

The chemistry of 1,3,5-triazacyclohexane complexes 5: cationic zinc(II) alkyl complexes of N-alkylated 1,3,5-triazacyclohexanes and 13-benzyl-1,5,9-triazatricyclo[7.3.1.0^{5,13}]-tridecane¹

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Received 5 February 1996

Abstract

Diethylzinc reacts with hydroperchlorates of N-alkylated 1,3,5-triazacyclohexanes (R_3TAC ; R = methyl (Me), benzyl (Bz), isopropyl (¹Pr)) and with the hydrotetrafluoroborate of 1,3,5-tris-(*para*-fluorobenzyl)-1,3,5-triazacyclohexane (FBz_3TAC) to give the corresponding cationic zinc ethyl complexes $[(R_3TAC)Zn(Et)]X$ ($X = ClO_4^-, BF_4^-$). Similar complexes were obtained from diethylzinc treated with $[HNMe_2Ph][BF_4]$ or $[HNMe_2Ph][B(C_6F_5)_4](Et_2O)$ in the presence of R_3TAC ($R = Bz, FBz, s$ -1-phenylethyl (*s*-PhMeCH)). A product of decomposition of $[(Bz_3TAC)Zn(Et)][ClO_4]$ was analyzed by X-ray diffraction. The structures of $[(s\text{-PhMeCH})_3TAC)Zn(Et)][BF_4]$ and $[(FBz_3TAC)Zn(Et)][BF_4]$ were estimated using nuclear Overhauser enhancement spectroscopy. Protonolysis of diethylzinc with $[HNMe_2Ph][BF_4]$ in the presence of 13-benzyl-1,5,9-triazatricyclo[7.3.1.0^{5,13}]-tridecane (BzTATC) yielded the complex $[(BzTATC)Zn(Et)][BF_4]$.

Keywords: Zinc; Ethyl; 1,3,5-Triazacyclohexane; Orthoamides; Trisaminomethanes; Tricyclic; 13-Benzyl-1,5,9-triazatricyclo[7.3.1.0^{5,13}]-tridecane; NMR spectroscopy

1. Introduction

We are investigating transition metal complexes containing N-alkylated 1,3,5-triazacyclohexanes (R_3TAC) [1,2] with the goal of preparing cationic alkyl complexes of vanadium, chromium or iron as homogeneous model systems of the Phillips ethylene polymerization catalyst. While synthesis and characterization of the neutral alkyl complexes $(^1Pr_3TAC)Cr(CH_2SiMe_3)_2(Cl)$ and $(Bz_3TAC)Cr(CH_2-C_6H_5)_3$ were reported recently [2], the preparation of cationic species has not yet been successful.

As shown earlier [2], R_3TAC is more weakly bound than the larger homologues (e.g. triazacyclononanes) or non-cyclic amines due to the increased ring strain. Therefore, the common methods of preparation of cationic transition metal amine complexes in aqueous media were not successful. We are now exploring protonolysis of organometallic compounds as a method

for the preparation of cationic transition metal amine complexes in non-aqueous media. The present investigation deals with the preparation of new cationic ethyl zinc complexes with R_3TAC (R = methyl (Me), benzyl (Bz), *p*-fluorobenzyl (FBz), isopropyl (¹Pr) and *s*-1-phenylethyl (*s*-PhMeCH)) and 13-benzyl-1,5,9-triazatricyclo[7.3.1.0^{5,13}]-tridecane (BzTATC) as structural models for future cationic complexes of other transition metals.

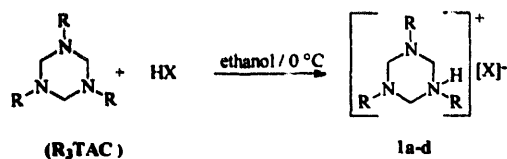
The acids $[H(OEt_2)_2][(3,5-(CF_3)_2C_6H_3)_4B]$ and $[HNMe_2Ph][B(C_6F_5)_4]$ have already been used for the generation of cationic complexes, e.g. of cobalt [3] and zirconium [4] respectively, and similarly protonolyses of amide complexes have been used, e.g. for synthesis of alkoxy complexes of chromium [5].

Only few mononuclear four-coordinated alkyl zinc complexes with tridentate ligands are known. First, are complexes $LZnR$ with L a tris-(pyrazolyl)-borato ligand and $R = Me, Et, ^1Bu$ or Ph [6–8]. Some of these were used as precursors of bioinorganic model systems [7].

In the past, many cationic complexes of several transition metals containing η^3 -coordinated 1,4,7-tri-

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¹ Dedicated to Professor H. Takaya.



Scheme 1. Reaction of R_3TAC with perchloric and fluoroboric acid to give **1a** ($R = Me$, $X = ClO_4^-$), **1b** ($R = Bz$, $X = ClO_4^-$), **1c** ($R = ^iPr$, $X = ClO_4^-$) and **1d** ($R = FBz$, $X = BF_4^-$) respectively.

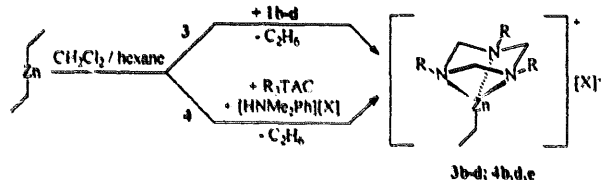
azacyclononanes and larger macrocyclic amines have been synthesized [9]. Among them are also monomeric alkyl complexes (e.g. with 1,4,7-triazacyclononanes [10,11]). However, no example of a cationic zinc complex with R_3TAC or $RTATC$, or even an alkyl zinc complex with a cyclic amine ligand, is reported. $RTATC$ complexes are only described with $CuCl_2$ ($R = Ph, Bz$) [12] and $Mo(CO)_3$ ($R = H, Me$) [13]. The known zinc complexes having R_3TAC or larger macrocyclic amines as ligands are either multinuclear or the amine is only η^1 -bound [14].

2. Results and discussion

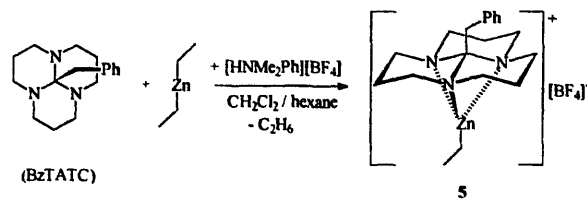
Reaction of R_3TAC ($R = Me, Bz, FBz$ or iPr) with perchloric acid and fluoroboric acid [15] yielded the mono hydroperchlorates **1a–c** and the mono hydrotetrafluoroborate **1d** respectively (Scheme 1).

While the results of elementary analysis of **1a–d** agree with the calculated values, the 1H NMR signals for the acidic protons could not be detected in solution of **1a–d** in $CDCl_3$ or CH_2Cl_2 . There is only a characteristic difference in chemical shifts between the ring protons or the benzylic protons in the amine and the corresponding ammonium salt. Compound **1c** is not stable at room temperature and decomposes within 24 h even in a dry atmosphere. Therefore it was prepared freshly prior to use without characterization.

Treating diethylzinc with one equivalent of **1b–d** respectively gave the cationic complexes $[(Bz_3TAC)Zn(Et)]ClO_4^-$ (**3b**), $[(^iPr_3TAC)Zn(Et)]ClO_4^-$ (**3c**) and $[(FBz_3TAC)Zn(Et)]BF_4^-$ (**3d**) in good yields (Scheme 2). An easier way to prepare the complexes



Scheme 2. Protonolysis of diethylzinc using **1b–d**, yielding **3b** ($R = Bz$, $X = ClO_4^-$), **3c** ($R = ^iPr$, $X = ClO_4^-$) and **3d** ($R = FBz$, $X = BF_4^-$) respectively. Protonolysis of diethylzinc with **2a** or **2b** in the presence of R_3TAC yields **4b** ($R = Bz$, $X = BF_4^-$), **4d** ($R = FBz$, $X = B(C_6F_5)_4^-$) and **4e** ($R = s-PhMeCH$, $X = BF_4^-$) respectively.



Scheme 3. Protonolysis of diethylzinc with **2a** in the presence of $BzTATC$, yielding **5**.

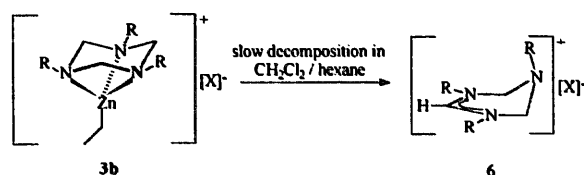
$[(R_3TAC)Zn(Et)]X^-$ is the protonolysis of diethylzinc with an N,N -dimethylanilinium salt $[HNMe_2Ph][X]$ (**2a,b**) in the presence of R_3TAC . Using this route the complexes $[(Bz_3TAC)Zn(Et)]BF_4^-$ (**4b**), $[(FBz_3TAC)Zn(Et)]B(C_6F_5)_4^-$ (**4d**) and the chiral complex $[(s-PhMeCH)_3TAC)Zn(Et)]BF_4^-$ (**4e**) have been synthesized. Complexes with the smallest N -alkylated 1,3,5-triazacyclohexane (Me_3TAC) could not be prepared by any of these routes.

Protonolyses of diethylzinc with **2a** in the presence of $BzTATC$ yielded the complex $[(BzTATC)Zn(Et)]BF_4^-$ (**5**) (Scheme 3). It is the first zinc complex with a 1,5,9-triazatricyclo[7.3.1.0^{5,13}]-tridecane ligand.

The 1H NMR spectra of the complexes **3b–d**, **4b,d,e** show the signals of the ethyl group ($\delta = 0.42–0.57$ ppm (q) and $\delta = 1.14–1.17$ ppm (t)) and two characteristic doublets in the range $\delta_1 = 3.1–3.7$ ppm and $\delta_2 = 4.0–4.4$ ppm. Using nuclear Overhauser enhancement spectroscopy (NOESY) the doublets were identified as the signals resulting from the exo (δ_1) and endo (δ_2) protons of the ring $-CH_2-$ groups. They became chemically different by ligand coordination to the zinc atom. However, the gated decoupled $^{13}C/^{1}H$ NMR of **3d** gave no indication of any agostic hydrogen–zinc interaction. The complex **3d** has been synthesized and investigated by ^{19}F NMR spectroscopy in order to determine the ligand to anion ratio. The measured intensities of the two ^{19}F NMR signals in **3d** support a ligand to anion ratio of 1:1.

The complexes **3b–d**, **4b,d,e** are sensitive towards moisture. Reaction with water yields ethane, zinc hydroxide and R_3TAC . The compounds also react with other protic agents like dimethylsulfoxide. No reaction is observed within 1 h when treating **4b** with benzophenone or the chiral **4e** with benzaldehyde. After stirring **4e** with benzaldehyde for 24 h at room temperature the characteristic 1H NMR signals of the ring protons have disappeared. However, no products could be identified.

From a solution of **3b** in dichloromethane/hexane, crystals were obtained after 14 days and analyzed by X-ray diffraction. Although the solid complexes **3b–d**, **4b,d,e** are stable for weeks when stored dry, we found the species **6** (Scheme 4) as one product of the slow decomposition of **3b** in CH_2Cl_2 solution. The molecular structure (Fig. 1) shows an organic cation and the ClO_4^- anion.



Scheme 4. Slow decomposition of **3b** in solution yielding **6** (R = Bz, X = ClO₄).

The structure is significantly different to that known for Bz₃TAC [16a] and similar to the cation derived from the oxidation of Me₃TAC with iodine [16b]. The N1–C1 and N2–C2 bond distances are short and C11, N1, C1, N2, C21, C3 and C2 are in one plane within the standard deviation. This indicates an sp² hybridization at the carbon atom C1 and **6** seems to be the product of oxidation with CH₂Cl₂ and a Lewis acid.

Since we were unable to grow crystals of [(R₃TAC)₂Zn(Et)][X] suitable for X-ray crystallography, we tried to use the well-resolved NMR spectra for structure refinement. The relative intensities of NOESY cross-peak signals ($I_{\text{det}}(\text{H}_A-\text{H}_B)$) are proportional to $1/(r_{A-B})^6$ where r_{A-B} is the distance between two hydrogen atoms A and B.

Crystal structures have shown that the R₃TAC ligand is relatively rigid and varies only in the conformation of the nitrogen substituent R. In the case of R = FBz or

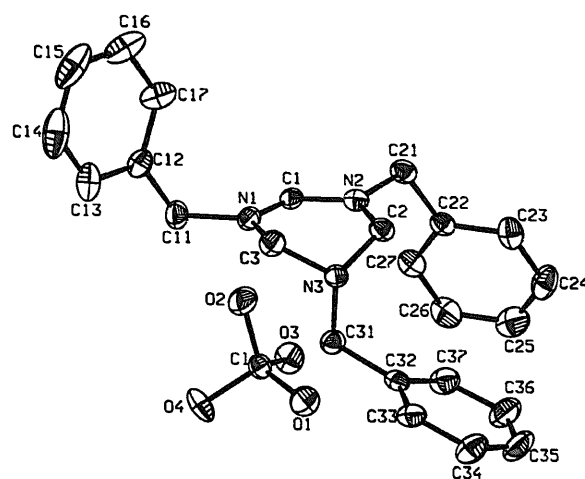


Fig. 1. A perspective ORTEP plot [28] of **6**, thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances (pm) and angles (°): C1–N1 130.2(5), C1–N2 133.2(5), N1–C11 147.5(5), N1–C3 147.6(6), N2–C7 148.4(5), N2–C21 146.9(5), C2–N3 142.7(5), C3–N3 145.0(6), C1–O1 143.2(3), N1–C1–N2 121.8(4), C1–N1–C3 119.8(4), C11–N1–C3 119.6(4), C11–N1–C1 120.6(4), C1–N2–C2 119.8(4), C1–N2–C21 120.9(4), C2–N2–C21 119.3(3), N2–C2–N3 111.7(3), C2–N3–C3 109.1(4), N1–C3–N3 110.4(4), O1–C1–O2 110.8(2).

s-PhMeCH, only the rotation around the N–C_{benz} and C_{benz}–C_{phen} bonds and the angle γ (describing the deviation of the N-substituent from the plane defined by the three nitrogen atoms) had to be varied (Fig. 2).

Table 1

Determined intensities $I_{\text{det}}(\text{H}_A-\text{H}_B)$ and their estimated standard deviations (SDs) and calculated intensities $I_{\text{calc}}(\text{H}_A-\text{H}_B)$ of NOESY cross-peak signals between two hydrogen atoms A and B in the cations of **3d** and **4e** respectively. When the standard deviation was below 10% a minimum error in the intensity of 10% was assumed, caused by integration. The intensities are scaled relative to $I_{\text{det}}(\text{H}_{\text{endo}}-\text{H}_{\text{exo}}) = 100$

H _A –H _B	Cation of 3d		Cation of 4e	
	$I_{\text{det}}(\text{H}_A-\text{H}_B)$ (SD)	$I_{\text{calc}}(\text{H}_A-\text{H}_B)$	$I_{\text{det}}(\text{H}_A-\text{H}_B)$ (SD)	$I_{\text{calc}}(\text{H}_A-\text{H}_B)$
H _{endo} –H _{exo}	100(10)	100	100(20)	100
H _{ortho} –H _{endo}	24(10)	21	26(27)	22
H _{ortho} –H _{exo}	^b	7	10(5)	9
H _{Me} –H _{endo}	—	—	33(8)	55
H _{Me} –H _{exo}	—	—	20(5)	27
H _{benz} –H _{endo}	65(10)	47	32(7)	31
H _{benz} –H _{exo}	46(7)	22	21(7)	11
H _{ortho} –H _{benz}	55(10)	40	40(15)	30
H _{ortho} –H _{Me}	—	—	19(7)	28
H _{benz} –H _{Me}	—	—	39(11)	45
H _{CH₂} –H _{CH₃}	^a	27	15(4)	27
H _{Me} –H _{CH₃}	—	—	1.0(0.3)	1.2
H _{ortho} –H _{CH₂}	^b	1.2	^b	4.1
H _{ortho} –H _{CH₃}	^b	0.9	^b	1.1
H _{benz} –H _{CH₂}	^b	0.3	^b	0.1
H _{benz} –H _{CH₃}	^b	0.8	^b	0.7
H _{endo} –H _{CH₂}	^b	0.4	^b	0.4
H _{endo} –H _{CH₃}	^b	0.6	^b	0.5
H _{exo} –H _{CH₂}	^b	0.0	^b	0.0
H _{exo} –H _{CH₃}	^b	0.0	^b	0.0

^a Not determined; ^b not observed.

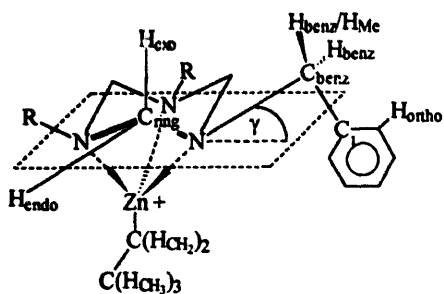


Fig. 2.

The highest signal intensity was obtained from the cross-peak between the hydrogen atoms in the endo (H_{endo}) and the exo (H_{exo}) position. Table 1 shows the relative intensities of all signals.

For all observed cross-peaks between ring hydrogen atoms and the nitrogen substituent (H_{ortho} , H_{benz} , and H_{Me} (in **4e**) the intensities of the H_{endo} signals are greater than the intensities of the H_{exo} signals. Therefore all averaged positions of these protons must be closer to the endo protons. However, the methyl and benzyl hydrogen atoms have only a small and nearly equal intensity ratio with the endo and exo positions. Compounds **3d** and **4e** have nearly the same intensities except for cross-peaks involving the benzyl groups which are twice as intense for **3d** compared with **4e**. Therefore we conclude that the two benzylic hydrogen atoms (or H_{Me} in **4e**) are in equivalent positions relative to the $R_3\text{TAC}$ ring and that the nitrogen substituents have either the conformation of Fig. 3(a) or 3(b). From the greater intensity for the cross-peak of the H_{ortho} compared with the H_{endo} protons, we conclude that conformation (a) gives the largest contribution.

The hypotheses of the unusual eclipsed conformation for a majority of the nitrogen substituents may be possible because of the relatively large distance between the ring protons and H_{benz} due to the large $C_{\text{ring}}-N-C_{\text{benz}}$ angle which is known from several X-ray structures of $R_3\text{TAC}$ complexes [1,2,17] to be larger than 120° . This results in a decreased torsion barrier in the direction of the $N-C_{\text{benz}}$ bond. As reported recently, the X-ray crystal structure and molecular mechanics studies of $R_3\text{TAC}$ ($R = \text{neopentyl}$) also indicate an eclipsed position of the N -substituents [18]. From X-ray struc-

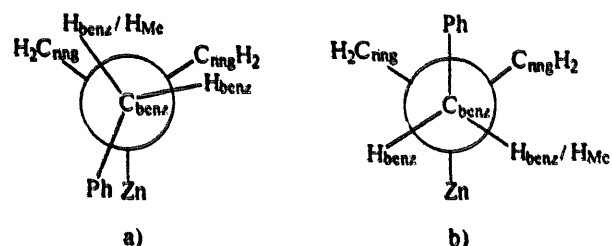


Fig. 3. Newman projection along the $N-C_{\text{benz}}$ bond in **3d** and **4e** respectively.

tures of $R_3\text{TAC}$ complexes with d^{10} metals (e.g. $[(Bz_3\text{TAC})\text{Cu}(\text{PPh}_3)]^+$ [17] and $[(\text{FBz}_3\text{TAC})_2\text{Zn}]^{2+}$ [19]), it is known that the phenyl groups are preferably allocated towards the zinc atom. This gives rise to supposing an attractive interaction between the zinc atom and the phenyl groups.

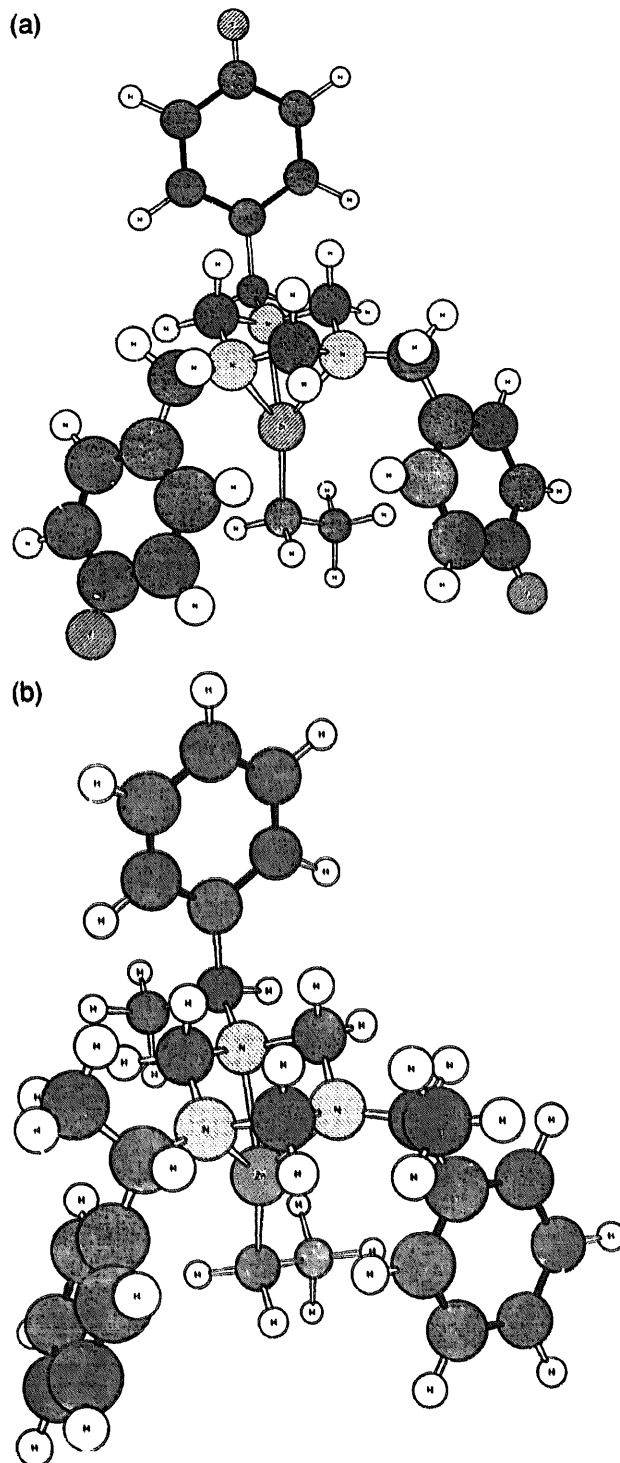


Fig. 4. Structures of the cations of (a) **3d** and (b) **4e** which give the largest contribution to the conformation of the molecules. The structures were estimated by NOESY spectroscopy.

Models with all substituents in conformation (a) did not agree with the intensities of the H_{benz} to H_{exo} cross-peaks and the fact that the cross-peak of H_{CH_3} and H_{Me} was the only (and therefore strongest) signal between $R_3\text{TAC}$ and the ethyl group. Both problems could be solved by assuming two nitrogen substituents in conformation (a) and one in conformation (b). For the structures shown in Fig. 4 the smallest angle γ (found in the X-ray structure of $[(\text{FBz}_3\text{TAC})_2\text{Zn}]^{2+}$ [19] was used ($\gamma = 5^\circ$).

Fig. 4 shows the plots with the best fit to the observed data of the cations of **3d** and **4e** respectively. The related calculated intensities (I_{calc}) are given in Table 1. All distances $r_{\text{A-B}}$ are very sensitive towards changing the $H_{\text{endo}}\text{-C}_{\text{ring}}\text{-H}_{\text{exo}}$ angle. This may explain why most of the calculated intensities are slightly lower than the measured ones. The intensity of the cross-peak between H_{Me} and H_{endo} in **4e** is very sensitive towards deviations from the torsion angle $\text{Zn-N-C}_{\text{benz}}\text{-C}_1$, set to zero. The differences in calculated and measured intensity may indicate a deviation from the ideal eclipsed position. However, because of the small number of signals observed we did not fit the model to more parameters.

The approximated structures of the cations of **3d** and **4e** show the cation is well protected by the aromatic groups of the N-substituents. This may be the reason for the observed decreased stability of the isopropyl compound **3c** and for the inertness of the complexes $[(R_3\text{TAC})\text{Zn}(\text{Et})][X]$ towards large reagents like benzophenone and benzaldehyde. Small agents should not be hindered from attacking the ethyl group.

3. Experimental details

All syntheses were carried out under deoxygenated and dried argon using standard Schlenk techniques. Moisture sensitive compounds were stored in a glove box. Hexane, pentane, ether and the chlorinated solvents were dried according to standard methods, stored over the drying agents and directly condensed into the reaction flasks prior to use. All other solvents were used as commercially obtained.

Elemental analyses were carried out using a Perkin-Elmer Series II CHNS/O analyzer 2400 and a Perkin-Elmer 2380 atomic absorption spectrophotometer. ^1H , ^{13}C and ^{19}F NMR were acquired on a Bruker ARX 200 FT-NMR spectrometer. For NOESY spectroscopy a Bruker ARX 400 FT-NMR spectrometer was used. IR spectra were recorded with a Perkin-Elmer IR 580B spectrophotometer.

The ligands were synthesized according to modified literature methods [20] (Bz_3TAC , FBz_3TAC , $^i\text{Pr}_3\text{TAC}$, $(\text{s-PhMeCH})_3\text{TAC}$) or used as commercially obtained

(Me_3TAC). The synthesis of BzTATC was described previously [13].

3.1. Synthesis of 1,3,5-tribenzyl-1,3,5-triazacyclohexanehydroperchlorate (**1b**) [15]

Crystalline Bz_3TAC (3.0 g, 8.39 mmol) was dissolved at room temperature in ethanol (20 ml). The solution was cooled to 0°C and aqueous perchloric acid (60%, 0.8 ml, 7.33 mmol) was added dropwise to the resulting white suspension. After stirring for 15 min, the volatile materials were removed in vacuo. The crude product was washed with ether and pentane, yielding a white solid (3.29 g, 98%).

Anal. Found: C, 62.24; H, 6.22; N, 9.06. $\text{C}_{24}\text{H}_{28}\text{N}_3\text{ClO}_4$ Calc.: C, 62.95; H, 6.16; N, 9.18%. M.p. 111°C . ^1H NMR (200 MHz, CD_2Cl_2): δ (ppm) 4.00 (s, 12H, $\text{N-CH}_2\text{-N}$ and $\text{Ph-CH}_2\text{-N}$), 7.31 (s, 15H, C_6H_5). ^{13}C NMR (50.29 MHz, CD_2Cl_2): δ (ppm) 56.1 ($\text{Ph-CH}_2\text{-N}$), 71.8 ($\text{N-CH}_2\text{-N}$), 128.9 (C_4), 129.2 ($\text{C}_{2/6}$), 129.8 ($\text{C}_{3/5}$). IR (KBr): ν (intensity) 625(s), 703(s), 745(s), 1057(s), 1108(s), 1122(s), 1456(s).

3.2. Synthesis of 1,3,5-trimethyl-1,3,5-triazacyclohexanehydroperchlorate (**1a**)

The same procedure was followed as for the preparation of **1b** except Me_3TAC (3.0 g, 23.22 mmol) instead of Bz_3TAC was used. The product precipitated when perchloric acid (2.0 ml, 18.33 mmol) was added (4.13 g, 98%).

Anal. Found: C, 31.96; H, 8.16; N, 18.94. $\text{C}_6\text{H}_{16}\text{N}_3\text{ClO}_4$ Calc.: C, 31.38; H, 7.02; N, 18.30%. M.p. 119°C . ^1H NMR (200 MHz, CD_2Cl_2): δ (ppm) 2.30 (s, 9H, $\text{CH}_3\text{-N}$), 3.59 (s, 6H, $\text{N-CH}_2\text{-N}$). ^{13}C NMR (50.29 MHz, CD_2Cl_2): δ (ppm) 39.2 ($\text{CH}_3\text{-N}$), 74.4 ($\text{N-CH}_2\text{-N}$). IR (KBr): ν (intensity) 444(m), 489(m), 623(s), 637(m), 889(m), 927(m), 982(m), 1096(s), 1178(m), 1259(m), 1283(m), 1447(m), 1455(m), 1479(m), 1525(m), 1576(m).

3.3. Synthesis of 1,3,5-tris-(para-fluorobenzyl)-1,3,5-triazacyclohexanehydrotetrafluoroborate (**1d**)

This compound was prepared in a manner analogous to that described for **1b**, except FBz_3TAC (2.7 g, 6.55 mmol) instead of Bz_3TAC and an etheric solution of HBF_4 (54%, 0.85 ml, 6.22 mmol) instead of perchloric acid were used. When the acid was added a clear solution resulted. The product precipitated after removing the solvent.

Anal. Found: C, 57.13; H, 4.68; N, 8.88. $\text{C}_{24}\text{H}_{25}\text{N}_3\text{BF}_4$ Calc.: C, 57.74; H, 5.05; N, 8.42%. M.p. 100°C . ^1H NMR (200 MHz, CD_2Cl_2): δ (ppm) 3.93

(s, 12H, N-CH₂-N and Ph-CH₂-N), 6.9–7.3 (m, 12H, C₅H₄F-CH₂). ¹³C NMR (50.29 MHz, CD₂Cl₂): δ (ppm) 55.1 (Ph-CH₂-N), 71.7 (N-CH₂-N), 116.0 (d, J[CF] = 21.6 Hz, C_{3/5}F), 129.9 (C₁), 131.7 (d, J[CF] = 8.2 Hz, C_{2/6}F), 163.1 (d, J[CF] = 247.0 Hz, C₄F). ¹⁹F NMR (188.15 MHz, CD₂Cl₂): δ (ppm) -37.05 (3F, C₄F), -72.00 (4F, BF₄). IR (KBr): ν(intensity) 751(m), 799(m), 826(m), 837(m), 863(m), 884(m), 1093(s), 1165(s), 1179(s), 1226(s), 1240(s), 1280(m), 1299(m), 1357(m), 1381(m), 1400(m), 1419(m), 1456(m), 1463(m), 1512(s), 1630(s), 3160(m).

3.4. Synthesis of *N,N*-dimethylaniliniumtetrafluoroborate (**2a**)

Freshly distilled *N,N*-dimethylanilin (2.24 g, 18.48 mmol) was dissolved in ether. To the stirred solution aqueous fluoroboric acid (7.75 M, 2 ml, 15.50 mmol) was added dropwise. After stirring for 10 min the aqueous phase was isolated. The water was removed in vacuo yielding a solid. After washing with ether and drying in vacuo a white solid was obtained (2.37 g, 73.2%).

Anal. Found: C, 45.84; H, 5.89; N, 6.77. C₈H₁₂NBF₄ Calc.: C, 45.98; H, 5.79; N, 6.70%. M.p. 52 °C. ¹H NMR (200 MHz, CDCl₃): δ (ppm) 3.37 (s, 6H, CH₃), 7.5–7.7 (m, 5H, C₆H₅), 9.17 (s, 1H, NH). ¹³C NMR (50.29 MHz, CDCl₃): δ (ppm) 47.8 (CH₃), 120.1 (C_{2/6}), 130.9 (C₄), 130.9 (C_{3/5}), 141.9 (C₁). IR (KBr): ν(intensity) 522(m), 534(m), 543(m), 575(m), 615(m), 685(m), 694(m), 746(m), 764(m), 771(m), 804(m), 898(m), 997(m), 1054(s), 1132(s), 1466(m), 1497(m), 2444(m), 2498(m), 2583(m), 2631(m).

3.5. Synthesis of *N,N*-dimethylaniliniumtetrakis-(pentafluorophenyl)-borate · (Et₂O) (**2b**)

A method for the preparation of the ether-free compound was described previously [4].

To a mixture of freshly distilled *N,N*-dimethylanilin (2.47 g, 20.41 mmol) and water (10 ml), hydrochloric acid (25%) was added dropwise until most of the dimethylanilin was dissolved. The solution was washed twice with ether. The colorless mixture was added to an intensively stirred solution of lithium tetrakis-(pentafluorophenyl)-borate (9.34 g, 13.61 mmol) in water (100 ml) in small portions. The white precipitate was filtered off and washed with water until chloride free. Washing with ether and drying in vacuo yielded the product as mono etherate (8.76 g, 73.5%).

Anal. Found: C, 49.47; H, 2.51; N, 1.79. C₃₆H₂₂NBF₂₀O Calc.: C, 49.39; H, 2.53; N, 1.60%. M.p. (decomp. without melt.) 120 °C. ¹H NMR (200 MHz, CD₂Cl₂): δ (ppm) 1.25 (t, J[HH] = 7.0 Hz, 6H, O(CH₂-CH₃)₂), 3.39 (s, 6H, N-(CH₃)₂), 3.62 (q, J[HH] = 7.0 Hz, 4H, O(CH₂-CH₃)₂), 5.94 (s, 1H,

NH), 7.3–7.7 (m, 5H, C₆H₅). ¹³C NMR (50.29 MHz, CD₂Cl₂): δ (ppm) 15.4 (O(CH₂-CH₃)₂), 48.8 (N-CH₃), 66.4 (O(CH₂-CH₃)₂), 119.6 (C_{2/6} in C₆H₅), 132.0 (C_{3/5} in C₆H₅), 134.1 (C₄ in C₆H₅), 140.9 (C₁ in C₆H₅), 136.9, 138.5, 148.5 (C₆F₅). ¹⁹F NMR (188.15 MHz, CD₂Cl₂): δ (ppm) -90.7 (t, J = 18.2 Hz, C_{2/6}F), -85.6 (t, J = 20.4 Hz, C₄F), -56.6 (m, C_{3/5}F). IR (KBr): ν(intensity) 662(m), 684(m), 689(m), 757(m), 768(m), 775(m), 979(s), 1084(s), 1094(s), 1182(w), 1278(m), 1374(m), 1463(s), 1514(s), 1646(m), 3251(m).

3.6. Synthesis of [(Bz₃TAC)Zn(Et)](ClO₄) (**3b**)

A solution of **1b** (0.17 g, 0.37 mmol) in dichloromethane (10 ml) was added to a stirred solution of diethylzinc in hexane (1 M, 0.3 g, 0.41 mmol) at 0 °C. After stirring for 15 min the volatile materials were removed. Washing with hexane the oily product obtained yielded a white moisture sensitive solid (0.14 g, 69%).

Anal. Found: C, 55.14; H, 5.51; N, 8.78; Zn, 12.70. C₂₆H₃₂N₃ClO₄Zn Calc.: C, 56.64; H, 5.85; N, 7.62; Zn, 11.86%. M.p. 113 °C. ¹H NMR (200 MHz, CDCl₃): δ (ppm) 0.48 (q, J[HH] = 8.0 Hz, 2H, Zn-CH₂), 1.17 (t, J[HH] = 8.0 Hz, 3H, CH₃), 3.19 (d, J[HH] = 8.6 Hz, 3H, N-CH_{endo}H_{exo}-N), 3.82 (s, 6H, Ph-CH₂-N), 4.20 (d, J[HH] = 8.6 Hz, 3H, N-CH_{endo}H_{exo}-N), 7.0–7.6 (m, 15H, C₆H₅). ¹³C NMR (50.29 MHz, CDCl₃): δ (ppm) 2.1 (Zn-CH₂), 11.6 (CH₃), 55.8 (Ph-CH₂-N), 73.4 (N-CH₂-N), 128.6 (C₄), 128.7 (C_{2/6}), 129.3 (C_{3/5}), 133.2 (C₁). IR (KBr): ν(intensity) 529(m), 618(s), 698(s), 745(s), 753(s), 922(s), 993(m), 1028(s), 1122(s), 1162(s), 1357(m), 1374(w), 1456(s), 1497(m), 2788(m), 2861(s), 2897(m), 2936(m), 3032(m), 3065(m), 3089(m).

3.7. Synthesis of [(FBz₃TAC)Zn(Et)](BF₄) (**3d**)

The same procedure was followed as for the preparation of **3b** except **1d** (0.2 g, 0.40 mmol) was used instead of **1b**.

Anal. Found: C, 51.40; H, 4.76; N, 8.16; Zn, 12.20. C₂₆H₂₉N₃BF₇Zn Calc.: C, 52.69; H, 4.93; N, 7.09; Zn, 11.03%. M.p. 96 °C. ¹H NMR (200 MHz, CDCl₃): δ (ppm) 0.42 (q, J[HH] = 8.0 Hz, 2H, Zn-CH₂), 1.14 (t, J[HH] = 8.0 Hz, 3H, CH₃), 3.39 (d, J[HH] = 8.4 Hz, 3H, N-CH_{endo}H_{exo}-N), 3.79 (s, 6H, C₆H₄F-CH₂-N), 4.17 (d, J[HH] = 8.4 Hz, 3H, N-CH_{endo}H_{exo}-N), 6.85–7.40 (m, 12H, C₆H₄F-CH₂). ¹³C NMR (50.29 MHz, CDCl₃, gated decoupled): δ (ppm) 1.8 (t, J[CH] = 121.4 Hz, Zn-CH₂), 11.4 (q, J[CH] = 124.6 Hz, CH₃), 54.7 (t, J[CH] = 137.9 Hz, Ph-CH₂-N), 75.1 (t, J[CH] = 147.0 Hz, N-CH₂-N), 116.0 (dd, J[CH] = 164.7 Hz, J[CF] = 21.3 Hz, C_{3/5}H), 129.2 (d, J[CF] = 3.0 Hz, C₁), 131.2 (dd, J[CH] = 160.6 Hz, J[CF] =

8.3 Hz, $C_{2/6}H$), 162.84 (d, $J[CF] = 247.8$ Hz, C_4F). ^{19}F NMR (188.15 MHz, $CDCl_3$): δ (ppm) -112.74 ($3F$, C_4F), -150.53 ($4F$, BF_4). IR (KBr): ν (intensity) 522(m), 766(m), 825(s), 835(s), 857(m), 1080(s), 1100(s), 1228(s), 1402(m), 1512(s), 1606(s).

3.8. Synthesis of $[(^iPr_3TAC)Zn(Et)]ClO_4$ (**3c**)

Aqueous perchloric acid (0.9 ml, 8.25 mmol) was added to a solution of iPr_3TAC (1.84 g, 8.63 mmol) in ethanol at 0 °C. A white precipitate appeared after stirring for some minutes. The solvents were removed at 0 °C in vacuo. The resulting white solid was washed with ether and pentane, dried in vacuo and then dissolved in dichloromethane. This solution was added to diethylzinc in hexane (1 M, 6.53 g, 8.99 mmol). The volatile materials were removed in vacuo after stirring for 15 min. The oily product was washed with pentane and ether to yield a white solid (3.05 g, 90.8%).

Anal. Found: C, 38.72; H, 7.73; N, 9.53. $C_{14}H_{32}N_3ClO_4Zn$ Calc.: C, 41.29; H, 7.92; N, 10.32%. M.p. (decomp.) 70 °C. 1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.42 (q, $J[HH] = 8.0$ Hz, 2H, $Zn-CH_2-CH_3$), 1.17 (d, $J[HH] = 6.7$ Hz, 18H, $CH(CH_3)_2$), 1.19 (t, $J[HH] = 8.0$ Hz, 3H, $Zn-CH_2-CH_3$), 3.32 (sept, $J[HH] = 6.7$ Hz, 3H, $N-CH(CH_3)_2$), 3.64 (d, $J[HH] = 8.8$ Hz, 3H, $N-CH_{endo}H_{exo}-N$), 4.21 (d, $J[HH] = 8.8$ Hz, 3H, $N-CH_{endo}H_{exo}-N$). ^{13}C NMR (50.29 MHz, $CDCl_3$): δ (ppm) 1.0 ($Zn-CH_2-CH_3$), 11.7 ($Zn-CH_2-CH_3$), 18.8 ($CH(CH_3)_2$), 52.5 ($N-CH(CH_3)_2$), 69.2 ($N-CH_2-N$). IR (KBr): ν (intensity) 522(m), 540(m), 623(s), 932(m), 1008(m), 1054(s), 1106(s), 1172(s), 1211(s), 1373(m), 1393(m), 1468(m), 1554(m), 1646(m), 1669(m), 2857(m), 2882(m), 2937(s), 2975(s), 3586(m).

3.9. Synthesis of $[(Bz_3TAC)Zn(Et)]BF_4$ (**4b**)

A solution of **2a** (4.43 g, 21.20 mmol) in dichloromethane was added to a stirred mixture of diethylzinc in hexane (15.4 g, 21.21 mmol) and Bz_3TAC (7.58 g, 21.20 mmol). After stirring for 15 min the volatile materials were removed in vacuo. After washing intensively with pentane the product was obtained as a white solid (10.94 g, 95.8%).

Anal. Found: C, 58.54; H, 5.96; N, 7.83. $C_{26}H_{32}N_3BF_4Zn$ Calc.: C, 57.97; H, 5.99; N, 7.80%. M.p. 100 °C. 1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.48 (q, $J[HH] = 8.0$ Hz, 2H, $Zn-CH_2-CH_3$), 1.17 (t, $J[HH] = 8.0$ Hz, 3H, $Zn-CH_2-CH_3$), 3.46 (d, $J[HH] = 8.6$ Hz, 3H, $N-CH_{endo}H_{exo}-N$), 3.80 (s, 6H, $Ph-CH_2-N$), 4.182 (d, $J[HH] = 8.6$ Hz, 3H, $N-CH_{endo}H_{exo}-N$), 7.10–7.40 (m, ca. 15H, $C_6H_5-CH_2$). ^{13}C NMR (50.29 MHz, $CDCl_3$): δ (ppm) 1.9 ($Zn-CH_2-CH_3$), 11.4 (CH_2-CH_3), 55.4 ($Ph-CH_2-N$), 73.6 ($N-CH_2-N$), 128.6 (C_4), 128.9 ($C_{2/6}$), 129.3 ($C_{3/5}$)

133.4 (C_7). IR (KBr): ν (intensity) 464(m), 518(m), 523(m), 613(m), 621(m), 664(m), 697(s), 703(s), 736(m), 751(m), 766(m), 920(m), 935(m), 979(s), 1001(s), 1025(s), 1081(s), 1146(s), 1165(s), 1208(m), 1214(m), 1237(m), 1265(m), 1280(m), 1290(m), 1303(m), 1320(m), 1335(m), 1349(m), 1357(m), 1363(m), 1371(m), 1455(s), 1497(m), 2721(m), 2794(m), 2814(s), 2855(m), 2933(m), 2948(m), 3034(m), 3065(m), 3089(m), 3108(m), 3537(m).

3.10. Synthesis of $[(FBz_3TAC)Zn(Et)]B(C_6F_5)_4$ (**4d**)

The same procedure was followed as for the preparation of **4b** except FBz_3TAC (0.24 g, 0.58 mmol) instead of Bz_3TAC , **2b** (0.40 g, 0.46 mmol) instead of **2a**, and diethylzinc in hexane (0.40 g, 0.55 mmol) were used. The product was a white solid (0.49 g, 82%).

Anal. Found: C, 49.86; H, 3.01; N, 3.31. $C_{50}H_{29}N_3BF_{23}Zn$ Calc.: C, 50.68; H, 2.47; N, 3.55%. M.p. 83 °C. 1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.57 (q, $J[HH] = 8.2$ Hz, 2H, $Zn-CH_2-CH_3$), 1.16 (t, $J[HH] = 8.2$ Hz, 3H, $Zn-CH_2-CH_3$), 3.42 (d, $J[HH] = 8.5$ Hz, 3H, $N-CH_{endo}H_{exo}-N$), 3.66 (s, 6H, $Ph-CH_2-N$), 4.09 (d, $J[HH] = 8.5$ Hz, 3H, $N-CH_{endo}H_{exo}-N$), 6.95–7.15 (m, ca. 12H, $C_6H_4F-CH_2$). ^{13}C NMR (50.29 MHz, $CDCl_3$): δ (ppm) 3.1 ($Zn-CH_2-CH_3$), 11.7 (CH_2-CH_3), 55.3 ($Ph-CH_2-N$), 74.2 ($N-CH_2-N$), 117.0 (d, $J[CF] = 20.4$ Hz, $C_{3/5}$ in C_5H_4F), 129.3 (d, $J[CF] = 3.0$ Hz, C_1 in C_5H_4F), 131.1 (d, $J[CF] = 8.5$ Hz, $C_{2/6}$ in C_5H_4F), 162.8 (d, $J[CF] = 248$ Hz, C_4 in C_5H_4F). ^{19}F NMR (188.15 MHz, $CDCl_3$): δ (ppm) -89.67 (m, $C_{2/6}F$), -85.60 (m, C_4F), -55.65 (m, $C_{3/5}F$), -34.17 (s, $C_6H_4F-CH_2$). IR (KBr): ν (intensity) 413(w), 423(w), 449(w), 551(w), 523(w), 527(w), 575(w), 610(w), 661(m), 684(m), 756(m), 769(m), 775(m), 832(m), 841(m), 852(m), 858(m), 980(s), 1029(m), 1064(m), 1089(s), 1159(m), 1225(s), 1230(s), 1262(m), 1274(m), 1356(m), 1367(m), 1374(m), 1464(s), 1513(s), 1604(m), 1643(m), 1687(m), 2868(m), 2955(m).

3.11. Synthesis of $[(s-PhMeCH)_3TAC]Zn(Et)]BF_4$ (**4e**)

This compound was prepared in a manner analogous to that described for **4b** except $(s-PhMeCH)_3TAC$ (0.52 g, 1.30 mmol) instead of Bz_3TAC , **2a** (0.25 g, 1.20 mmol) and diethylzinc in hexane (1.02 g, 1.40 mmol) were used. The procedure yielded a white solid (0.68 g, 97.6%).

Anal. Found: C, 59.94; H, 7.14; N, 7.89. $C_{29}H_{38}N_3BF_4Zn$ Calc.: C, 59.97; H, 6.59; N, 7.23%. M.p. 80 °C. 1H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.53 (q, $J[HH] = 8.2$ Hz, 2H, $Zn-CH_2-CH_3$), 1.16 (t, $J[HH] = 8.2$ Hz, 3H, CH_2-CH_3), 1.40 (t, $J[HH] = 6.9$ Hz, 9H, $CH(CH_3)$), 3.21 (d, $J[HH] = 9.0$ Hz, 3H,

N-CH_{endo}H_{exo}-N), 4.18 (q, J [HH] = 6.9 Hz, 3H, Ph-CH(CH₃)-N), 4.33 (d, J [HH] = 9.0 Hz, 3H, N-CH_{endo}H_{exo}-N), 7.05–7.45 (m, ca. 15H, C₆H₄F-CH₂). ¹³C NMR (50.29 MHz, CDCl₃): δ (ppm) 2.6 (Zn-CH₂-CH₃), 12.1 (CH₂-CH₃), 17.1 (CH(CH₃)), 60.1 (Ph-CH₂-N), 70.5 (N-CH₂-N), 127.7 (C_{2/4}), 129.0 (C₁), 129.5 (C_{3/5}), 138.5 (C₄). IR (KBr): ν (intensity) 518(w), 546(w), 565(w), 623(w), 703(s), 747(w), 763(m), 1087(s), 1102(s), 1209(m), 1243(m), 1281(m), 1310(m), 1331(m), 1362(m), 1380(m), 1456(s), 1496(m), 1603(w).

3.12. Synthesis of [(BzTATC)Zn(Et)][BF₄] (5)

5 was prepared according to the manner described for **4b** except BzTATC (0.22 g, 0.81 mmol) instead of Bz₃TAC, **2a** (0.22 g, 0.81 mmol) and diethylzinc in hexane (1 M, 0.17 g, 0.81 mmol) were used.

Anal. Found: C, 49.70; H, 6.66; N, 9.06. C₁₉H₃₀N₃BF₄Zn Calc.: C, 50.41; H, 6.68; N, 9.28%. M.p. 152 °C. ¹H NMR (200 MHz, CDCl₃): δ (ppm) 0.59 (q, J [HH] = 8.0 Hz, 2H, Zn-CH₂-CH₃), 1.20 (t, J [HH] = 8.0 Hz, 3H, Zn-CH₂-CH₃), 1.96 (m, 6H, CH₂-CH₂-CH₂), 2.9 (m, 6H, N-CH_{endo}H_{exo}-CH₂), 3.3 (m, 6H, N-CH_{endo}H_{exo}-CH₂), 3.63 (s, 2H, C-CH₂-C₆H₅), 7.15–7.60 (m, ca. 5H, CH₂-C₆H₅). ¹³C NMR (50.29 MHz, CDCl₃): δ (ppm) 1.7 (Zn-CH₂-CH₃), 11.5 (Zn-CH₂-CH₃), 25.2 (CH₂-CH₂-CH₂), 26.3 (C-CH₂-C₆H₅), 48.7 (N-CH₂-CH₂), 90.9 ((N)₃-C-CH₂), 128.9 (C₄), 128.9 (C_{2/6}), 132.5 (C_{3/5}), 133.8 (C₁). IR (KBr): ν (intensity) 462(m), 478(m), 494(m), 520(m), 536(m), 547(m), 647(m), 711(s), 768(m), 964(m), 998(s), 1003(s), 1027(s), 1056(s), 1075(s), 1144(s), 1163(m), 1177(m), 1184(m), 1201(m), 1214(m), 1230(m), 1273(m), 1284(m), 1294(m), 1327(m), 1333(m), 1357(m), 1379(m), 1389(m), 1429(m), 1441(m), 1455(m), 1466(m), 1485(m), 1496(m), 1578(s), 2829(s), 2864(m), 2925(m), 2935(m), 3342(m).

3.13. X-ray diffraction analysis of **6**

Data collection was carried out with an Enraf-Nonius CAD-4 automatic diffractometer, controlled by a PC and fitted with a low-temperature equipment. The cell parameters were obtained from the angles of 25 reflections in the range 10.0° < 2 θ < 20.0°. Reflections were scanned with variable scan time, depending on intensities, with 2/3 of the time used for scanning the peak and 1/6 for measuring each of the left and right background. The intensities of three check reflections monitored after 2 h showed only statistical fluctuations during the course of the data collection. The crystal orientation was checked every 200 intensity measurements by scanning three reflections. A new orientation matrix was automatically calculated from a list of 25

recentered reflections if the angular change was greater than 0.1%. The raw data were corrected for Lorentz polarization and absorption effects [21].

Refinement in space group *P* $\bar{1}$ was successful. The structures were solved with direct methods (SHELXS 86 [22]) and refined by full-matrix least-squares using SHELXL 93 [23], which minimizes R_w^2 (based on F^2). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated in idealized positions (C–H 0.96 Å, $U_{iso} = 0.08$ Å²). Scattering factors were taken from Refs. [24–26]. After all atoms were added to the model of the structure, an empirical absorption correction was applied (DIFABS [27]; min. and max. correction factors 0.578 and 1.202). Final residuals of least-squares $R = 5.7\%$.

Data reduction was performed using the PC software package [21]. All other calculations were undertaken with SHELXL 93 [23]. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-391007, the names of the authors and the journal citation.

3.14. Molecular mechanics calculations of **3d** and **4e**

The structure models of cations of **3d** and **4e** (shown in Fig. 4) were estimated using a molecular mechanics program [29] and parameters from the literature [30,31]. To calculate the models the following parameters were fixed: (a) the bond lengths and angles in the triazacyclohexane ring to averaged values obtained from X-ray structures [1,2,17] (C_{ring}-N 147.0 pm, C_{benz}-N 149.0 pm, C_{ring}-N-C_{ring} 109.0°, N-C_{ring}-N 105.6°), (b) the N-Zn bond lengths to 217 pm, (c) the Zn-C_{CH₂} bond length to 195 pm, (d) the torsion angles Zn-N-C_{benz}-C₁ to 0° and 180° and (e) the H_{endo}-C_{ring}-H_{exo} angle to 113°. The expected intensities $I_{calc}(H_A-H_B)$ of a cross-peak between two hydrogen atoms A and B were obtained by summation $1000/(r_{A-B})^6$ of all distances r_{A-B} existing in the molecule and scaling to the value of 100 for H_{endo}-H_{exo} cross-peak intensity.

4. Supplementary material available

Crystallographic data of **6**, lists of coordinates with isotropic displacement factors and anisotropic temperature factors of non-hydrogen atoms, a list of coordinates of hydrogen atoms as well as tables of bond lengths and angles (4 pages) have been deposited. Furthermore, calculated atom positions of **3d** and **4e** as well as X-ray structure data of [(FBz₃TAC)₂Zn][BF₄]₂ are available. Ordering information can be obtained from the authors.

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. R.D. Köhn thanks the Deutsche Forschungsgemeinschaft for a Habilitation Fellowship and Professor H. Schumann for support of this work.

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