filtered. Evaporation to dryness led to a very viscous yellow oil in quantitative yield (3.88 g). ^{1}H NMR (C_6D_6): δ 7.17 (t, 6H, $^{3}J_{H-H} = 7.5$ Hz, H_{meta}), 6.77 (t, 3H, $^{3}J_{H-H} = 7.5$ Hz, H_{para}), 6.62 (d, 6H, $^{3}J_{H-H} = 7.5$ Hz, H_{ortho}), 3.19 (s, 3H, NH), 2.98 (s, 12H, CH_2), 0.15 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 147.47 (C_{ipso}), 129.55 (C_{meta}), 118.22 (C_{para}), 116.76 (C_{ortho}), 50.41 (CH_2), −1.15 (CH_3). Anal. Calcd for $C_{30}H_{48}N_6Si_3$: C, 62.42; H, 8.39; N, 14.57. Found: C, 62.74; H, 8.40; N, 14.15. IR (KBr): 3381, 2954, 2910, 1920, 1829, 1769, 1697, 1600, 1497, 1382, 1291, 1255, 1151, 1109, 1077, 993, 966, 890, 824, 786, 751, 690, 626, 452 cm^{-1}. MS (EI) *m/z*: 577 (35, $[M]^{+}$), 484 (100, $[M - PhNH2]^{+\cdot}$).

[1,4,7-{N(Li)PhSiMe$_2$}$_3$-tacn] (3). Treatment at −78 °C of a suspension of 1,4,7-{[N(H)Ph]SiMe$_2$}$_3$-tacn (2.50 g, 4.33 mmol) in 60 mL of pentane with a 1.6 M solution of n-LiBu in hexanes (8.1 mL, 12.98 mmol) led to the quantitative formation of Li$_3${1,4,7-[(NPh)SiMe$_2$]$_3$-tacn} that was obtained as a pale yellow solid (2.57 g, 4.33 mmol) after evaporation of the solvent. ^{1}H NMR (C_6D_6): δ 7.08 (t, 6H, $^{3}J_{H-H} = 7.8$ Hz, H_{meta}), 6.69 (t, 3H, $^{3}J_{H-H} = 7.8$ Hz, H_{para}), 6.68 (d, 6H, $^{3}J_{H-H} = 7.8$ Hz, H_{ortho}), 2.88 (m, 6H, CH_2 syn), 2.31 (m, 6H, CH_2 anti), 0.27 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 156.63 (C_{ipso}), 130.86 (C_{meta}), 121.93 (C_{ortho}), 116.35 (C_{para}), 48.14 (CH_2), −0.15 (CH_3).

[1,4,7-{N(Li)PhSiMe$_2$}$_3$-tacn](THF)$_2$ (3·THF). Yellow crystals of **3·THF** have been obtained at −20 °C from a concentrated solution of **3** in THF. ^{1}H NMR (C_6D_6): δ 7.14 (t, 6H, $^{3}J_{H-H} = 7$ Hz, H_{meta}), 7.05 (d, 6H, $^{3}J_{H-H} = 7$ Hz, H_{ortho}), 6.61 (t, 3H, $^{3}J_{H-H} = 7$ Hz, H_{para}), 2.96 (m, 8H, OCH_2, THF), 2.93 (m, 6H, CH_2 syn), 2.44 (m, 6H, CH_2 anti), 1.00 (m, 8H, CH_2, THF), 0.40 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 157.9 (C_{ipso}), 130.0 (C_{meta}), 123.1 (C_{ortho}), 115.3 (C_{para}), 67.98 (OCH$_2$, THF), 48.2 (CH_2), 25.14 (CH_2, THF), −0.1 (CH_3). Anal. Calcd for $C_{38}H_{61}N_6Li_3O_2Si_3$: C, 61.73; H, 8.32; N, 11.37. Found: C, 61.54; H, 9.07; N, 11.07.

[1,4,7-{N(Na)PhSiMe$_2$}$_3$-tacn]·2THF (4). A solution of 1,4,7-{[N(H)Ph]SiMe$_2$}$_3$-tacn (6.42 g, 11.14 mmol) in THF (25 mL) was added dropwise to a suspension of NaH (1.2 g, 50 mmol) in THF (100 mL) cooled at −40 °C. The temperature was allowed to rise until room temperature, and the mixture was then heated at 50 °C for 12 h. The solution was filtered, and the residue of NaH was washed with THF (30 mL). The evaporation of the THF led to a greenish solid in quantitative yield (8.76 g). ^{1}H NMR (C_6D_6): δ 7.04 (t, 6H, $^{3}J_{H-H} = 7.2$ Hz, H_{meta}), 6.68 (d, 6H, $^{3}J_{H-H} = 7.2$ Hz, H_{ortho}), 6.43 (t, 3H, $^{3}J_{H-H} = 7.2$ Hz, H_{para}), 3.29 (m, 8H, OCH_2, THF), 2.70 (m, 6H, CH_2, syn), 2.53 (m, 6H, CH_2, anti), 1.26 (m, 8H, CH_2, THF), 0.26 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 160.71 (C_{ipso}), 130.48 (C_{meta}), 121.91 (C_{ortho}), 112.82 (C_{para}), 67.82 (OCH$_2$, THF), 48.42 (CH_2, tacn), 25.52 (CH_2, THF), 0.04 (CH_3).

[Ti{N(Ph)SiMe$_2$}$_3$-tacn] (5). Method 1 was performed as follows: TiCl$_4$ (0.408 g, 2.15 mmol) was added at −70 °C to a solution of Li$_3$[1,4,7-{(NPh)SiMe$_2$}$_3$-tacn] (1.59 g, 2.15 mmol) in toluene (30 mL). The color darkened immediately, and a precipitate appeared. The mixture was allowed to warm to room temperature while being stirred overnight. The solution was filtered through a Celite layer and the solvent evaporated to dryness to give a dark green material. Washing with hexane led to a dark yellow powder. Method 2 was performed as follows: A suspension of [TiCl$_3$(THF)$_3$] (8.07 g, 21.8 mmol) in toluene (200 mL) was rapidly added to a suspension of Na$_3$[1,4,7-{(NPh)SiMe$_2$}$_3$-tacn]·2THF (17.13 g, 21.72 mmol) in toluene (300 mL) at −60 °C. The mixture was allowed to warm to room temperature while being stirred for 12 h. The solution was filtered through a Celite layer, and the residue was washed with THF and toluene. The solvents were evaporated under vacuum, and the compound was washed at −30 °C with hexane (3 × 30 mL). Yield, 81% (13.53 g). Anal. Calcd for $C_{30}H_{45}N_6Si_3Ti$: C, 57.92; H, 7.30; N, 13.52. Found: C, 56.60; H, 7.56; N, 12.93. IR (KBr): 2959 (m), 1622 (mw), 1603 (s), 1492 (s), 1409 (w), 1362 (w), 1287 (m), 1259 (s), 1028 (s), 904 (s), 800 (s), 752 (s), 693 (s), 506 (mw) cm^{-1}. MS (EI) *m/z*: 621(50, $[M]^{+}$), 472 (100, $[M - PhNSiMe2]^{+\cdot}$).

[Ti{N(Ph)SiMe$_2$}$_3$-tacn]X (6). The experimental procedure used to prepare the cationic complexes **6** is described for **6a**: Treatment of a toluene solution of [Ti{N(Ph)SiMe$_2$}$_3$-tacn] (3.112 g, 5.00 mmol) with 0.5 equiv of solid I$_2$ (0.640 g, 2.50 mmol) at −60 °C, followed by slow warming until room temperature, lead to the precipitation of a dark red solid. The solvent was removed, and the residue was washed with hexane and then Et$_2$O. The product obtained is analytically pure. Yield, 100%. For **6a**, ^{1}H NMR (CD_2Cl_2): δ 6.96 (t, 6H, $^{3}J_{H-H} = 7.5$ Hz, H_{meta}), 6.92 (t, 3H, $^{3}J_{H-H} = 7.5$ Hz, H_{para}), 6.16 (d, 6H, $^{3}J_{H-H} = 7.5$ Hz, H_{ortho}), 3.9−4.0 (m, br, 6H, CH_2, anti), 3.55−3.65 (m, br, 6H, CH_2, syn), 0.47 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 151.89 (C_{ipso}), 128.89 (C_{meta}), 122.84 (C_{ortho}), 123.63 (C_{para}), 51.70 (CH_2, tacn), −0.39 (CH_3). Anal. Calcd for $C_{36}H_{50}BrIN_6Si_3Ti$ [with 1 equiv (C_6H_5Br)]: C, 47.71; H, 5.57; N, 9.28. Found: C, 47.68; H, 5.56; N, 9.26. IR (KBr): 2957 (mw), 1621 (mw), 1602 (m), 1589 (m), 1499 (m), 1481 (ms), 1443 (ms), 1255 (s), 1072 (ms), 1041 (m), 1026 (m), 1004 (m), 910 (s), 870 (ms), 831 (s), 781 (s), 735 (ms), 696 (ms), 642 (ms), 513 (ms), 477 (mw), 437 (mw) cm^{-1}. MS (FAB) *m/z*: 621(100, $[M]^{+}$). For **6b**, ^{1}H NMR (CD_2Cl_2): δ 6.95 (t, 6H, $^{3}J_{H-H} = 7.8$ Hz, H_{meta}), 6.88 (t, 3H, $^{3}J_{H-H} = 7.8$ Hz, H_{para}), 6.17 (d, 6H, $^{3}J_{H-H} = 7.8$ Hz, H_{ortho}), 4.0−4.1 (m, br, 6H, CH_2, anti), 3.5−3.6 (m, br, 6H, CH_2, syn), 0.45 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 152.0 (C_{ipso}), 128.89 (C_{meta}), 123.55 (C_{para}), 122.86 (C_{ortho}), 51.70 (CH_2, tacn), −0.45 (CH_3). Anal. Calcd for $C_{30}H_{45}ClN_6Si_3Ti$: C, 54.79; H, 6.90; N, 12.79. Found: C, 54.85; H, 6.92; N, 12.70. IR (KBr): 2960 (mw), 1708 (mw), 1627 (mw), 1605 (mw), 1500 (mw), 1456 (w), 1363 (w), 1258 (w), 1030 (w), 908 (s), 833 (w), 797 (w), 696 (mw), 509 (mw) cm^{-1}. MS (FAB) *m/z*: 621(100, $[M]^{+}$). For **6c**, ^{1}H NMR (C_6D_5Br): δ 7.45 (t, 6H, $^{3}J_{H-H} = 7.5$ Hz, H_{meta}), 7.34 (t, 3H, $^{3}J_{H-H} = 7.5$ Hz, H_{para}), 6.65 (d, 6H, $^{3}J_{H-H} = 7.5$ Hz, H_{ortho}), 4.23 (s, br, 6H, CH_2, anti), 4.1 (s, br, 6H, CH_2, syn), 0.85 (s, 18H, CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_5Br): δ 152.0 (C_{ipso}), 128.54 (C_{meta}), 123.22 (C_{para}), 122.57 (C_{ortho}), 51.39 (CH_2, tacn), −0.86 (CH_3). Anal. Calcd for $C_{31}H_{45}N_7SSi_3Ti$: C, 54.73; H, 6.67; N, 14.42; S, 4.72. Found: C, 54.73; H, 6.51; N, 14.12; S, 5.10. IR (KBr): 2956 (w), 2361 (s), 1591 (mw), 1483 (m), 1255 (s), 1075 (mw), 1043 (w), 1005 (w), 910 (s), 874 (m), 832 (ms), 813 (m), 781 (s), 735 (mw), 698 (m), 645 (m), 516 (m). MS (FAB) *m/z*: 621 (100, $[M]^{+}$). For **6d**, ^{1}H NMR (CD_2Cl_2): δ 7.0 (t, 6H, $^{3}J_{H-H} = 7.5$ Hz, H_{meta}), 6.94 (t, 3H, $^{3}J_{H-H} = 7.5$ Hz, H_{para}), 6.16 (d, 6H,

Table 4. Experimental Results on Crystal Data and Structure Refinement for Compounds **3**, **5**, **6a** and **6e**

	3	**5**	**6a**	**6e**
formula	$C_{80}H_{106}Li_6N_{12}O_6Si_6$	$C_{30}H_{45}N_6Si_3Ti$	$C_{36}H_{50}BrIN_6Si_3Ti$	$C_{108}H_{130}B_2N_{12}Si_6Ti_2$
M_r	1541.95	621.89	905.80	1882.20
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$
unit cell dimensions	$a = 11.639(4)$ Å $b = 20.362(7)$ Å $c = 20.463(9)$ Å $\alpha = 103.70(3)°$ $\beta = 89.81(3)°$ $\gamma = 106.66(3)°$	$a = 11.788(2)$ Å $b = 16.385(4)$ Å $c = 17.460(3)$ Å $\beta = 101.03(1)°$	$a = 10.659(4)$ Å $b = 20.557(3)$ Å $c = 19.492(3)$ Å $\beta = 104.70(4)°$	$a = 25.875(5)$ Å $b = 13.974(8)$ Å $c = 28.679(9)$ Å $\beta = 93.51(9)°$
V	4503(3) Å^3	3310.0(11) Å^3	4131.3(18) Å^3	10350(5) Å^3
Z	2	4	4	4
ρ_{calcd} mg/m^3	1.137	1.248	1.456	1.208
absn coeff	0.146 mm^{-1}	0.396 mm^{-1}	2.041 mm^{-1}	0.276 mm^{-1}
reflns collected/unique	24774/21630 [R(int) = 0.0286]	5963/5764 [R(int) = 0.0542]	10307/7968 [R(int) = 0.1017]	18688/18252 [R(int) = 0.1655]
final R indices [$I > 2\sigma(I)$]	R1 = 0.0839; wR2 = 0.1962	R1 = 0.0807; wR2 = 0.1392	R1 = 0.0848; wR2 = 0.1494	R1 = 0.2468; wR2 = 0.4482

$^3J_{H-H} = 7.5$ Hz, H_{ortho}), 3.61 (s, 12H, CH_2), 0.49 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 151.85 (C_{ipso}), 129.02 (C_{meta}), 123.87 (C_{para}), 122.92 (C_{ortho}), 51.22 (CH_2, tacn), −0.60 (CH_3). Anal. Calcd for $C_{30}H_{45}F_6N_7PSi_3Ti$: C, 46.96; H, 5.92; N, 10.96. Found: C, 46.83; H, 6.01; N, 10.96. IR (KBr): 2953 (w), 1592 (mw), 1484 (m), 1248 (m), 1078 (mw), 1045 (w), 1009 (w), 919 (m), 877 (m), 844 (s), 811 (m), 779 (m), 694 (w), 648 (w), 558 (w). MS (FAB) m/z: 621(100, [M]$^+$). For **6e**, ^1H NMR (CD_2Cl_2): δ 7.34 (t, br, 8H, H_{ortho} BPh_4), 7.06 (t, 8H, $^3J_{H-H} = 7$ Hz, H_{meta} BPh_4), 6.88−7.02 (m, 13H, $H_{meta} + H_{para} + H_{para}$ BPh_4), 6.09 (t, 6H, $^3J_{H-H} = 7$ Hz, H_{ortho}), 2.96−3.08 (m, 6H, CH_2, anti), 2.24−3.36 (m, 6H, CH_2, syn), 0.41 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 151.68 (C_{ipso}), 136.39 (C_{ortho} BPh_4), 129.05 (C_{meta}), 126.1 (t, $^1J_{B-C} = 3$ Hz, C_{ipso} BPh_4), 126.0 (C_{meta} BPh_4), 123.98 (C_{para}), 122.84 (C_{ortho}), 122.36 (C_{para} BPh_4), 51.05 (CH_2, tacn), −0.54 (CH_3). Anal. Calcd for $C_{54}H_{65}BN_6Si_3Ti$: C, 68.89; H, 6.97; N, 8.94 Found: C, 68.89; H, 7.01; N, 8.91. IR (KBr): 3055 (mw), 2983 (mw), 1591 (m), 1483 (ms), 1254 (s), 1075 (m), 1040 (w), 1005 (w), 910 (s), 872 (m), 833 (s), 806 (s), 777 (s), 735 (s), 706 (s), 646 (m), 613 (m), 515 (mw), 434 (w). MS (FAB) m/z: 621 (100, [M]$^+$).

[Ti{N(Ph)SiMe$_2$}$_3$-tacn][W(CO)$_5$I], 7. A THF solution of $W(CO)_6$ (0.716 g; 2.03 mmol) was added at room temperature to a dispersion of **6a** (1.44 g, 1.92 mmol) in THF (40 mL). The mixture was warmed at 70 °C for 4 days and after cooling was filtered, and the solvent and the excess of $W(CO)_6$ were removed under vacuum. The solid was extracted in CH_3CN and, from this solution, pure **7** precipitated off in quantitative yield, on cooling to −20 °C. Crystals of **7** were obtained from CH_2Cl_2 at −20 °C.

^1H NMR (CD_2Cl_2): δ 7.45 (t, 6H, $^3J_{H-H} = 7.5$ Hz, H_{meta}), 7.37 (t, 3H, $^3J_{H-H} = 7.5$ Hz, H_{para}), 6.52 (d, 6H, $^3J_{H-H} = 7.5$ Hz, H_{ortho}), 3.94 (m, br, 6H, CH_2, anti), 3.76 (m, br, 6H, CH_2, syn), 0.65 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 197.94 (CO), 151.41 (C_{ipso}), 128.66 (C_{meta}), 122.45 (C_{ortho}), 123.56 (C_{para}), 50.75 (CH_2, tacn), −1.21 (CH_3). Anal. Calcd for $C_{35}H_{36}IN_6O_5Si_3TiW$: C, 39.52; H, 3.41; N, 7.90. Found: C, 39.61; H, 3.47; N, 7.96. IR (KBr): 2060.8 (w), 1920.6 (sh), 1906.8 (s), and 1844.4 (m)

X-ray Experimental Details. X-ray data for the 4 compounds were collected using a MACH3 Nonius diffractometer equipped with Mo radiation ($\lambda = 0.71069$ Å), at room temperature. Solution and refinement were made using SIR97[39] and SHELXL[40] included in the package of programs WINGX-Version 1.64.03b.[41] For compound **3**, two trisamidotacn fragments, four THF molecules, and six Li atoms were found in the asymmetric unit and refined exhibiting slight differences in the geometric parameters. Two solvent molecules (THF) were found to be disordered near two centers of symmetry. The refinement did not improve using different approaches to a disorder model. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were inserted in idealized positions riding in the parent C atom. For compounds **5** and **6**, the same procedure was performed. In complexes **5** and **6a**, one molecule was found per asymmetric unit, and a bromobenzene molecule (solvent) in **5** and an iodine ion in **6a** were also found. In compound **6e**, two molecules were found in the asymmetric unit exhibiting slight differences in the geometric parameters. These crystals were of very poor quality (lower crystallinity) as can be seen in the R_{int} and R_{sigma}, values and they had a very poor diffraction quality (very weak high angle data). The structure was determined in order to have an idea of the counterion influence in the molecular geometry.

All the details concerning data collection and refinement of the 4 compounds are present in Table 4.

Figures were made with ORTEP3.[42]

Data were deposited in CCDC under the deposit numbers 194896−194899 for compounds **3**, **5**, **6a**, and **6e**, respectively.

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