

Ion Pairing in Ti(IV) Trisamidotriazacyclononane Compounds

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[Ti{N(Ph)SiMe₂}₃-tacn]X complexes (X = Cl, **1**; I, **2**; PF₆⁻, **3**; BPh₄⁻, **4**) were studied by NMR and electron absorption and emission methods, which showed that these compounds exist in bromobenzene and dichloromethane solutions as ion pairs. The significant modifications observed in the proton resonances of tacn in C₆D₅Br, which follow the sequence BPh₄⁻ ≥ PF₆⁻ ≥ I⁻ ≈ Cl⁻, are a qualitative indication of the strength of the interactions that depend on the anion. The reaction of **2** with LiNMe₂ led to [Ti(NPh){NPh(SiMe₂)₂-tacn], **5**, that forms upon attack of Me₂N⁻ at one SiMe₂ group. The formation of **5** is discussed on the basis of the interactions identified in solution.

Introduction

The relevance of ion pairing in determining the structures and reactivity of transition metal complexes is now widely recognized and sustained by a rising number of reports.^{1–4}

Strongly related to the latest and most significant advances in the understanding of ion pair interactions are NMR methodologies, as NOE and PGSE,^{5–8} which give information about solution structural features and allow the comparison between solution and solid-state structures, where packing forces may originate specific interactions, not necessarily relevant to the reactivity in solution.

The interference of halide and formerly thought “non-coordinating” anions in many stoichiometric and catalytic reactions^{9,10} pushed the search for weakly coordinating anions, intended to promote the dissolution of ionic compounds in nonpolar solvents and also to explore the reactivity of the cation in condensed phase without, or with minimal,

counterion participation.¹¹ Despite the success in reducing or modifying the nature of ion-pair interactions, these are intimately related to the driving force of key aspects of chemical processes such as conversion and stereochemistry.^{12–14}

Considering transition metal hydrides, hydrogen bonding revealed to be critical to many aspects of their chemistry such as the equilibrium ratio between isomers, the pathways of protonation reactions, the stability of dihydrogen complexes, and the kinetic features of dihydrogen complexes reactions.^{15,16}

Studies on Diels–Alder reactions¹⁷ and homogeneous polymerization^{18–21} also showed the dependence of the activity and the selectivity on ion pair interactions.

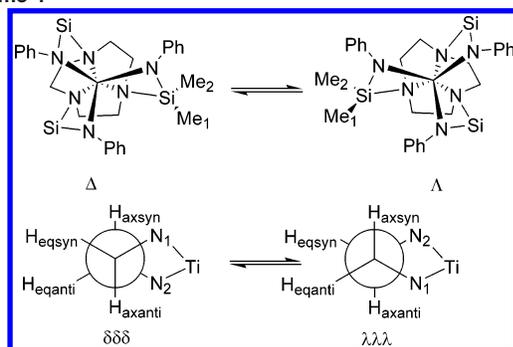
In this work, we present NMR and UV–vis data for Ti(IV) trisamido-tacn cations of general formula [Ti{N(Ph)SiMe₂}₃-tacn]X and discuss ion pair interactions in those complexes. These results are compared to the solid-state structures of [Ti{N(Ph)SiMe₂}₃-tacn]X (X = I, BPh₄). The reaction of

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Scheme 1



[Ti{N(Ph)SiMe₂}₃-tacn]I with LiNMe₂ is also reported and discussed in the light of the interactions described.

Results and Discussion

Cationic [Ti{N(Ph)SiMe₂}₃-tacn]X (X = Cl, **1**; I, **2**; PF₆, **3**; BPh₄, **4**; tacn = triazacyclononane) have been recently reported by some of us.²² The complexes, which are readily prepared by oxidation of the neutral Ti(III) precursor, were characterized by X-ray diffraction (**2** and **4**) and NMR that confirmed the titanium coordination to six nitrogen atoms in a distorted trigonal prismatic geometry.

In solution, a fluxional process consisting in the trigonal twist of the amido and amine nitrogen planes is accompanied by a change in the conformation of the five-member Ti–NCH₂CH₂N metalocycles, in such a way that the overall process corresponds to the intramolecular conversion of enantiomers (Δ(λλλ)/Λ(δδδ)) (Scheme 1). An analogous equilibrium was identified for [Ti{N(Ph)SiMe₂}₃-tacu]I (tacu = triazacycloundecane).²³ In this case, due to the different macrocycle chain lengths (C₂ and C₃), the global fluxional process has a further component that is the boat/chair conversion of the six-member metalocycles formed by the bonding of the NC₃N moieties to the titanium. Although a static ¹H spectrum was not obtained until –70 °C in CD₂Cl₂ and overlapping resonances did not allow the estimation of activation parameters, variable-temperature NMR studies allowed the differentiation of the three independent processes and gave information about their limit temperatures. δ/λ isomerization is the higher-activation-energy process, being blocked at –40 °C, Δ/Λ equilibrium stops at –70 °C and the chair/boat conversion is still operative at –70 °C.

In addition to the intramolecular processes mentioned, the solutions of cations [Ti{N(Ph)SiMe₂}₃-tacn]X also disclose ion pair formation that have a deep influence on the ¹H NMR and UV–vis absorption and emission spectra.

As shown in Figure 1 and Table 1, at 23 °C, the tacn methylenic proton resonances and the dimethylsilyl proton resonances of complexes [Ti{N(Ph)SiMe₂}₃-tacn]X are strongly dependent on the solvent and counterions.

In *d*₅-bromobenzene, all complexes display an AA'BB' pattern for the methylenic H_{syn} and H_{anti} resonances that is maintained in CD₂Cl₂, except for **3** that leads to a deceptively simple AA'BB' spectrum. In CD₃CN, the H_{syn} and H_{anti} resonances of **1** and **2** appear superimposed in an apparent singlet whereas **3** and **4** give rise to a more complex AA'BB' pattern. In *d*₂-dichloromethane and *d*₅-bromobenzene, H_{syn} resonances appear at higher field than H_{anti} for complexes **1**, **2**, and **3**, although for complex **4**, those resonances invert their relative positions, with H_{anti} being observed at higher field than H_{syn}. In both solvents, H_{syn} and H_{anti} resonances are more shielded in complex **4** than in complexes **1**, **2**, and **3**. The shifts to high field registered in all complexes are more pronounced for H_{anti} than for H_{syn}.

The NOESY spectrum of complex **4** in CD₂Cl₂ (Figure 2) shows (i) strong interactions between the ortho- and meta-phenyl anion protons (δ 7.34 and 7.06, respectively) and the cation H_{anti} resonance (δ 3.08–2.96), (ii) weak interaction between the ortho-Ph anion protons (δ 7.34) and the cation H_{syn} (δ 3.36–3.24), and (iii) medium interactions between all BPh₄[–] protons and the Si(CH₃)₂ protons (δ 0.41). These results show that the BPh₄[–] anions are located at the macrocycle side, close to H_{anti} and to the dimethylsilyl groups, with which nonbonded interactions between atoms of the two ionic moieties are the strongest exhibited (Scheme 2). The lack of NOE between the BPh₄[–] and NPh protons further confirms the anion preference to locate on the side of the triazacyclononane ring.

Thus, the shifts to high field observed for the macrocyclic protons are consistent with the BPh₄[–] ring current effects. The outcome is mainly noticed in the H_{anti} resonance because the anion is closer to H_{anti} than to H_{syn} protons. The shielding of Si(CH₃)₂ signals, more pronounced in *d*₅-PhBr than in dichloromethane, also reflect the proximity of the anion and, as expected due to the lower dielectric constant of bromobenzene, ion pairing is more effective in this solvent than in dichloromethane.

To evaluate the importance of ion pairing in the solutions of complexes **2** and **3**, absorption and emission spectra were recorded in CH₂Cl₂ and CH₃CN (Figures 3 and 4). In CH₃CN, the two electronic absorption spectra are identical, with maximum, λ_a, at 285 nm for **2** and at 286 nm for **3**. Electronic excitation at higher and lower energies relative to the maximum of the band centered at λ_a around 285 nm produces similar emission spectra. Accordingly, luminescence collected at higher and lower energies relative to the emission maximum also gives rise to similar spectral distributions corresponding well to the respective absorption profiles. Thus, the **2** and **3** emitting states in CH₃CN can be ascribed to the directly excited (relaxed) electronic states of the cation. In CH₃CN, the emission spectra of **2** displays more intense fluorescence than that of **3**. In spite of the extremely high dielectric constant of the solvent, the PF₆[–] anion may act as a more efficient quencher, thereby

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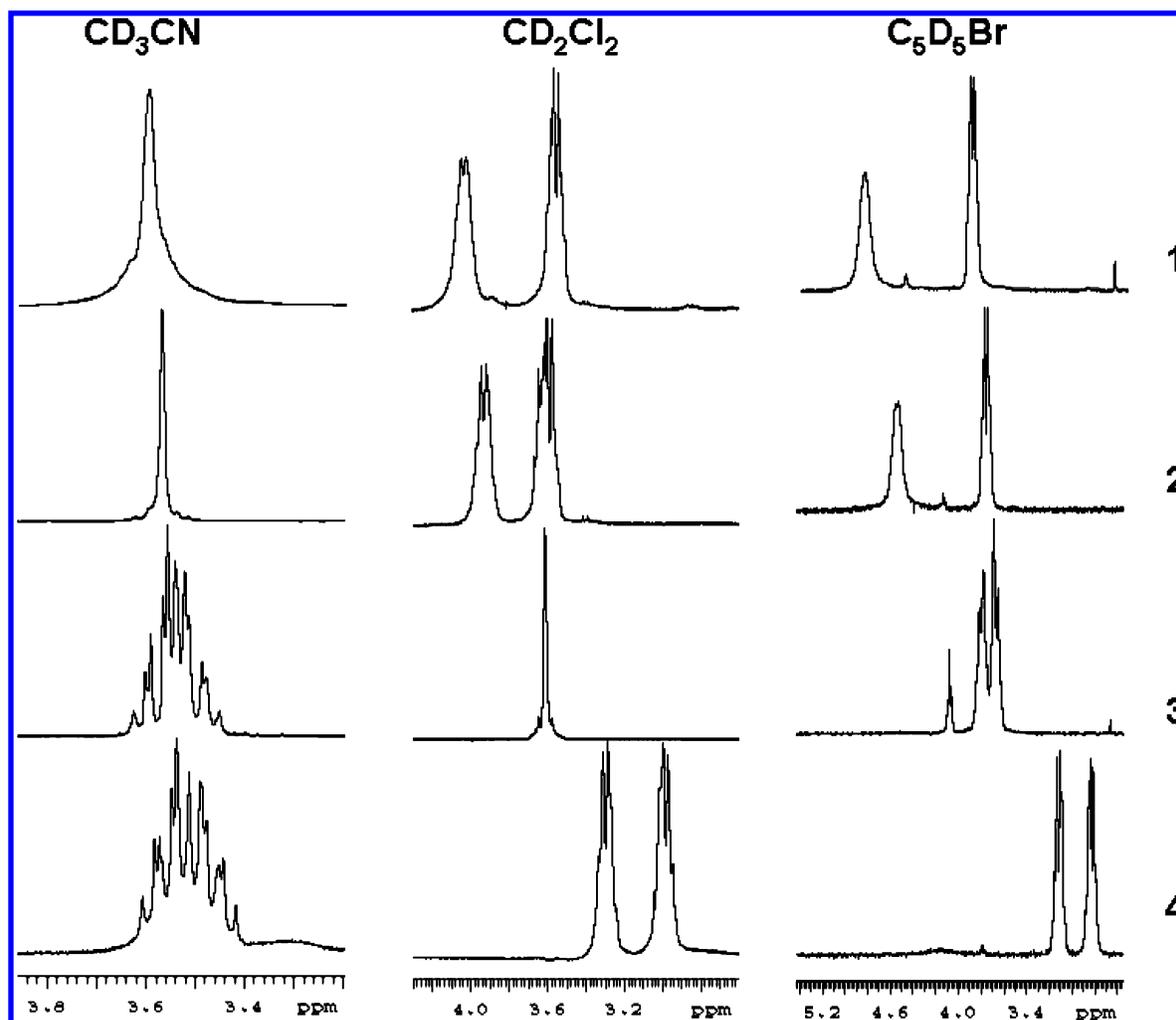


Figure 1. Selected ^1H methylenic resonances of $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{X}$ in CH_3CN , CD_2Cl_2 , and d_5 -bromobenzene.

Table 1. Selected ^1H NMR Data for $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{X}$ ($\text{X} = \text{Cl}$, **1**; I , **2**; PF_6 , **3**; BPh_4 , **4**)

	δH_{anti}			δH_{syn}			$\delta \text{Si}(\text{CH}_3)_2$		
	CD_3CN	CD_2Cl_2	$\text{C}_6\text{D}_5\text{Br}$	CD_3CN	CD_2Cl_2	$\text{C}_6\text{D}_5\text{Br}$	CD_3CN	CD_2Cl_2	$\text{C}_6\text{D}_5\text{Br}$
1	3.59	4.10–4.00	4.96–4.78	3.59	3.60–3.50	4.00–3.80	0.48	0.45	0.76
2	3.57	4.00–3.90	4.70–4.50	3.57	3.65–3.55	3.95–3.75	0.48	0.47	0.71
3	3.62–3.44	3.61	3.86–3.73	3.62–3.44	3.61	3.72–3.69	0.48	0.49	0.62
4	3.61–3.41	3.08–2.96	2.93–2.78	3.61–3.41	3.36–3.24	3.20–3.05	0.48	0.41	0.33

reducing the emission of **3**. In CH_2Cl_2 , both compounds display very broad additional absorption bands with λ_a at 325 nm for **2** and at 320 nm for **3**, consistent with stronger anion–cation interactions and higher extinction coefficients in the main absorption band. The shifts to higher wavelength and broadening registered in CH_2Cl_2 vs CH_3CN are indicative of the existence of contact ion pairs in dichloromethane, and the higher shift for **3** reflects a stronger anion–cation interaction in this complex.²⁴ This conclusion was supported for **2** and **3** in CH_2Cl_2 by the lack of fluorescent emission that is probably strongly quenched by charge-transfer processes between the ions.^{25,26}

The occurrence of ion pair association in $\text{C}_6\text{D}_5\text{Br}$ solutions of **3** is clearly expressed in the significant high-field shifts

of H_{anti} and $\text{Si}(\text{CH}_3)_2$ resonances. In CH_2Cl_2 and CD_3CN , the methylenic protons NMR patterns observed are not symptomatic.

The differences observed in the proton NMR spectra of complexes **1** and **2** in CD_2Cl_2 and $\text{C}_6\text{D}_5\text{Br}$ are slight and suggest that, regardless the solvent, Cl^- and I^- interact similarly with the macrocyclic protons. However, a minor effect that is reflected in both solvents by a small shielding of H_{anti} in **2** may be noted (in CD_2Cl_2 , δH_{anti} is 4.25 in **1** and 3.95 in **2** and in $\text{C}_6\text{D}_5\text{Br}$, δH_{anti} is 4.87 in **1** and 4.61 in **2**, whereas δH_{syn} is the same for **1** and **2**: 3.60 in CD_2Cl_2 and 3.90 in $\text{C}_6\text{D}_5\text{Br}$). Although the significance of this difference is questionable, it is consistent with the higher polarizability

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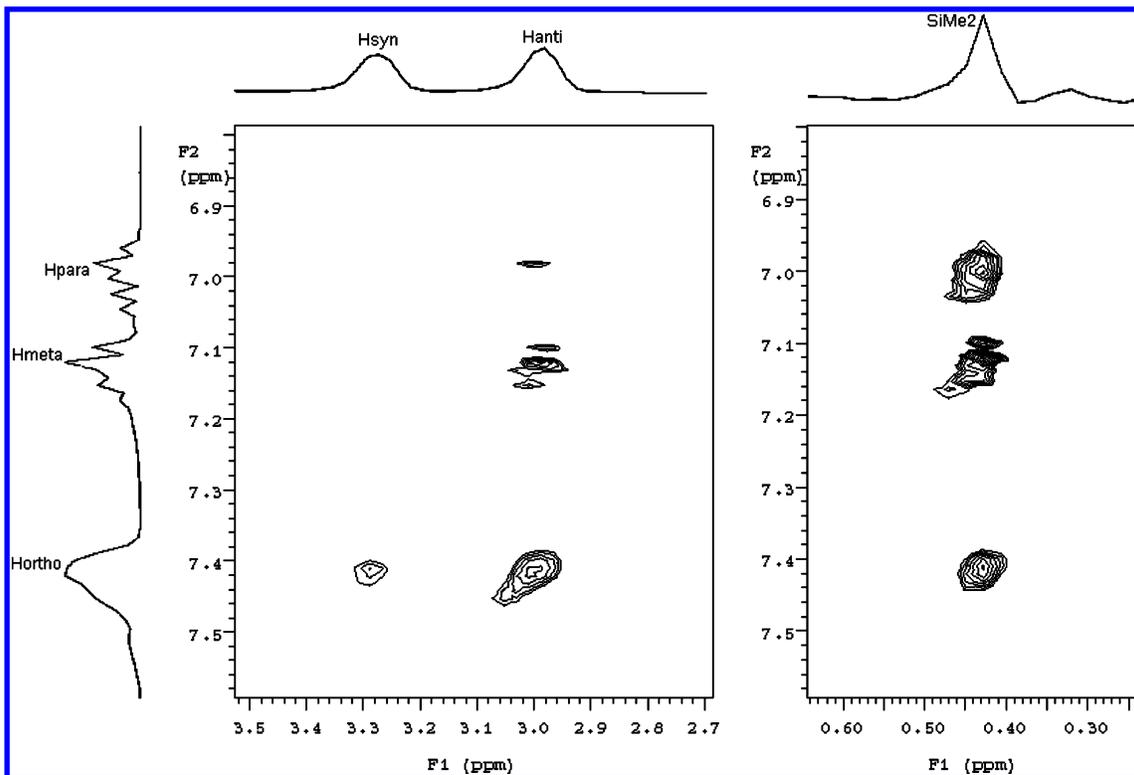
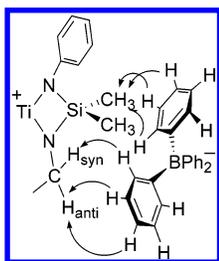


Figure 2. Section of the ^1H NOESY spectrum of $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{BPh}_4$ showing the interaction between the anion and the cation.

Scheme 2



of I^- versus Cl^- and may thus reflect a preference of I^- to be closer to the cation.

The ion pair structure identified in solution for **4** is also observed in the solid-state structure (Figure 4) that shows the proximity of the anion phenyl rings and the macrocycle.²² The orientation of one of the phenyls is such that one H_{anti} ($\text{H}(1)$) points to the aromatic π system, with short contact distances to the meta and para phenyl carbons ($\text{C}(75)$) and $\text{C}(74)$) and protons ($\text{H}(75)$ and $\text{H}(74)$). This arrangement approaches the ortho proton of the same phenyl ring ($\text{H}(76)$) to the methyl protons of the $\text{Si}(\text{CH}_3)_2$ group ($\text{H}(8)$). Short contact distances are also observed between the ortho and meta protons of other anion phenyl group ($\text{H}(52)$ and $\text{H}(53)$) and the $\text{Si}(\text{CH}_3)_2$ protons $\text{H}(8)$ (Table 2) and between BPh_4^- H_{ortho} ($\text{H}(42\text{A})$) and macrocyclic H_{anti} (2.812 \AA) and H_{syn} (3.896 \AA) generated by symmetry in the solid-state structure, which allow for the strongest spatial interactions observed in the NOESY spectrum.

In the solid-state structure of **2**, iodine is located in a "hole" defined by the atoms $\text{CH}_2\text{-N}(\text{SiMe}_2)\text{-CH}_2$ (Figure 5).

The shortest distance between I^- and the dimethylsilyl protons is 3.179 \AA ($\text{I-H}(18)$) and the distances to the

macrocyclic H_{anti} protons are 3.593 \AA ($\text{I-H}(5)$) and 3.256 \AA ($\text{I-H}(4)$). Taking into account the difference between carbon and iodine covalent radii, the two anions approach the cation similarly, and given that stereochemical constraints are less important in the case of I^- , its proximity to $\text{Si}(\text{CH}_3)_2$ is most probably the reflection of the electrophilicity of this fragment.

To test this assumption, we carried out reactions of **2** with nucleophiles. Although we have not been able to isolate any product from the reaction with LiCH_3 , the reaction of $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{I}$, **2**, with LiNMe_2 led to the formation of $[\text{Ti}\{\text{N}(\text{Ph})\{\text{NPh}(\text{SiMe}_2)_2\}_2\text{-tacn}]\text{I}$, **5**, which results from the nucleophilic attack of dimethylamido on one SiMe_2 pendant group (Scheme 3). The cleavage of the Si-NPh bond, leading to the formation of an imido ligand, is a consequence of the addition of NMe_2 . The intermediate aminal formed decomposes, giving rise to a neutral secondary amine function in the tacn ring. The origin of this reaction is uncertain. Although accidental hydrolysis may not be ruled out, the reproducibility and low yield (η ca. 30%) observed for the reaction may suggest an intrinsic instability of the aminal. Indeed, this result sustains our previous observations on the lack of success in the synthesis of $\{\text{NH}(\text{R})\text{SiMe}_2\}_3\text{-tacn}$ compounds with R groups other than Ph, suggesting that the stabilization of the N-Si-N fragment requires the presence of electron acceptor groups on the nitrogen.

The reaction sequence shown in Scheme 3 is straightforwardly reasoned on the basis of the ion pair interactions discussed for complexes $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{X}$.

The ^1H NMR data for **5** display two resonances for the methyl groups of the SiMe_2 fragments, six multiplets for the methylenic protons, two sets of aromatic resonances integrating 2:1 for the phenyl rings, and one signal at 3.94 ppm

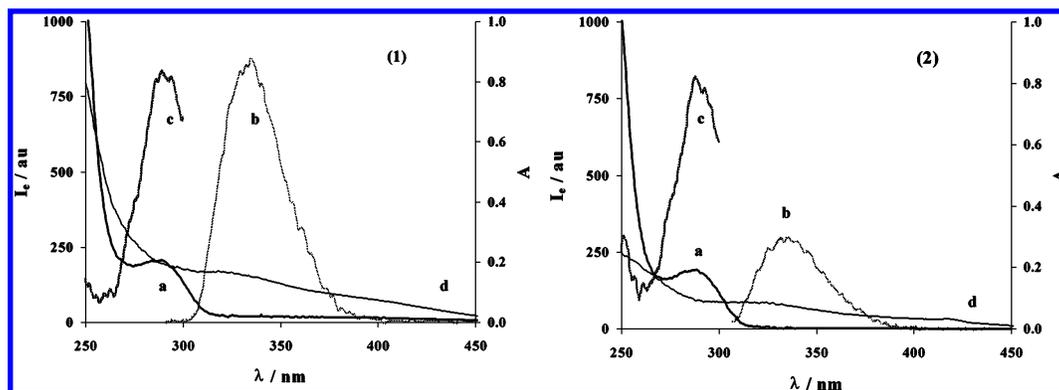


Figure 3. (1) $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{I}$, (2) $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{PF}_6$: (a) electronic absorption, (b) emission, $\lambda_{\text{exc}} = 280$ nm and (c) excitation $\lambda_{\text{em}} = 350$ nm spectra in acetonitrile, and (d) electronic absorption in dichloromethane. (a) and (d) right scale (A); (b) and (c) left scale (I_e).

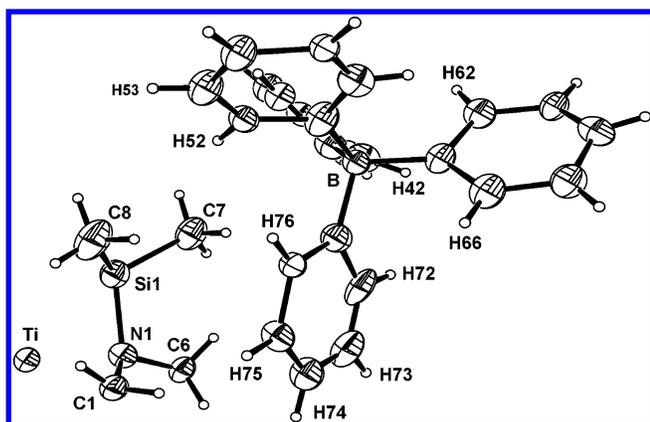


Figure 4. Section of the ORTEP representation of **4** showing the proximity of two anion phenyl rings and the macrocycle (N(1), C(1), and C(6)) and one pending arm (Si(1), C(7), and C(8)).²²

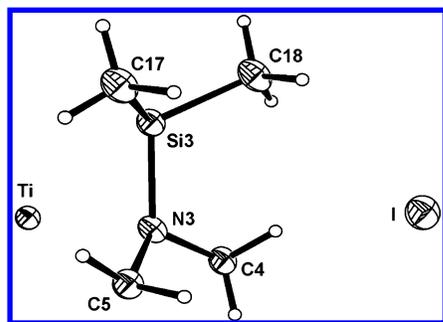


Figure 5. Section of the ORTEP representation of **2** showing the location of the anion between the macrocycle (N(3), C(4), and C(5)) and one pending arm (Si(3), C(17), and C(18)).²²

Table 2. Shortest Contact Distances (Å) for **4**

H(anion)⋯H(cation)		C(anion)⋯H(cation)	
H(76)⋯H(8)	3.111	C(76)⋯H(8)	3.198
H(75)⋯H(1) _{anti}	2.666	C(75)⋯H(1) _{anti}	2.841
H(74)⋯H(1) _{anti}	2.647	C(74)⋯H(1) _{anti}	2.839
H(52)⋯H(8)	2.899	C(52)⋯H(8)	2.763
H(53)⋯H(8)	3.057	C(53)⋯H(8)	2.885

corresponding to the NH proton of tacn. The ^{13}C NMR spectrum is consistent with the C_s symmetry observed in the proton NMR spectrum. The ipso carbon of the imido ligand appears at 161.0 ppm, in agreement with values for $\text{Ti}=\text{NPh}$ complexes.²⁷

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Two possible isomers may be drawn for **5**. One, presenting C_s symmetry, would display the imido ligand and the tacn NH fragment in the trans position, **5a** (shown in Scheme 3), the other, having a NSi tacn amine trans to the imido ligand, is a chiral molecule, **5b** (Scheme 4). In solution, however, **5b** may be involved in a fluxional process that creates an average C_s symmetry, as represented in Scheme 4. The distinction between the two structures would be possible if low-temperature NMR experiments stopped the fluxional process, which did not happen until -90 °C. The assignment of a definite structure to **5** is therefore not possible. (The authors believe that, by analogy to other unpublished compounds which structures have been characterized by X-ray diffraction, **5b** reflects the actual structure of the complex.)

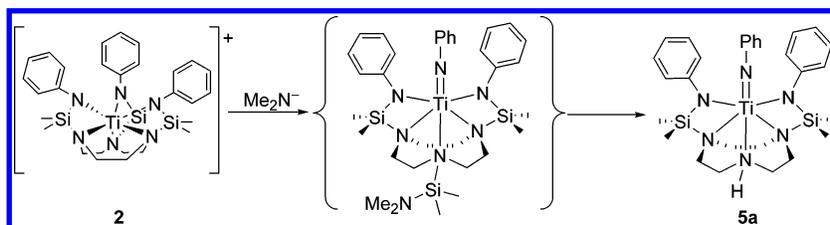
Conclusion

NMR and UV-vis experiments have shown that complexes $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{X}$ ($\text{X} = \text{Cl}$, **1**; I , **2**; PF_6 , **3**; BPh_4 , **4**) exist in bromobenzene and dichloromethane solutions as ion pairs. The proximity of the BPh_4^- anion to the H_{anti} methylenic protons of tacn and to the bridging $\text{Si}(\text{CH}_3)_2$ protons was deduced from the NOESY spectrum of **4** in $\text{CD}_2\text{-Cl}_2$. The interactions between the iodine and PF_6^- anions and the cation were supported by electron absorption and emission measurements in CH_2Cl_2 and CH_3CN . The results showed a stronger interaction in complex **3** solutions and also pointed out the influence of the solvent dielectric constant and polarizability. Ion pairing is responsible for the differences observed in the proton resonances of tacn and $\text{Si}(\text{CH}_3)_2$ in CD_3CN , CD_2Cl_2 and $\text{C}_6\text{D}_5\text{Br}$. These differences are particularly significant in $\text{C}_6\text{D}_5\text{Br}$, the less-polar solvent, where the macrocyclic H_{anti} and the $\text{Si}(\text{CH}_3)_2$ proton resonances are progressively shifted from **1** to **4** ($\text{BPh}_4^- \geq \text{PF}_6^- \geq \text{I}^- \approx \text{Cl}^-$). The interactions with the macrocyclic protons are consistent with the trend observed for other nitrogen-based ligands such as diimine and (polypyrazolyl)-borate and -methane, for which a preferential interaction with the protons α to the nitrogen donors are observed.^{28,29} The results

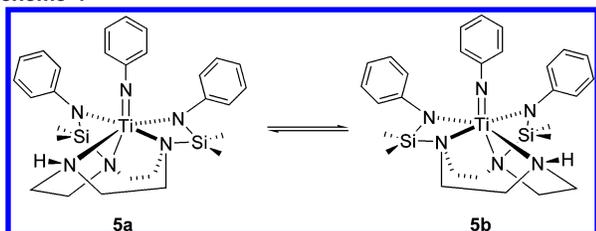
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Scheme 3



Scheme 4



described also provide an interpretation for the unusual ring opening of a tacn-derived amido ligand ($[\text{Pr}_2\text{-tacn}]^-$) reported by Arnold et al., where an intramolecular acid–base reaction between one benzyl ligand and one $[\text{Pr}_2\text{-tacn}]^-$ proton is responsible for the elimination of toluene and the formation of a new acyclic diamino-amino pincer ligand.³⁰ The interactions with dimethylsilyl protons, on the other hand, have not been previously reported, but we estimate that it may be common on the basis of the reactivity displayed by dimethylsilylamido metal derivatives that are prone to dimethylsilyl C–H bond cleavage.³¹ The formation of **5** is thus a direct consequence of the steric protection of titanium and the positive charge at silicon.

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 (*n*-hexane) under a nitrogen atmosphere and distilled. 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 (0 ppm). 10^{-2} M solutions of complexes **1–4** were used to run the NMR spectra. Electronic absorption spectra were recorded using a Jasco double-beam spectrophotometer (model Jasco V-560). Emis-

sion and excitation spectra were recorded using a Perkin-Elmer spectrofluorimeter (model LS-50B). Absorption and fluorescence 10-mm quartz cells were used. Temperature was kept within $T = 296 \pm 1$ K using circulating water streams on both apparatus' cell holders. Samples (5 mL) were prepared from stock solutions of each solvent from where aliquots were taken and diluted by addition of pure solvent. The final concentration was kept at 30 μM (to avoid aggregation and inner filter effects). Fresh samples were used in all the measurements. Elemental analyses were obtained from Laboratório de Análises do IST, Lisbon, Portugal. $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{X}$ (**1–4**) were prepared according to described procedures.²²

[Ti(NPh){NPh(SiMe₂)₂-tacn}, (5**).** A THF solution of $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{-tacn}]\text{I}$ (1.62 g, 2.16 mmol) cooled at -60 °C was treated with a suspension of LiNMe_2 (0.12 g, 2.27 mmol) in 10 mL of THF. The temperature was allowed to rise slowly to room temperature, and the mixture was stirred during 24 h. The volatiles were evaporated to dryness, and the residue was washed with a small portion of cold hexane. The product was extracted in diethyl ether, and a concentrate solution was cooled at -20 °C to afford 0.36 g of **5**. Yield, 30%. ^1H NMR (C_6D_6): δ 7.32 (t, 4H, $^3J_{\text{H}_\text{O}-\text{H}_\text{m}} = ^3J_{\text{H}_\text{p}-\text{H}_\text{m}} = 7.8$ Hz, H_m , Me_2SiNPh), 7.27 (t, 2H, $^3J_{\text{H}_\text{O}-\text{H}_\text{m}} = ^3J_{\text{H}_\text{p}-\text{H}_\text{m}} = 6.6$ Hz, H_m , TiNPh), 7.11 (t, 2H, $^3J_{\text{H}_\text{p}-\text{H}_\text{m}} = 7.8$ Hz, H_p , Me_2SiNPh), 6.87 (t, 1H, $^3J_{\text{H}_\text{p}-\text{H}_\text{m}} = 6.9$ Hz, H_p , TiNPh), 6.82 (d, 4H, $^3J_{\text{H}_\text{O}-\text{H}_\text{m}} = 7.8$ Hz, H_O , Me_2SiNPh), 6.17 ((d, 2H, $^3J_{\text{H}_\text{O}-\text{H}_\text{m}} = 7.8$ Hz, H_O , TiNPh), 3.94 (s, 1H, NH), 3.05–2.80 (m, 4H, H_{syn} , $\text{SiN}(\text{CH}_2)_2\text{NSi}$, H_{syn} , $\text{SiNCH}_2\text{CH}_2\text{NH}$), 2.55–2.45 (m, 2H, H_{syn} , $\text{SiNCH}_2\text{CH}_2\text{NH}$), 2.19–1.92 (m, 4H, H_{anti} , $\text{SiN}(\text{CH}_2)_2\text{NSi}$, H_{anti} , $\text{SiNCH}_2\text{CH}_2\text{NH}$), 1.75–1.62 (m, 2H, H_{anti} , $\text{SiNCH}_2\text{CH}_2\text{NH}$), 0.32 (s, 6H, SiCH_3), 0.20 (s, 6H, SiCH_3). ^{13}C - $\{^1\text{H}\}$ NMR (C_6D_6): δ 161.0 (C_{ipso} , TiNPh), 155.8 (C_{ipso} , Me_2SiNPh), 128.7 (C_m , $\text{Me}_2\text{-SiNPh}$), 128.6 (C_m , TiNPh), 123.3 (C_O , TiNPh), 122.7 (C_O , $\text{Me}_2\text{-SiNPh}$), 118.5 (C_p , Me_2SiNPh), 117.9 (C_p , TiNPh), 48.2 ($\text{SiNCH}_2\text{-CH}_2\text{NH}$), 48.0 ($\text{SiN}(\text{CH}_2)_2\text{NSi}$), 46.7 ($\text{SiNCH}_2\text{CH}_2\text{NH}$), 1.54 (SiCH_3), –1.62 (SiCH_3). Anal. Calcd for $\text{C}_{28}\text{H}_{40}\text{N}_6\text{Si}_2\text{Ti}$: C, 59.55; H, 7.14; N, 14.88. Found: C, 59.36; H, 7.04; N, 14.14.

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