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Amido/Amine Triazacyclononane-Based Zirconium Complexes: Syntheses, Reactivity, and Structures

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The reactions of $[Zr(NMe_2)_4]_2$ with triamido–triazacyclonane ligand precursors, $\{NH(Ph)SiMe_2\}_3$tacn ($H_3N_3[9]N_3$) and $\{NH(C_6H_4F)SiMe_2\}_3$tacn ($H_3N_{3-F}[9]N_3$), led to the formation of complexes $[Zr(NMe_2)_2\{N(Ph)SiMe_2\}_2\{NH(Ph)SiMe_2\}tacn]$, **1**, and $[Zr(NMe_2)_2\{N(o\text{-}C_6H_4F)SiMe_2\}_2\{NH(o\text{-}C_6H_4F)SiMe_2\}\ tacn]$, **2**, where the zirconium is coordinated to two remaining dimethylamido ligands and to a dianionic tacn-based ligand, $[\{N(Ph')SiMe_2\}_2\{NH(Ph')SiMe_2\}tacn]^{2-}$, that formed from deprotonation of two amine pendent arms of the ligands' precursors. The third pendent arm of $H_3N_3[9]N_3$ and $H_3N_{3-F}[9]N_3$ remains neutral and not bonded to the zirconium. Treatment of **1** with NaH led to the synthesis of $[Zr(NMe_2)\{N(Ph)SiMe_2\}_2tacn]$, **3**, that results from the cleavage of the N–Si bond of the original neutral pendent arm. Complexes $[ZrCl\{N(Ph')SiMe_2\}_2tacn]$ ($Ph' = C_6H_5$, **4**, and C_6H_4F, **5**) have been obtained by reactions of $ZrCl_4$ with $\{MN(Ph')SiMe_2\}_3tacn{\cdot}2THF$ (M = Li, Na). Reactions of **4** and **5** with $LiC{\equiv}CPh$ led to the syntheses of $[Zr(CCPh)\{N(Ph')SiMe_2\}_2tacn]$ ($Ph' = C_6H_5$, **6**, and C_6H_4F, **7**). The solid-state structure of **3** shows a chiral metal center.

Introduction

Amido ligands (R_2N^-) proved to be very useful tools for the design of new polydentate ligand frameworks[1−3] where peculiar balances of electronic and steric properties, resulting from variations of the nitrogen substituents and combinations with other functionalities, led to new and varied metal reactivity patterns.[4−9] In this context, the incorporation of amido ligands in macrocyclic topologies, either as pendent arms of macrocyclic backbones[10−17] or in the macrocyclic skeleton,[18−20] was explored. Ligands obtained by combining tacn and imido donors or anionic amido tacn-derived moieties, in particular, have been thought as alternatives to cyclopentadienyl ligands.[19,21] The results reported so far have shown that, despite the classical role of neutral macrocycles as support ligands of transition metals chemistry, anionic macrocyclic−amido transition metal derivatives are versatile compounds that require extensive studies before a pattern of their reactivity might be established. Our previous work

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(1) Kempe, R. *Eur. J. Inorg. Chem.* **2003**, 791.
(2) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487.
(3) Kempe, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 468.
(4) Axenov, K. V.; Kilpelainen, I.; Klinga, M.; Leskela, M.; Repo, T. *Organometallics* **2006**, *25*, 463.
(5) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822.
(6) Mendiratta, A.; Cummins, C. C. *Inorg. Chem.* **2005**, *44*, 7319.
(7) Stephens, F. H.; Johnson, M. J. A.; Cummins, C. C.; Kryatov, O. P.; Kryatov, S. V.; Rybak-Akimova, E. V.; McDonough, J. E.; Hoff, C. D. *J. Am. Chem. Soc.* **2005**, *127*, 15191.
(8) Morello, L.; Yu, P. H.; Carmichael, C. D.; Patrick, B. O.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 12796.
(9) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke, F. G. N. *J. Am. Chem. Soc.* **1999**, *121*, 10444.
(10) Bambirra, S.; Van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **2001**, 637.
(11) Robson, D. A.; Rees, L. H.; Mountford, P.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **2000**, 1269.
(12) Schlager, O.; Wieghardt, K.; Grondey, H.; Rufinska, A.; Nuber, B. *Inorg. Chem.* **1995**, *34*, 6440.
(13) Dias, A. R.; Martins, A. M.; Ascenso, J. R.; Ferreira, H.; Duarte, M. T.; Henriques, R. T. *Inorg. Chem.* **2003**, *42*, 2675.
(14) Martins, A. M.; Ascenso, J. R.; Azevedo, C. G.; Dias, A. R.; Duarte, M. T.; Ferreira, H.; Ferreira, M. J.; Henriques, R. T.; Lemos, M. A.; Li, L.; Ferreira da Silva, J. L. *Eur. J. Inorg. Chem.* **2005**, 1689.
(15) Monteiro, B.; Roitershtein, D.; Ferreira, H.; Ascenso, J. R.; Martins, A. M.; Domingos, A.; Marques, N. *Inorg. Chem.* **2003**, *42*, 4223.
(16) Martins, A. M.; Ascenso, J. R.; Costa, S. M. B.; Dias, A. R.; Ferreira, H.; Ferreira, J. A. B. *Inorg. Chem.* **2005**, *44*, 9017.
(17) Bambirra, S.; Tsurugi, H.; Van Leusen, D.; Hessen, B. *Dalton Trans.* **2006**, 1157.
(18) Porter, R. M.; Danopoulos, A. A.; Reid, G.; Titcomb, L. R. *Dalton Trans.* **2005**, 427.
(19) Schmidt, J. A. R.; Giesbrecht, G. R.; Cui, C. M.; Arnold, J. *Chem. Commun.* **2003**, 1025.
(20) Fletcher, J. S.; Male, N. A. H.; Wilson, P. J.; Rees, L. H.; Mountford, P.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4130.
(21) Male, N. A. H.; Skinner, M. E. G.; Bylikin, S. Y.; Wilson, P. J.; Mountford, P.; Schroder, M. *Inorg. Chem.* **2000**, *39*, 5483.

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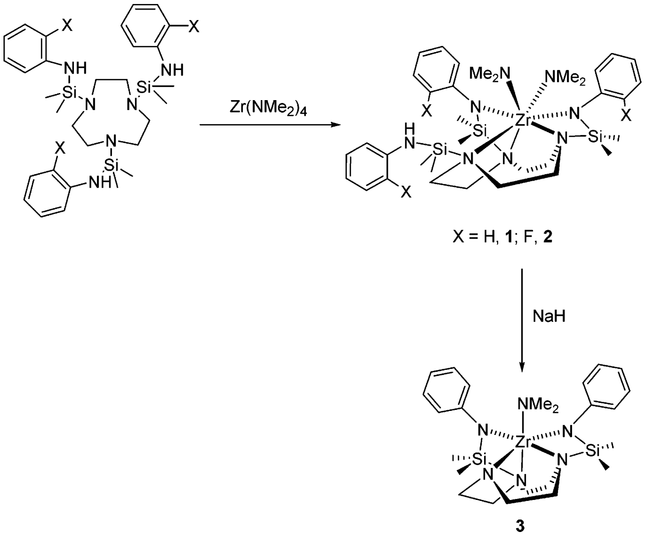
Scheme 1



Scheme 2

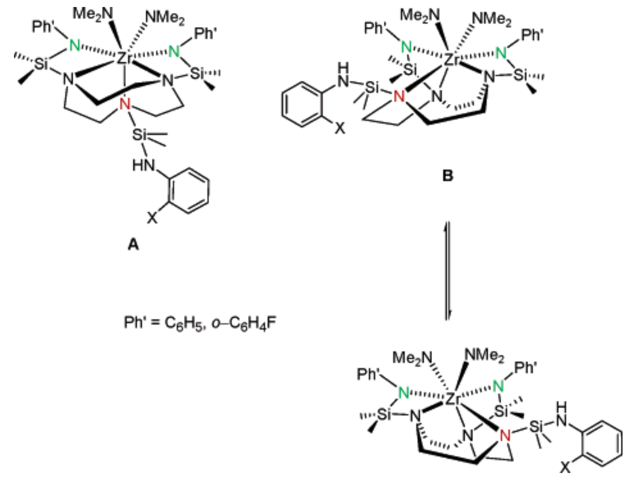
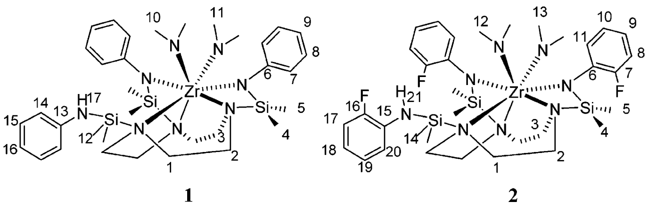


Chart 1



on titanium triamido−triazacyclononane compounds has shown that although the hexadentate ligand prevents the approach to the metal center, radical transfer from Ti(III) led to a singular reactivity.[16,22] The results here described extend the work to zirconium complexes, which reveal a very different behavior from that of titanium.

Results and Discussion

The reactions of $[Zr(NMe_2)_4]_2$ with triamido−triazacyclonane ligand precursors, $\{NH(Ph)SiMe_2\}_3$tacn ($H_3N_3[9]N_3$)[13] and $\{NH(C_6H_4F)SiMe_2\}_3$tacn ($H_3N_{3-F}[9]N_3$),[14] are represented in Scheme 1.

As shown, acid−base reactions between $[Zr(NMe_2)_4]_2$ and $H_3N_3[9]N_3$ or $H_3N_{3-F}[9]N_3$ led to the formation of complexes **1** and **2** where the zirconium is coordinated to two remaining dimethylamido ligands and to a dianionic tacn-based ligand, $[\{N(Ph')SiMe_2\}_2\{NH(Ph')SiMe_2\}tacn]^{2-}$ that formed from deprotonation of two amine pendent arms of the ligands' precursors. The third pendent arm of $H_3N_3[9]N_3$ or $H_3N_{3-F}[9]N_3$ remains neutral and not bonded to zirconium. The ^1H NMR spectra of **1** and **2** display an average C_s symmetry with two dimethylamido resonances, two different sets of phenyl resonances integrating 2:1, three different silicon methyl groups, six multiplets due to the methylenic macrocyclic protons, and one singlet due to the NH proton. The carbon spectra of **1** and **2** are also consistent with the presence of an average symmetry plane that contains the NMe_2 nitrogen atoms, the noncoordinated pendent arm and bisects the opposite C−C bond of the tacn ring. The proton and carbon NMR patterns observed for the $[\{N(Ph')SiMe_2\}_2\{NH(Ph')SiMe_2\}tacn]^{2-}$ moieties in **1** and **2** (Ph′ = C_6H_5, C_6H_4F) may be assigned to two different structures, as depicted in Scheme 2. In **A** the macrocyclic amine bearing the noncoordinated pendent arm (represented in red) bisects the $Me_2N-Zr-NMe_2$ angle and the two Zr−N−Si−N metallocycles are symmetrically arranged in relation to a plane containing the two dimethylamido ligands, the metal and the tacn nitrogen atom opposite to the NMe_2 ligands (represented in red). **B** represents a chiral molecule which NMR spectra may display an average C_s symmetry plane if a fluxional process, corresponding to a pendulum movement of the tacn nitrogen atom attached to the noncoordinated pendent arm, interconverts the two Zr−N−Si−N metallacycles. The definite assignment of a type **A** or **B** structure to complexes **1** and **2** was not possible on the basis of VT NMR experiments. Nevertheless, on the basis of the molecular structure of **3** (Scheme 1) obtained by single-crystal X-ray diffraction (see below), it is likely that **1** and **2** have type **B** structures for which low activation energy racemization equilibrium is responsible by the average C_s symmetry observed. An analogous situation was identified to take place with titanium triamido−tacn complexes.[16,22]

The unequivocal confirmation that the NH proton resonance (δ 3.12 ppm) is due to a protonated pendent arm rather than being part of a NMe_2H ligand was obtained through a $^1H-^{15}N$ HMBC of **1** (Supporting Information, Figure S1) that showed the coupling between the proton at 3.12 ppm and a nitrogen atom ($^1J_{NH} = 75$ Hz) that is simultaneously coupled to the dimethylsilyl (δ 0.11 ppm, H12 in Chart 1) and the *ortho*-phenyl protons (δ 6.56 ppm, H14 in Chart 1) of the noncoordinated pendent arm. Consistent with this result is the observation of two resonances in the ^{19}F NMR spectrum of **2**, one broad singlet at −44.4 ppm that correspond to the metal-coordinated $N(C_6H_4F)SiMe_2$ fragments and one multiplet at −57.1 ppm due to the noncoordinated pendent arm. The fluorine chemical shift and the signal multiplicity of the free pendent arm (δ −57.1 ppm) are reminiscent of what is observed for the ligand precursor $H_3N_{3-F}[9]N_3$ (δ −57.5 ppm), where the couplings with the

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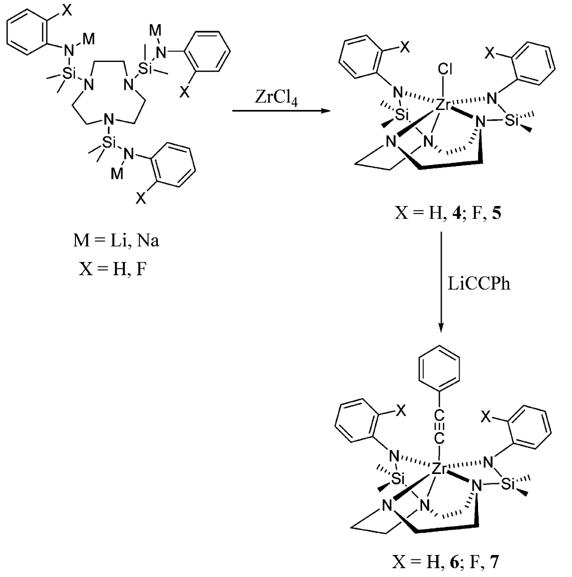
[22] Barroso, S.; Cui, J. L.; Dias, A. R.; Duarte, M. T.; Ferreira, H.; Henriques, R. T.; Oliveira, M. C.; Ascenso, J. R.; Martins, A. M. *Inorg. Chem.* **2006**, *45*, 3532.

Scheme 3



NH and the aromatic protons are responsible for the splitting of the ^{19}F resonance into a multiplet.[14]

Treatment of **1** with NaH led to the synthesis of $[Zr(NMe_2)\{N(Ph)SiMe_2\}_2tacn]$, **3** (Scheme 1), that results from the cleavage of the N−Si bond of the original neutral pendent arm. This reaction transforms the tacn amine into one anionic nitrogen moiety and requires the elimination of one dimethylamido ligand. This pathway is sustained by the reactions of $ZrCl_4$ with $M_3N_3[9]N_3(THF)_2$ and $M_3N_{3-F}[9]N_3(THF)_2$ (M = Li, Na), which give rise to $[ZrCl\{N(Ph')SiMe_2\}_2tacn]$ (Ph′ = C_6H_5, **4**, and C_6H_4F, **5**) (see Scheme 3). A related N−Si bond cleavage was observed in cationic titanium complexes $[Ti\{N_3[9]N_3\}]^+$ ($N_3[9]N_3$ = $N(Ph)SiMe_2\}_3tacn$) in consequence of nucleophilic attack at the silicon of one pendent arm.[22]

The molecular structure of **3** is shown in Figure 1, and relevant bond lengths and angles are presented in Table 1.

The zirconium is coordinated by the five nitrogen atoms of the ligand framework and by an NMe_2 in an asymmetric environment. Coordination geometry is best described as a distorted pseudooctahedron, with atoms N(4) and N(1) occupying apical positions (N(4)−Zr−N(1) angle of 163.62(19)°). Atoms N(2), N(3), N(11), and N(21) define an equatorial plane that is highly distorted toward a tetrahedral arrangement.The N−Zr−N angles within the macrocycle are similar to the ones found in similar Ti complex,[13,16,22] with a mean value of 73°. Considering the planes defined by atoms N(1)−N(2)−N(3) and N(4)−N(21)−N(11) and the centroids of those triangles, cent(1) and cent(2), respectively, the angle cent(1)−Zr−cent(2) is 156.1(7)°, the dihedral angle between the two planes is 8.2(2)°, and the torsion angles, θ, that characterize the distortion of the octahedral structure between N(i)−cent(1)−Zr−cent(2)−N(j) (where N(i) = N(1)−N(3) and N(j) = N(4), N(21), and N(31)) are respectively 27.6(8), 30.1(8), and 30.8(8)°. The angles N(3)−Zr(1)−N(4) and N(1)−Zr(1)−N(4) that are not constrained by the ligand frame have values close to those expected for the octahedral coordination geometry being respectively 93.5(2) and 163.62(19)°.

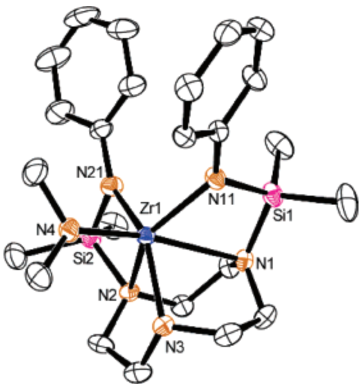


Figure 1. View of complex **3** along the equatorial plane, showing the octahedral coordination of zirconium and the labeling scheme adopted. Thermal ellipsoids are drawn at 30% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **3**

Zr(1)−N(4)	2.061(5)	N(1)−C(1)	1.479(7)
Zr(1)−N(3)	2.088(5)	N(1)−C(6)	1.490(8)
Zr(1)−N(11)	2.134(5)	N(4)−C(17)	1.453(8)
Zr(1)−N(21)	2.197(5)	N(4)−C(18)	1.455(8)
Zr(1)−N(2)	2.418(5)	N(21)−C(21)	1.396(7)
Zr(1)−N(1)	2.528(5)	N(2)−C(2)	1.483(7)
N(11)−C(11)	1.412(7)	N(2)−C(3)	1.492(8)
N(3)−C(4)	1.461(8)	C(1)−C(2)	1.511(8)
N(3)−C(5)	1.465(8)		

(4)−Zr(1)−N(3)	93.5(2)	N(11)−Zr(1)−N(2)	137.43(17)
N(4)−Zr(1)−N(11)	109.16(19)	N(21)−Zr(1)−N(2)	67.19(18)
N(3)−Zr(1)−N(11)	109.8(2)	N(4)−Zr(1)−N(1)	163.62(19)
N(4)−Zr(1)−N(21)	97.1(2)	N(3)−Zr(1)−N(1)	73.43(18)
N(3)−Zr(1)−N(21)	140.2(2)	N(11)−Zr(1)−N(1)	67.69(17)
N(11)−Zr(1)−N(21)	102.6(2)	N(21)−Zr(1)−N(1)	99.23(18)
N(4)−Zr(1)−N(2)	113.05(18)	N(2)−Zr(1)−N(1)	73.28(16)
N(3)−Zr(1)−N(2)	73.34(18)		

The angles $N_{macrocycle}$−Zr−N_{amido}, imposed by the ligand backbone, have values of 67.7(2)° (N(1)−Zr(1)−N(11)) and 67.2(2)° (N(2)−Zr(1)−N(21)), and the angle between the two planes defined by these atoms is 10°. The sum of angles around the amido nitrogens is close to 360° for N(4), N(21), and N(11), but due to constrains imposed by the macrocycle framework, the sum of angles around N(3) is only 345.6. This constraint, however, does not imply a weaker metal−nitrogen bond as confirmed by the Zr−N(3) and Zr−N(4) distances that are very similar (2.088(5) and 2.061(5) Å, respectively)[23−25] and slightly shorter than the Zr−N(21) and Zr−N(11) bond lenghts (2.197(5) Å and 2.134(5) Å). These values reflect the influence of the nitrogen substituents on the metal−amido bonding and evidence the role of the $SiMe_2$ and phenyl groups as electron density acceptors.[26−28] The two Zr−N_{amine} bond lengths also differ, with Zr−N(1) (2.528(5) Å) being considerably longer than Zr−N(2) (2.418(5) Å) in consequence of the trans effect caused by N(4).

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(23) Morton, C.; Munslow, I. J.; Sanders, C. J.; Alcock, N. W.; Scott, P. *Organometallics* **1999**, *18*, 4608.

(24) Gade, L. H.; Renner, P.; Memmler, H.; Fecher, F.; Galka, C. H.; Laubender, M.; Radojevic, S.; McPartlin, M.; Lauher, J. *Chem.*—Eur. J. **2001**, *7*, 2563.

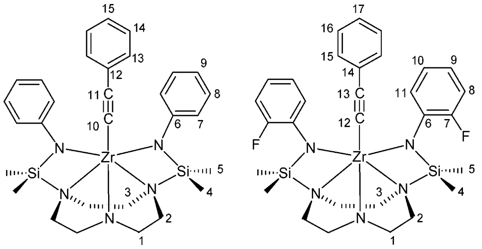
(25) Skinner, M. E. G.; Li, Y. H.; Mountford, P. *Inorg. Chem.* **2002**, *41*, 1110.

(26) Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742.

(27) Turculet, L.; Tilley, T. D. *Organometallics* **2002**, *21*, 3961.

(28) Doufou, P.; Abboud, K. A.; Boncella, J. M. *J. Organomet. Chem.* **2000**, *603*, 213.

Chart 2



6 **7**

The proton and carbon NMR data for **3** show C_s average symmetry which is consistent with a rapid exchange that corresponds to the compound's racemization by a process similar to that proposed in Scheme 2 for **1** and **2**. Thus, the two phenyl rings exhibit one set of three aromatic resonances, the methylenic macrocyclic proton resonances appear as six multiplets that correlate to three carbon resonances, and the dimethylsilyl protons give rise to one apparent singlet that shows a correlation with two different carbon resonances.

The most remarkable difference between the macrocyclic resonances of **3** and those of **1** is the shift to low field of H_{1syn} (δ 3.86−3.78 ppm vs δ 3.29 ppm in **1**) that is adjacent to the macrocyclic anionic nitrogen. This shift is symptomatic of the formation of an anionic nitrogen functionality in the macrocycle by cleavage of one N−Si bond. In reality, the methylenic macrocyclic proton resonances of **3** result from two different spin systems. Four multiplets corresponding to H_{1syn}, H_{2syn}, H_{1anti}, and H_{2anti} constitute an ABCD system whereas the protons H_{3syn} and H_{3anti} give rise to an AA′XX′ system. The simulation of the signals allowed the estimation of the coupling constants for the two spin systems (Supporting Information, Figure S2 and Table S1).

As mentioned above, complexes $[ZrCl\{N(Ph')SiMe_2\}_2$-tacn] ($Ph' = C_6H_5$, **4**, and C_6H_4F, **5**) have been obtained by reactions of $ZrCl_4$ with $\{MN(Ph)SiMe_2\}_3tacn\cdot 2THF$ ($M_3N_3[9]N_3(THF)_2$)) and $\{MN(C_6H_4F)SiMe_2\}_3tacn\cdot 2THF$-($M_3N_{3-F}[9]N_3(THF)_2$) (M = Li, Na) (Scheme 3). These complexes have not been fully characterized since it was not possible to obtain them free of solvents and LiCl or NaCl that result from the chloride metathesis reactions. The formulation of **4** and **5** as neutral rather than anionic ate complexes was inferred from ^1H and ^{13}C NMR data, which are closely related to those of **3**. The macrocyclic resonance patterns confirm the cleavage of one tacn pendent arm, and the similarity between these spectra and those of **3** suggests that the zirconium coordination sphere in all compounds should be comparable. Particularly noteworthy are the low-field shift of H_{1syn} and the high-field shifts of C_2 and C_3 macrocyclic resonances. Further evidence on the formulation of **4** and **5** was obtained through their reactions with LiC≡CPh that led to the syntheses of $[Zr(CCPh)\{N(Ph')$-$SiMe_2\}_2tacn]$ ($Ph' = C_6H_5$, **6**, and C_6H_4F, **7**) (Scheme 3).

The NMR spectra of **6** and **7** (Chart 2) are consistent with C_s symmetry and the occurrence of racemization through an exchange process analogous to that discussed for **1**−**3** (Scheme 2). The methylenic proton resonances display a pattern similar to the one observed for **3**, namely an ABCD system for H_1 and H_2 and an AA′XX′ system for H_3. The shift to low field of the H_{1syn} resonances in **6** (δ 3.90−3.82 ppm) and **7** (δ 4.01−3.93 ppm) is more pronounced than that observed in **3** (δ 3.86−3.78 ppm). This effect reflects that in the alkynyl derivatives **6** and **7** the macrocyclic amido moiety acts as a better electron donor than in **3** where the dimethylamido ligand reduces the electropositive character of the metal center. The result is thus in agreement with the higher basicity of the dimethylamido ligand when compared to the alkynyl moiety. The fact that the metal coordination to anionic amido diamine tacn-based ligands is mainly reflected in the chemical shift of the macrocyclic H_{syn} protons differs from what we have observed for Ti(IV) complexes of general formula $[Ti\{N(Ph)SiMe_2\}_3tacn]^+$, for which metal coordination induces a high-field shift that mainly affects the H_{anti} resonances.[16] In the ^{13}C NMR spectra of **6** and **7**, the C_1 carbon resonances suffer a high-yield shift whereas an opposite shift occurs in the C_2 carbon resonance. These modifications in the macrocyclic resonances allow a definite distinction between anionic and neutral tacn-derived macrocycles. The coupling between the *ortho*-fluorine phenyl substituents and the C_α of Zr*C*CPh in **7** gives rise to a triplet in the carbon NMR spectrum (δ 140.6 ppm)[29−31] with a coupling constant of 9 Hz, and the ^{19}F NMR resonance of **7** is observed as a broad singlet at δ −43.2 ppm. These data are indicative of Zr···F interactions in solution that have previously been reported to occur in polyamidozirconium complexes.[32]

The trends observed in the NMR spectra are consistent with the acidity increase of the H_α protons of amido moieties, frequently observed upon coordination to electrophilic metal centers, which often lead to C−H bond activation.[33−35] This effect may also originate competitive secondary reactions when compounds suitable to act either as bases or nucleophiles are used, as is the case of halide metathesis reactions carried out with alkylating reagents. Attempts to prepare other compounds of general formula $[Zr(R)\{N(Ph')SiMe_2\}_2$-tacn] (R = Me, NMe_2, CH_2Ph) have been unsuccessful, and the yields attained in the syntheses of **6** and **7** are low (ca. 20%).

Conclusions

The reactions of ligand precursors $H_3N_3[9]N_3$ and $H_3N_{3-F}[9]N_3$ with $Zr(NMe_2)_4$ led to the formation of complexes **1** and **2** that maintain two original dimethylamido ligands. The metals' coordination sphere is completed through the bonding of three tacn amines and two amide pendent arms. The noncoordinated pendent arm remains

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(29) Findeis, B.; Schubert, M.; Gade, L. H.; Möller, F.; Scowen, I. J.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1996**, 125.

(30) Kempe, R.; Brenner, S.; Arndt, P. *Organometallics* **1996**, *15*, 1071.

(31) Black, D. G.; Swenson, D. C.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3539.

(32) Memmler, H.; Walsh, K.; Gade, L. H.; Lauher, J. W. *Inorg. Chem.* **1995**, *34*, 4062.

(33) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.* **2003**, 1554.

(34) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.

(35) Giesbrecht, G. R.; Shafir, A.; Arnold, J. *J. Chem. Soc., Chem. Commun.* **2000**, 2135.

neutral. Cleavage of one $N_{tacn}-Si$ bond and transformation of one neutral tacn nitrogen into an anionic nitrogen moiety contained in the macrocycle occurs upon deprotonation of the amine pendent arms of **1** and **2**. The reaction converts the neutral tris(amine) macrocycle into an anionic amido−bis(amine) moiety. Thus, complexes of the general formula $[Zr(X)\{N(Ph')SiMe_2\}_2tacn]$, where X = NMe_2, **3**, Cl, **4** and **5**, and CCPh, **6** and **7**, display an amido fragment in the tacn framework formed by cleavage of a N−Si bond. In these complexes, the α-nitrogen H_{syn} resonances are sensitive to the X ligands that are coordinated to the zirconium. In the case of the alkynyl derivatives **6** and **7** the shift of H_{syn} resonances to high field is more pronounced than those for the other complexes that have π-donor ligands (NMe_2 and Cl) coordinated to the zirconium. In complex **7** the fluorine atoms of the phenyl rings interact with the metal and give rise to a triplet for the Zr−*C*CPh resonance ($^2J_{F-C}$ = 9 Hz) in the carbon NMR spectrum.

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 an atmosphere of nitrogen 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 (δ 0). The complete assignment of proton and carbon resonances of all complexes was based on HETCOR, NOESY, and COSY experiments. Elemental analyses were obtained from Laboratório de Análises, IST, Lisbon, Portugal. $\{NH(Ph)SiMe_2\}_3tacn$, $\{NH(C_6H_4F)SiMe_2\}_3tacn$, $\{NaN(Ph)SiMe_2\}_3tacn\cdot 2THF$, $\{NaN(C_6H_4F)SiMe_2\}_3tacn\cdot 2THF$,[13,14] and $[Zr(NMe_2)_4]_2$[36] were prepared according to described procedures. $ZrCl_4$ and LiCCPh were purchased from Aldrich and used as received.

$[Zr(NMe_2)_2\{N(Ph)SiMe_2\}_2\{NH(Ph)SiMe_2\}tacn]$ (1). A solution of $\{NH(Ph)SiMe_2\}_3tacn$ (1.62 g; 2.81 mmol) in 10 mL of toluene was added to a suspension of $[Zr(NMe_2)_4]_2$ (0.83 g; 3.12 mmol) in 30 mL of the same solvent, and the mixture was heated at 60 °C during 24 h. The volatiles were evaporated to dryness, and the residue was extracted at −30 °C with hexane. The solution was filtered and the solvent evaporated to dryness leading to a vitreous material that was cooled to liquid-nitrogen temperature and scraped. The pale yellow solid obtained was allowed to warm to room temperature under vacuum. Yield: 1.99 g, 94%. ^1H NMR (C_6D_6): δ 7.09 (m, 6H, H_8, H_{15}), 6.85 (d, $^3J_{HH}$ = 7.2, 4H, H_7), 6.75 (m, 3H, H_9, H_{16}), 6.56 (d, $^3J_{HH}$ = 7.2 Hz, 2H, H_{14}), 3.38−3.20 (m, 6H, H_{1syn}, H_{2syn}, H_{3syn}), 3.12 (s br, 1H, H_{17}), 3.05−2.98 (m, 2H, H_{3anti}), 2.79−2.71 (m, 2H, H_{1anti}), 2.73 (s, 6H, H_{10}), 2.48−2.40 (m, 2H, H_{2anti}), 2.42 (s, 6H, H_{11}), 0.16 (s, 6H, H_5), 0.11 (s, 6H, H_{12}), 0.09 (s, 6H, H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 153.9 (C_6), 147.1 (C_{13}), 129.6 (C_{15}), 128.3 (C_8), 126.0 (C_7), 120.6 (C_9), 118.6 (C_{14}), 54.5 (C_1), 54.1 (C_2), 51.5 (C_3), 42.9 (C_{11}), 41.6 (C_{10}), 0.6 (C_5), −0.5 (C_4), −1.1 (C_{12}). MS (EI), *m/z*: 737 ($[M - CH_4]^+$). Anal. Calcd for $C_{34}H_{58}N_8Si_3Zr$: C, 54.11; H, 7.75; N, 14.86. Found: C, 53.85; H, 8.01; N, 14.67.

$[Zr(NMe_2)_2\{N(o\text{-}C_6H_4F)SiMe_2\}_2\{NH(o\text{-}C_6H_4F)SiMe_2\}tacn]$ (2). A solution of $\{NH(o\text{-}C_6H_4F)SiMe_2\}_3tacn$ (1.32 g; 2.09 mmol) in 15 mL of toluene was added to a suspension of $[Zr(NMe_2)_4]_2$ (0.59 g; 2.12 mmol) in 40 mL of the same solvent, and the mixture was heated at 60 °C during 24 h. The solvent was evaporated to dryness, and the residue was extracted at −30 °C with hexane. The solution was filtered and the solvent evaporated to dryness leading to a vitreous material that was cooled to liquid-nitrogen temperature and scrapped. The pale yellow solid obtained was allowed to warm to room temperature under vacuum. A contamination of **2** with free ligand in ca. 20% was determined by NMR. ^1H NMR (C_6D_6): δ 7.03−6.95 (m, 2H, H_{11}), 6.96−6.89 (m, 1H, H_{17}), 6.91−6.84 (m, 3H, H_8, H_{19}), 6.89−6.81 (m, 3H, H_{10}, H_{20}), 6.60−6.48 (m, 3H, H_9, H_{18}), 3.77 (m, 1H, H_{21}), 3.48−3.39 (m, 2H, H_{1syn}), 3.37−3.31 (m, 2H, H_{3syn}), 3.31−3.22 (m, 2H, H_{2syn}), 3.10−3.02 (m, 2H, H_{3anti}), 2.83 (s, 6H, H_{12}), 2.80−2.68 (m, 2H, H_{2anti}), 2.56−2.47 (m, 2H, H_{1anti}), 2.55 (s, 6H, H_{13}), 0.29 (s, 6H, H_5), 0.20 (s, 6H, H_4), 0.12 (s, 6H, H_{14}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 157.6 (d, $^1J_{CF}$ = 236, C_7), 153.2 (d, $^1J_{CF}$ = 237, C_{16}), 142.1 (d, $^2J_{CF}$ = 13.5, C_6), 135.6 (d, $^2J_{CF}$ = 13.6, C_{15}), 128.2 (C_{11}), 124.7 (C_{19}), 123.6 (C_{10}), 120.8 (d, $^3J_{CF}$ = 6.7, C_9), 118.5 (d, $^3J_{CF}$ = 6.8, C_{18}), 117.3 (C_{20}), 115.4 (d, $^2J_{CF}$ = 19.3, C_{17}), 114.8 (d, $^2J_{CF}$ = 22.2 Hz, C_8), 54.1 (C_1, C_2), 51.3 (C_3), 43.1 (C_{13}), 41.8 (C_{12}), 0.6 (C_5), −0.6 (C_4), −1.4 (C_{14}). ^{19}F NMR (C_6D_6): δ −44.4 (br, 2F, F_{16}), −57.1 (m, 1F, F_7).

$[Zr(NMe_2)\{N(Ph)SiMe_2\}_2tacn]$ (3). A solution of **1** (4.33 g; 5.75 mmol) in THF (120 mL) was treated with an excess of NaH (0.24 g; 10 mmol) during 20 h under reflux. The solvent was evaporated to dryness, and the residue was extracted with hexane and filtered. The hexane was removed in vacuum, and the complex was dissolved in diethyl ether. The solution was cooled until −20 °C leading to the formation of white crystals that were separated by filtration and dried in vacuum. Yield: 2.08 g, 64%. ^1H NMR (C_6D_6): δ 7.21 (t, $^3J_{H_8H_7} = {}^3J_{H_8H_9}$ = 7.8, 4H, H_8), 6.99 (d, $^3J_{H_7H_8}$ = 7.8, 4H, H_7), 6.80 (t, $^3J_{H_9H_8}$ = 7.8 Hz, 2H, H_9), 3.86−3.78 (m, 2H, H_{1syn}), 3.16 (s, 6H, H_{10}), 3.09−3.00 (m, 2H, H_{2syn}), 2.85−2.80 (m, 2H, H_{3syn}, $H_{3'syn}$), 2.80−2.73 (m, 2H, H_{1anti}), 2.45−2.37 (m, 2H, H_{2anti}), 2.31−2.24 (m, 2H, H_{3anti}, $H_{3'anti}$), 0.29 (s, 6H, H_4), 0.27 (s, 6H, H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.3 (C_6), 129.3 (C_8), 122.1 (C_7), 119.2 (C_9), 54.2 (C_1), 50.5 (C_2), 48.7 (C_3), 46.3 (C_{10}), 0.2 (C_5), −0.5 (C_4). MS (EI), *m/z*: 559 ($[M]^+$). Anal. Calcd for $C_{24}H_{40}N_6Si_2Zr$: C, 51.45; H, 7.20; N, 15.01. Found: C, 51.14; H, 7.47; N, 14.94.

$[ZrCl\{N(Ph)SiMe_2\}_2tacn]$ (4). A solution of $\{NaN(Ph)SiMe_2\}_3tacn\cdot 2THF$ (1.00 g; 1.28 mmol) in diethyl ether (15 mL) was added at −60 °C to a suspension of $ZrCl_4$ (0.31 g; 1.32 mmol) in 30 mL of the same solvent. The mixture was stirred for 26 h, and the temperature was allowed to warm until room temperature. The solution was filtered, and the filtrate was concentrated and cooled at −20 °C leading to the formation of a small amount of a white solid that was separated of the mother liquor by filtration. ^1H NMR (C_6D_6): δ 7.16 (t, $^3J_{H_8H_7} = {}^3J_{H_8H_9}$ = 7.8 Hz, 4H, H_8), 6.90−6.68 (m, 6H, H_7, H_9), 3.64 (m, 2H, H_{1syn}), 2.99 (m, 2H, H_{2syn}), 2.71 (m, 2H, H_{3syn}, $H_{3'syn}$), 2.58 (m, 2H, H_{1anti}), 2.40 (m, 2H, H_{2anti}), 2.33 (m, 2H, H_{3anti}, $H_{3'anti}$), 0.29 (s, 12H, H_4, H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.1 (C_6), 129.2 (C_8), 121.6 (C_7), 120.2 (C_9), 54.1 (C_1), 50.1 (C_2), 48.7 (C_3), 0.2, −0.5 (C_4, C_5).

$[Zr(C{\equiv}CPh)\{N(Ph)SiMe_2\}_2tacn]$ (6). A solution of $\{NaN(Ph)SiMe_2\}_3tacn\cdot 2THF$ (1.15 g; 1.46 mmol) in diethyl ether (15 mL) was added at −40 °C to a suspension of $ZrCl_4$ (0.36 g; 1.55 mmol) in 40 mL of the same solvent. The mixture was stirred for 15 h, and the temperature was allowed to warm until room temperature. The precipitate was filtered off and washed with Et_2O. The filtrate was cooled to −60 °C, and a 1 M solution of LiCCPh (1.50 mL;

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(36) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.

1.50 mmol) in THF was added. The mixture was again allowed to warm to room temperature, and the volatiles were then removed in vacuum. The residue was extracted with hexane and filtered. The concentrate solution was cooled to −20 °C overnight, and a powder formed. The solvent was filtered off, and the solid was extracted in Et_2O. Slow diffusion of hexane into the ether solution led to the formation of a white microcrystalline precipitate that was separated by filtration. Yield: 20% (0.18 g). ^{1}H NMR (C_6D_6): δ 7.41 (d, $^3J_{H_{13}H_{14}} = 7.2$, 2H, H_{13}), 7.04−7.02 (m, 2H, H_9), 7.02 (d, $^3J_{H_7H_8} = 7.8$, 4H, H_7), 6.99 (t, $^3J_{H_{14}H_{15}} = {}^3J_{H_{14}H_{13}} = 7.2$, 2H, H_{14}), 6.90 (t, $^3J_{H_{14}H_{15}} = 7.2$, 1H, H_{15}), 6.74 (t, $^3J_{H_8H_7} = {}^3J_{H_8H_9} = 7.8$ Hz, 4H, H_8), 3.90−3.82 (m, 2H, H_{1syn}), 3.71−3.63 (m, 2H, H_{2syn}), 3.17−3.09 (m, 2H, H_{3syn}), 2.85−2.76 (m, 2H, H_{1anti}), 2.49−2.40 (m, 4H, H_{2anti}, H_{3anti}), 0.59 (s, 6H, H_4), 0.30 (s, 6H, H_5). ^{13}C{^{1}H} NMR (C_6D_6): δ 153.1 (C_6), 141.9 (C_{10}), 131.6 (C_{13}), 128.2 (C_9, C_{14}), 127.4 (C_{12}), 126.2 (C_{15}), 124.5 (C_7), 119.1 (C_8), 111.5 (C_{11}), 56.2 (C_1), 50.5 (C_3), 50.0 (C_2), 0.7 (C_5), 0.3 (C_3). Anal. Calcd for $C_{30}H_{39}N_5Si_2Zr$: C, 58.39; H, 6.37; N, 11.35. Found: C, 58.46; H, 6.47 N, 11.26.

[Zr(C≡CPh){N(C_6H_4F)SiMe$_2$}$_2$tacn] (7). The synthetic procedure used for **4** was applied to prepare **5** using {NaN(C_6H_4F)SiMe$_2$}$_3$tacn·2THF (1.32 g; 1.15 mmol), $ZrCl_4$ (0.28 g; 1.24 mmol), and a 1 M solution of LiCCPh (1.10 mL; 1.10 mmol) in THF. The product was obtained in 22% yield (0.13 g) from diethyl ether/hexane as described for **4**. ^{1}H NMR (C_6D_6): δ 7.38 (d, $^3J_{H_{15}H_{16}} = 6.9$, 2H, H_{15}), 7.11 (d br, 2H, H_{11}), 6.98 (t, $^3J_{H_{16}H_{15}} = {}^3J_{H_{16}H_{17}} = 6.9$, 2H, H_{16}), 6.90 (d, $^3J_{H_{17}H_{16}} = 6.9$, 1H, H_{17}), 6.81 (t br, ^{3}JH14H15 = 7.2 Hz, 2H, H_{10}), 6.56 (m br, 2H, H_8), 6.38 (m br, 2H, H_9), 4.01−3.93 (m, 2H, H_{1syn}), 3.67−3.58 (m, 2H, H_{2syn}), 3.29−3.22 (m, 2H, H_{3syn}), 2.87−2.79 (m, 2H, H_{1anti}), 2.50−2.42 (m, 4H, H_{2anti}, H_{3anti}), 0.65 (s, 6H, H_4), 0.35 (s, 6H, H_5). ^{13}C{^{1}H} NMR (C_6D_6): δ 157.8 (d, $^1J_{CF} = 236$, C_7), 141.3 (d, $^2J_{CF} = 7$, C_6), 140.6 (t, $^2J_{CF} = 9$, C_{12}), 131.6 (C_{15}), 128.1 (C_{16}), 127.5 (C_{14}), 126.1 (C_{17}), 124.2 (C_{11}), 123.5 (C_{10}), 118.6 (d, $^3J_{CF} = 7.5$, C_9), 114.4 (d, $^2J_{CF} = 21$ Hz, C_8), 109.6 (C_{13}), 57.3 (C_1), 50.4 (C_3), 49.7 (C_2), −0.1 (C_5), −0.5 (C_4). ^{19}F NMR (C_6D_6): δ −43.2 (br). Anal. Calcd for $C_{30}H_{37}N_5F_2Si_2Zr$: C, 55.18; H, 5.71; N, 10.72. Found: C, 55.26; H, 5.77 N, 10.36.

X-ray Experimental Details. Data were collected, at room temperature, on a MACH3 Bruker Nonius diffractometer equipped with Mo (0.710 69 Å) radiation. Data were corrected for Lorentz and polarization effects but not for absorption. Cell dimensions were determined from the setting angles of 25 reflections, within θ values of 15−17°. Structure was solved by direct methods using SIR97[37] and refined using SHELXL[38] within the pack of programs WINGX.[39] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Data have been deposited under CCDC 164823. Data collection and refinement details are presented in Table 2.

Table 2. Data Collection and Refinement Parameters for Complex **3**

cryst system, space group	monoclinic, $P2_1/c$
unit cell dimens	$a = 15.446(3)$, $b = 11.050(2)$, $c = 18.125(6)$ Å; $\beta = 114.55(2)$°
V	2813.9(12) Å^3
Z	4
calcd density	1.322 Mg/m^3
abs coeff	0.499 mm^{-1}
F(000)	1176
θ range for data collcn	2.22−25.99°
limiting indices	$0 \le h \le 19$, $-13 \le k \le 0$, $-22 \le l \le 20$
reflcns collcd/unique	5726/5515 [R(int) = 0.0402]
completeness to θ (25.99°)	99.7%
refinement method	full-matrix least-squares on F^2
data/restraints/params	5515/0/338
goodness-of-fit on F^2	1.042
final R indices [$I > 2\sigma(I)$]	R1 = 0.0513, wR2 = 0.1165
R indices (all data)	R1 = 0.1001, wR2 = 0.1723
largest diff peak and hole	0.450 and −0.740 e Å^{-3}

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Supporting Information Available: NMR spectra, ^{1}H−^{15}N HMBC of **1** (Figure S1), experimental and simulated ABCD and AA′BB′ spin systems of **3** (Figure S2), simulated coupling constants for the macrocycle proton spins systems of **3** (Table S1), and crystallographic data for **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Sparna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(38) Sheldrick, G. M. *SHELXL-97: A program for refining crystal structures (208)*; Univ. of Göttingen: Göttingen, Germany, 1998.

(39) *WINGIX, version 1.64.05, An Integrated System of Window Programs for the Solution, Refinement of Single Crystal X-ray Diffraction Data*; 1999.