Polyhedron 29 (2010) 1399–1404

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Unsymmetrically substituted triazacyclohexanes and their chromium complexes

Saïda Latreche [a], Abdelhamid Mousser [b], Gabriele Kociok-Köhn [c], Randolf D. Köhn [c,*], Frank Schaper [d,*]

[a] Département de chimie, Université Tébessa, 12000 Tébessa, Algeria
[b] Département de chimie, Université Montouri Constantine, 25000 Constantine, Algeria
[c] Department of Chemistry, University of Bath, Bath BA2 7AY, UK
[d] Département de chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7

ARTICLE INFO

*Article history:*
Received 1 November 2009
Accepted 6 January 2010
Available online 28 January 2010

*Keywords:*
Triazacyclohexane
Chromium complexes
Chromium(III)
Selective crystallisation

ABSTRACT

The unsymmetrically N-substituted N,N′-$Ar_2$-N″-R-1,3,5-triazacyclohexanes **1**–**4** (Ar = *ortho*- or *para*-fluorophenyl, *R* = *n*- or *iso*-propyl) can be obtained in good yields from a one-step condensation reaction with excess amine. Solid state structures of **1**–**4** resemble closely those of their triaryl-substituted analogues. The condensation reaction to **4** was looked at by detailed NMR investigations and revealed that amine/aniline exchange is occurring in solutions containing free aniline even at ambient conditions setting up an equilibrium between all possible symmetrical and unsymmetrical triazacylcohexanes. Selective crystallisation of **4** from the solution drives the reaction to high yields of **4**. Complexes **1**–**4** react readily with $CrCl_3$ or $CrCl_3(THF)_3$ to form the corresponding $CrCl_3$ complexes. The complexes are insoluble in non-polar solvents and decompose under decomplexation in coordinating solvents.



## 1. Introduction

1,3,5-Triazacyclohexanes (TAC) are tripodal ligands, which tend to adopt a *fac*-coordination in octahedral metal complexes. In this they resemble their triazacyclononane analogues, but are synthetically more easily accessible by simple condensation from primary amines and formaldehyde. With the exception of recent examples of $Ph_3$TAC-complexes of W(0) [1], their metal complexes have so far been restricted to triazacyclohexanes (TAC) ligands carrying three aliphatic substituents. We have previously investigated the coordination of aryl-substituted TACs (Ar = *ortho*-$C_6H_4F$, *para*-$C_6H_4F$, *para*-anisyl, and *para*-tolyl) to $CrCl_3$ as part of the investigations into the coordination chemistry of N-substituted 1,3,5-triazacyclohexanes undertaken in the Köhn group [2–6] and found that the purple complexes formed upon those reactions are extremely sensitive to moisture, insoluble in non-coordinating solvents and rapidly dissolve in coordinating solvents under decomplexation of the TAC ligand [7]. We thus decided to investigate the chemistry of unsymmetrically substituted TAC ligands, carrying aliphatic as well as aromatic substituents.

## 2. Results and discussion

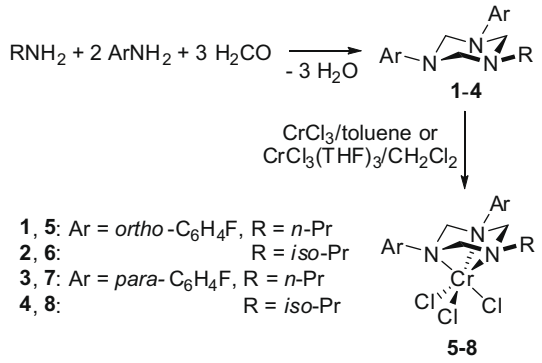
### 2.1. Ligand syntheses

Reactions of formaldehyde with equimolar mixtures of primary amines and anilines tend to give triaryl-substituted TACs as the major products, seemingly indicating a higher reactivity of anilines in TAC formation. Analytically pure, unsymmetrically substituted ligands can be isolated, however, in greater than 50% yield from the product mixtures obtained by reactions of a 2:1 mixture of primary amine:aniline with 1 equiv. of formaldehyde per equivalent of $NH_2$ group (**1** and **3** in Scheme 1). When the amount of formaldehyde is limited to the amount required for the desired product (about 0.5 equiv. per $NH_2$ group) the yield could be raised to 73% and 91% for **2** and **4**, respectively. The bisarylalkyl substituted triazacyclohexanes crystallise from the reaction mixture either during the reaction or from a cooled hexane solution and can therefore be obtained analytically pure. *Ortho*- and *para*-fluoro-substituted anilines were employed to utilise the high sensitivity and resolution of $^{19}$F NMR for the analysis product mixtures and complexes [8].

Crystals of **4**, suitable for an X-ray diffraction study, were obtained by slow diffusion of hexane into a dichloromethane solution of the ligand (Fig. 1). Preliminary results of the crystal structure determinations of **1**–**3** have been reported independently [9–11] and we will focus here on similarities and differences between ligands **1**–**4**. All four triazacylcohexane ligands adopt the diaxial-equatorial chair conformation typically observed in most aryl-substituted and all mono-fluorophenyl-substituted triazacyclohexanes in the solid state [12]. The alkyl substituent in **1**–**4** occupies the equatorial position, indicating higher 1,4-interactions for alkyl than for aryl substituents. The $C_{ipso}$–$C_{ipso}$ distances of 3.22–3.30 Å between the phenyl-substituents (Table 1) are notably shorter than the optimal π-stacking distance expected for a sandwiched or parallel-displaced benzene dimer [13,14]. Consequently, the aromatic rings are angled away from each other with angles

* Corresponding authors.
*E-mail addresses:* r.d.kohn@bath.ac.uk (R.D. Köhn), Frank.Schaper@umontreal.ca (F. Schaper).

0277-5387/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.01.008




**Scheme 1.**

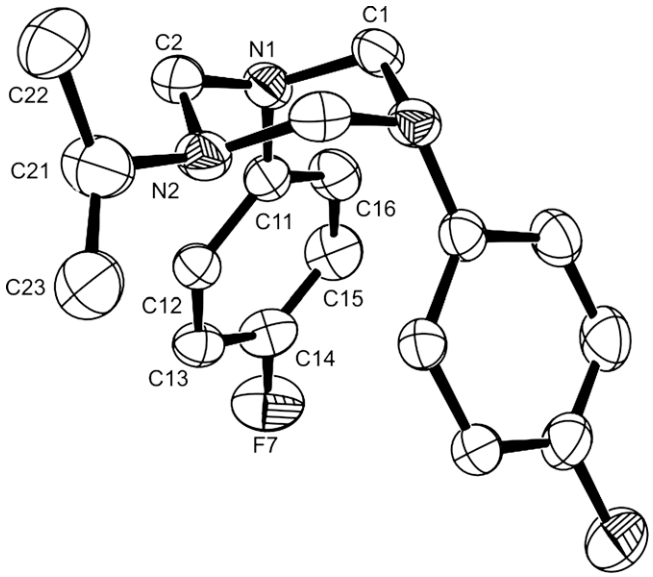



**Fig. 1.** Crystal structure of ligand **4**. Hydrogen atoms and the second disordered site for C23 omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

between their mean planes of 33–44° and $C_{para}$–$C_{para}$ distances approx. 2 Å longer than the distance of the respective *ipso*-carbon atoms. Despite their V-like conformation, the rings remain surprisingly coplanar, with tilt-angles of less than 10° (Table 1). In general, TAC **1**–**4** show identical structures with insignificant differences in bond lengths and with close resemblance to the structures of their tris(monofluorophenyl)-substituted analogues.

A DFT calculation on the structure of **4** reproduces the geometry well except for a larger repulsion between the aryl groups ($C_{ipso}$–$C_{ipso}$ 3.56 and $C_{para}$–$C_{para}$ 6.08 Å). DFT is known to underestimate long-range van der Waals interactions and introduction of Grimme's semiempirical van der Waals correction [15] to the DFT calculation optimises to a structure with much closer aryl groups ($C_{ipso}$–$C_{ipso}$ 3.16 and $C_{para}$–$C_{para}$ 4.52 Å) similar to the observed contacts. Thus, an attractive van der Waals interaction between the aryl groups is responsible for the stability of the conformation found in **1**–**4**.

### 2.2. Selectivity in ligand synthesis

The high yield for **1**–**4** from reaction mixtures containing very different aniline to amine ratios (1:2 rather than 2:1) was surprising given that mixtures of two different amines tend to result in roughly statistical mixtures of unsymmetrically substituted TACs [16–20]. Therefore we investigated the formation of **4** in more detail. When all volatiles are removed from the reaction solution, the NMR spectrum showed the oily residue to contain mostly **4**, but also significant amounts of free aniline, all other combinations of aryl and *i*Pr substituted triazacyclohexanes and some products assigned to intermediates containing ring-opened, iminium cations (*vide supra*).

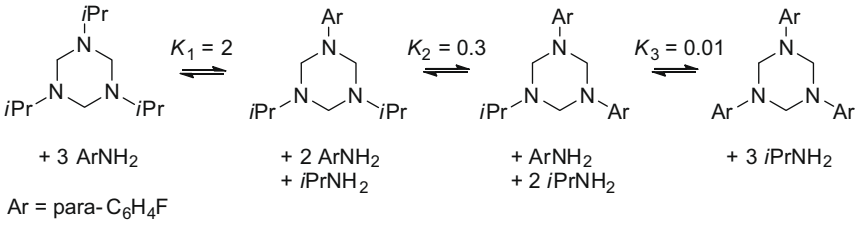
Addition of *p*-fluoroaniline to the NMR sample resulted in a significant change of the product distribution favouring the more aniline rich products with release of free $i\text{PrNH}_2$ within minutes. A new equilibrium distribution is reached after a few days. The same redistribution can be observed when *p*-fluoroaniline is added to a $CDCl_3$ solution of $i\text{Pr}_3$TAC. Fast initial change is leading to equilibrium distribution after about one week. The rate of redistribution is influenced by the acidity of the solution. While the equilibration is expected to follow complex kinetics the decrease of the free aniline concentration follows approximately a first order exponential rate law and can be used as an estimate of the rate. A wet or even acid containing sample shows much faster reaction than a solution containing base ($NEt_3$). Commercial wet aniline (a few% water) had a half life toward equilibrium of about 10 min. Addition of 50 mol% $NEt_3$ per amine slowed down the reaction to about 130 min half life, while the equilibrium was reached by the time the first NMR spectrum was taken upon addition of 4 mol% triflic acid or extra water. Dried aniline ($MgSO_4$) showed much slower reaction (half life of 500 min, details in Supporting material). This fast exchange by the addition of aniline was unexpected as previous unpublished results in the Köhn group showed amine exchange with triazacylohexanes taking place at 100 °C or more.

Similarly, isolated (>95 wt.% pure) **4** showed significant redistribution with 1.4 equiv. *p*-fluoro-aniline within hours and reached equilibrium within two days containing $Ar_3$TAC, $Ar_2i\text{PrTAC}$ and $Ar i\text{Pr}_2$TAC in a ratio of 1:33:8 besides free isopropyl amine, aniline and the side products/intermediates discussed below. Thus more isopropyl rich triazacyclohexanes are formed in the mixture upon addition of the aniline (remaining aniline fragments are found in

**Table 1**
Comparison of structural parameters (distances (Å), angles (°)) for TAC **1**–**4** and their symmetrically substituted analogues.[a]

| | 1 | 2 | 3 | 4 | ($o$-$^F$Ph$_3$)TAC[b] | ($p$-$^F$Ph$_3$)TAC[b] |
|---|---|---|---|---|---|---|
| N1–C11 | 1.422(3)–1.425(3) | 1.413(8)–1.420(8) | 1.421(3)–1.422(4) | 1.420(2) | 1.412–1.417 | 1.424 |
| N1–C2 | 1.437(3)–1.478(3) | 1.449(3)–1.46(2) | 1.451(4)–1.474(3) | 1.452(2) | 1.443–1.479 | 1.442–1.476 |
| C11–C11A | 3.22 | 3.25 | 3.30 | 3.30 | 3.28 | 3.38 |
| C14–C14A | 4.83 | 5.04 | 5.33 | 5.16 | 6.05 | 5.03 |
| Ph–Ph[c] | 33 | 39 | 44 | 40 | 58 | 40 |
| Tilt angle[d] | 4 | 9 | 7 | 1 | 10 | 2 |

Crystal structures of TACs **1**–**3** were subject of preliminary communications.
[a] Numeration as shown in Fig. 1 for TAC **4**.
[b] See Ref. [12].
[c] Angle between the mean planes (C11–C16, F7) and (C11A–C16A, F7A).
[d] Average deviation of C12–C16–C16A and C16–C12–C12A from 90°.




**Scheme 2.** Approximate equilibrium constants for the differently substituted triazacyclohexanes.

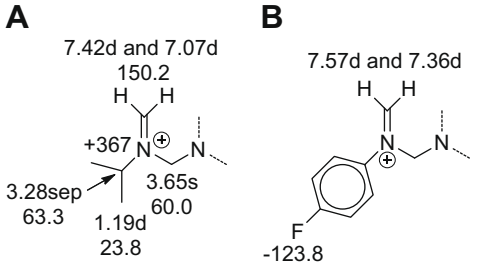
the side products) which therefore acts foremost as a catalyst to reach the equilibrium composition.

The final equilibrium concentrations allow an approximate determination of equilibrium constants for the possible mixed triazacyclohexanes in $CDCl_3$ as shown in Scheme 2.

Thus, **4** (or generally aniline versus isopropylamine) is not favoured by thermodynamics in this series. Indeed, directly observed NMR spectra of the EtOH/water reaction solution in the ratio of $ArNH_2$:*i*PrNH$_2$:$CH_2O$ of 1:2:2 showed $Ar_3TAC$, $Ar_2$*i*PrTAC (**4**), Ar*i*Pr$_2$TAC and *i*Pr$_3$TAC (Ar = *p*-fluoroaniline) in the ratio of 0:3:34:24, besides excess amine, aniline and some side products, before the final product **4** started to crystallise from the solution. This corresponds to similar equilibrium constants of $K_1 = 1.0$ and $K_2 = 0.1$ in ethanol/water. Crystallisation from the reaction solution and vacuum removal of excess isopropyl amine shifted the equilibrium towards **4** and resulted in a product highly enriched in **4** in high yield. Once all free aniline is used up or removed, solutions of **4** in $CDCl_3$ are stable.

The observed acid catalysis led us to propose the mechanism shown in Scheme 3 for the exchange of N-substituents in triazacyclohexanes for the first aniline. An initial DFT exploration at the BP86/SVP level indicates much easier ring-opening after protonation with barriers of less than 20 kcal/mol.

Additional support for this mechanism is gained from intermediates or side products observed during the formation of **4**. A characteristic pair of doublets was found above 7 ppm in $^1$H NMR spectra, which were correlated by HMBC experiments to two far down-field shifted signals in $^{13}$C and $^{15}$N NMR spectra (150 and 367 ppm, respectively; Scheme 4, Supplementary material). Long range HMBC correlation experiments link these signals to an isopropyl and a methylene group and they were consequently assigned to the iminium species **A** in Scheme 4. The remaining NMR signals are likely to be similar to the dominant TAC signals and could not be identified. A second pair of doublets, present in lower concentrations, was tentatively assigned to iminium species **B** carrying a fluorophenyl group. These ring-opened intermediates are observed in small concentrations throughout the reactions

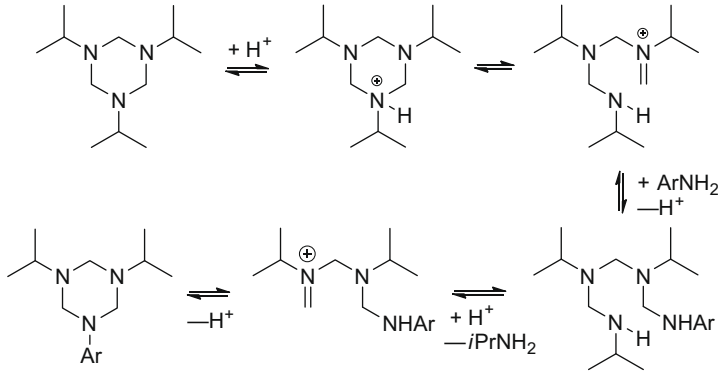



**Scheme 4.** Characteristic NMR signals for terminal groups in ring-opened intermediates ($^1$H with, hetero nuclei without multiplicity). Assignments confirmed by HMBC experiments.

while the TAC concentrations change towards their equilibrium. Other major side products were found to be aminals, mostly $(ArNH)_2CH_2$ and small amounts of ArNHCH$_2$NH*i*Pr. The $^1$H NMR resonances of the former (see Supplementary material) had been confirmed as the major product of the direct reaction of formaldehyde with 2 equiv. of *p*-fluoroaniline [21].

### 2.3. Complex syntheses

Addition of **1** or **2** to $CrCl_3(THF)_3$ in dichloromethane at room temperature or of **3** or **4** to anhydrous $CrCl_3$ in hot toluene at 110 °C yielded the corresponding purple coloured $CrCl_3$ complexes **5**–**8** in good to moderate yields. The isolated complexes gave correct elemental analyses, with the exception of **6** which may contain a $CH_2Cl_2$ solvent molecule. Analyses of the ether phase used to separate the unreacted ligand from the formed complex showed only the presence of unchanged ligand, indicating that TAC isomerisation does not take place under the conditions employed here. As previously observed for their $(Ar_3TAC)CrCl_3$ analogues, complexes **5**–**8** proved to be insoluble in non-coordinating solvents, such as toluene, dichloromethane and ether, even at elevated temperatures, which prevented further purification of **6** and characterizations of **5**–**8** by $^{19}$F




**Scheme 3.** Proposed mechanism for the exchange via ring-opened intermediates.

**Table 2**
Observed and selected calculated IR frequencies in $cm^{-1}$ for **4** and **8** (intensity, $^{15}N$ isotope shift for **8**).

| Exp of **4** | Calc. of **4** | Exp of **8** | Calc. of **8** |
|---|---|---|---|
| 517 | 505(28) | 522s | 519(17, 5) |
| 530 | 527(30) | 527s | 529(26, 0) |
| 561w | 547(2) | 542w | 552(36, 2) |
| | 573(2) | | |
| 582w | 581(4) | 554 | 568(1, 4) |
| 619 | 621(27) | 573w | 585(7, 4) |
| 643w | 640(37) | 639 | 327(1, 0) |
| 700w | 694(5) | 713w | 704(4, 0) |
| | 697(23) | | 708(4, 0) |
| | 700(5) | | |
| 727 | 720(8) | 746w | 748(42, 8) |
| 818s | 813(131) | 768w | 772(8, 7) |
| | | | 792(7, 0) |
| 826s | 823(36) | 836s | 828(79, 0) |
| 852w | | | |
| 877 | 866(52) | | |

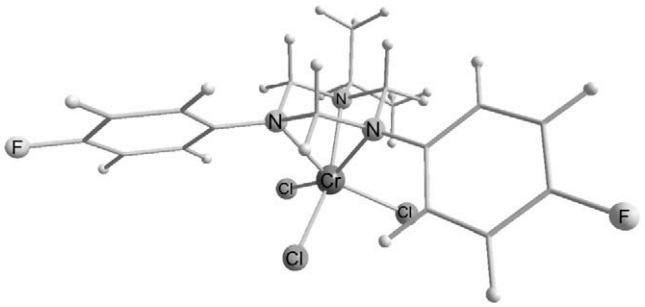



**Fig. 2.** DFT calculated structure of **8**.

NMR or UV–Vis spectroscopy. Solubilisation in polar solvents such as THF or acetonitrile led to decomplexation of the TAC ligand and, despite repeated attempts, only crystals of the TAC ligand or of $CrCl_3(THF)_3$ were obtained in recrystallisation experiments. However, the limited solubility in dry dichloromethane allowed analysis of **8** by ESI–MS and showed a weak signal for an ammonium adduct with the correct high resolution mass and isotope pattern. IR spectra of both the ligand **4** and the complex **8** showed significant differences in the region just above 500 $cm^{-1}$ were rocking vibrations of the triazacyclohexanes are observed in analogy to those observed for trioxane at 469 and 521 $cm^{-1}$ [22]. This assignment can be confirmed by DFT calculated IR spectra where significant N involvement is indicated by the calculated $^{15}N$ isotope shifts as shown in Table 2. Such vibrations also involve N–Cr stretching and are therefore an indication of ligand bonding.

Therefore the structure and bonding of **8** was further investigated by DFT methods which were found to reproduce crystallographic Cr-ligand distances within 2 pm for trialkylsubstituted $CrCl_3$ complexes. Fig. 2 shows the calculated structure of **8**. The Cr–N(aniline) bonds (2.18 Å) are significantly longer than the Cr–N*i*Pr bond (2.15 Å) also when compared to calculated $iPr_3TACCrCl_3$ (2.14 Å). This result is supported by the experimental observation that aniline based triazacyclohexanes undergo ligand substitution with donor solvent while all-alkyl substituted complexes are inert.

## 3. Conclusions

Unsymmetrical TAC ligands with one alkyl and two aryl substituents can be prepared in good yields employing an excess of the alkyl amine. Detailed NMR studies have shown that the high yield is due to favourable crystallisation behaviour coupled with fast redistribution of N-substituents catalysed by free aniline and high volatility of the propylamines during work-up under vacuum. Under homogeneous conditions alkyl substituents are favoured thermodynamically over aromatic substituents in triazacyclohexanes. The new ligands readily form $CrCl_3$ complexes, which are, however, insoluble in unpolar solvents and unstable against decomplexation in polar solvents. Thus, aniline based triazacyclohexanes are much less suitable for coordination chemistry than their trialkyl analogues.

## 4. Experimental

All manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk-line or glove box techniques. Solvents were dried according to standard methods and collected by distillation or dried by passage through activated aluminum oxide and de-oxygenated by repeated extraction with nitrogen. $CrCl_3(THF)_3$ was prepared according to literature methods [23]. $^1H$, $^{13}C$, $^{19}F$ and $^{15}N$ NMR spectra were recorded on Bruker MXR-300, ARX-400, Acance-400 or -500 spectrometers and referenced to residual solvent ($CHCl_3$: $\delta$ 7.26, $CDCl_3$: $\delta$ 77.00), to internal TMS when added or external $CFCl_3$ (0 ppm for $^{19}F$) or $MeNO_2$ (381.5 ppm rel. to liq. ammonia). $^{15}N$ NMR shifts were obtained be $^1H$–15N HMBC using a pulsed field gradient for long range coupling of 7 Hz. Elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal). High resolution electrospray mass spectra were obtained on a Bruker TOF instrument in dichlormethane solution. Isotope pattern match the assigned ion and only the monoisotopic signal is stated.

### 4.1. 1-Pr-3,5-bis(o-$C_6H_4F$)-1,3,5-triazacyclohexane (1)

*n*-Propylamine (3.95 mL, 48 mmol) and *o*-fluoroaniline (2.32 mL, 24 mmol) were dissolved in ethanol (20 mL). An aqueous solution of formaldehyde in water (37%, 5.4 mL, 72 mmol) was added under stirring. The reaction mixture was kept at room temperature for 2 days. The solution was concentrated to half its volume and left for another day, after which the remaining solvent was evaporated. Recrystallisation from hexane at −20 °C yielded 2.6 g (68%) of colorless microcrystals. *Anal.* Calc. for $C_{18}H_{21}N_3F_2$ (317.38): C, 68.12; H, 6.67; N, 13.24. Found: C, 67.51; H, 6.41; N, 12.93%. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 7.28–6.85 (m, 8H, Ph), 4.73 (s, 2H, –N(Ar)C*H*$_2$N(Ar)–), 4.29 (s, 4H, –N(Pr)C*H*$_2$N(Ar)–), 2.61 (t, 2H, NC*H*$_2$Et), 1.54–1.42 (m, 2H, NCH$_2$C*H*$_2$Me), 0.86 (*t*, 3H, NCH$_2$CH$_2$*Me*). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 155.6 (d, $J$ = 245 Hz, 2C, $C_{Ar}F$), 137.5 (d, $J$ = 9 Hz, 2C, –NAr), 124.5 (d, $J$ = 4 Hz, 2C, Ar), 122.7 (d, $J$ = 8 Hz, 2C, Ar), 120.4 (d, $J$ = 3 Hz, 2C, Ar), 115.8 (d, $J$ = 21 Hz, 4C, Ar), 71.2 (d, $J$ = 4 Hz, 2C, –N(Pr)*C*H$_2$N(Ar)–), 69.5 (t, $J$ = 3 Hz, 1C, –N(Ar)CH$_2$N(Ar)–), 54.1 (s, 1C, NCH$_2$Et), 20.9 (s, 1C, NCH$_2$CH$_2$Me), 11.9 (s, 1C, NCH$_2$CH$_2$*Me*). $^{19}F$ NMR ($CDCl_3$, 282 MHz): $\delta$ −125.1 (m).

### 4.2. 1-iPr-3,5-bis(o-$C_6H_4F$)-1,3,5-triazacyclohexane (2)

Isopropylamine (4.10 mL, 48 mmol) and *ortho*-fluoroaniline (2.27 mL, 24 mmol) were dissolved in ethanol (20 mL). An aqueous solution of formaldehyde in water (37%, 2.7 mL, 36 mmol) was added under stirring. The reaction mixture was kept at room temperature for 8 h. The solution was concentrated to half its volume and left for another day, after which the remaining solvent was evaporated. Recrystallisation from hexane at −20 °C yielded 2.78 g (73%) of colorless microcrystals. *Anal.* Calc. for $C_{18}H_{21}N_3F_2$: C, 68.12; H, 6.67; N, 13.24. Found: C, 68.83; H, 6.20; N, 13.37%. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 7.30–6.83 (m, 8H, Ar), 4.70 (s, 2H, –N(Ar)C*H*$_2$N(Ar)–), 4.37 (s, 4H, –N(Pr)C*H*$_2$N(Ar)–), 3.12 (sep.,

$J$ = 6 Hz, 1H, –C*H*Me$_2$), 1.07 (d, $J$ = 6 Hz, 6H, –CH*Me*$_2$). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 155.6 (d, $J$ = 245 Hz, 2C, $C_{Ar}F$), 137.5 (d, $J$ = 9 Hz, 2C, $C_{Ar}N$), 124.4 (d, $J$ = 4 Hz, 2C, Ar), 122.7 (d, $J$ = 8 Hz, 2C, Ar), 120.6 (d, $J$ = 3 Hz, 2C, Ar), 115.8 (d, $J$ = 21 Hz, 2C, Ar), 69.9 (t, $J$ = 4 Hz, 1C, –N(Ar)C$H_2$N(Ar)–), 68.4 (d, $J$ = 3 Hz, 2C, –N(Pr)C$H_2$-N(Ar)–), 49.0 (s, 1C, –CHMe$_2$), 20.4 (s, 2C, –CH*Me*$_2$). $^{19}$F NMR ($CDCl_3$, 282 MHz): $\delta$ −125.1 (m).

### 4.3. 1-Pr-3,5-bis(p-$C_6H_4$)F-1,3,5-triazacyclohexane (3)

*n*-Propylamine (7.9 mL, 96 mmol) and *p*-fluoroaniline (4.54 mL, 48 mmol) were dissolved in ethanol (20 mL). An aqueous solution of formaldehyde in water (37%, 10.8 mL, 144 mmol) was added under stirring. The reaction mixture was kept at room temperature for 1 days. The resulting precipitate was filtered and dried to yield the required product. 4.0 g (52%). *Anal.* Calc. for $C_{18}H_{21}N_3F_2$: C, 68.12; H, 6.67; N, 13.24. Found: C, 67.87; H, 6.56; N, 13.06%. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 6.90–6.84 (m, 8H, Ph), 4.63 (s, 2H, –N(Ar)C$H_2$N(Ar)–), 4.18 (s, 4H, –N(Pr)C$H_2$N(Ar)–), 2.50 (t, $J$ = 7 Hz, 2H, NC$H_2$Et), 1.47 (sex., $J$ = 7 Hz, 2H, NCH$_2$C$H_2$Me), 0.86 (t, $J$ = 7 Hz, 3H, NCH$_2$CH$_2$*Me*). $^{13}$C NMR ($CDCl_3$, 75 MHZ): $\delta$ 157.6 (d, $J$ = 240 Hz, 2C, $C_{Ar}F$), 145.8 (s, 2C, $C_{Ar}N$), 119.5 (d, $J$ = 8 Hz, 4C, Ar), 115.6 (d, $J$ = 22 Hz, 4C, Ar), 72.0 (s, 2C, –N(Pr)C$H_2$N(Ar)–), 70.3 (s, 1C, –N(Ar)C$H_2$N(Ar)–), 54.1 (s, 1C, NC$H_2$Et), 20.82 (s, 1C, NCH$_2$C$H_2$-Me), 11.9 (s, 2C, NCH$_2$CH$_2$*Me*). $^{19}$F NMR ($CDCl_3$, 282 MHz): $\delta$ −124.6 (m).

### 4.4. 1-iPr-3,5-bis(p-$C_6H_4F$)-1,3,5-triazacyclohexane (4)

#### 4.4.1. Experiment A

Isopropylamine (4.09 mL, 48 mmol) and *p*-fluoroaniline (2.27 mL, 24 mmol) were dissolved in ethanol (20 mL). An aqueous solution of formaldehyde in water (37%, 2.7 mL, 36 mmol) was added under stirring. The reaction mixture was kept at room temperature for 8 h. The resulting precipitate was filtered and dried to yield the required product after recrystallisation from hexane 3.49 g (91%). *Anal.* Calc. for $C_{18}H_{21}N_3F_2$: C, 68.12; H, 6.67; N, 13.24. Found: C, 68.09; H, 6.46; N, 13.10%. $^1$H NMR ($CDCl_3$, 400 MHZ): $\delta$ 6.95–6.85 (m, 8H, Ph), 4.58 (s, 2H, –N(Ar)C$H_2$N(Ar)–), 4.24 (s, 4H, –N(*i*Pr)C$H_2$N(Ar)–), 3.00 (sep., $J$ = 7 Hz, 1H, –C*H*Me$_2$), 1.07 (d, $J$ = 6 Hz, 6H, –CH*Me*$_2$). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 157.6 (d, $J$ = 242 Hz, 2C, $C_{Ar}F$), 145.7 (s, 2C, $C_{Ar}N$), 119.6 (d, $J$ = 8 Hz, 4C, Ar), 115.6 (d, $J$ = 22 Hz, 4C, Ar), 70.9 (s, 1C, –N(Ar)C$H_2$-N(Ar)–), 69.1 (s, 2C, –N(*i*Pr)C$H_2$N(Ar)–), 49.2 (s, 1C, –CHMe$_2$), 18.5 (s, 2C, –CH*Me*$_2$). $^{19}$F NMR ($CDCl_3$, 282 MHz): $\delta$ *−125.2* (m).

#### 4.4.2. Experiment B

Isopropylamine (3.5 mL, 41 mmol) and *p*-fluoroaniline (2.26 g freshly vacuum-transfered, 20.3 mmol) were dissolved in ethanol (16 mL). An aqueous solution of formaldehyde in water (37%, 2.3 mL, 31 mmol) was added under stirring. The reaction mixture was kept at room temperature for 15 h. Even cooling to −20 °C for 1 day gave no precipitate. The solvent was removed in vacuo and trapped in liquid nitrogen and contained *i*PrNH$_2$ and *i*Pr$_3$TAC (about 2:1 by weight) besides EtOH and water by NMR. The remaining oil was analysed by NMR (containing 48 mol% (25 wt.%) "ArNH$_2$" (13:8:1 mixture of the aniline and two aniline like compounds with overlapping aromatic $^1$H signals and $^{19}$F signals at −126.9, −126.4 and −127.3 ppm, respectively), 0.2 mol% (0.3 wt.%) Ar$_3$TAC, 41 mol% (61 wt.%) Ar$_2$*i*PrTAC, 13 mol% (4 wt.%) Ar*i*Pr$_2$TAC and 1 mol% (1 wt.%) *i*Pr$_3$TAC) and then recrystallised from hexane to obtain nearly pure **4** (only significant impurity is ArNH$_2$ at <10%). Addition of free aniline identified the NMR signals for ArNH$_2$ but also rearranged the product mixture within minutes to release free *i*PrNH$_2$ with a loss of *i*Pr$_3$TAC and Ar*i*Pr$_2$TAC forming more Ar$_2$*i*PrTAC and some Ar$_3$TAC.

### 4.5. {Pr(o-$C_6H_4F$)$_2$TAC}$CrCl_3$ (5)

TAC **1** (41 mg, 0.11 mmol) and $CrCl_3(THF)_3$ (35 mg, 0.11 mmol) were stirred in $CH_2Cl_2$ (2 mL) for 20 h. Filtration, repeated washings with ether and drying in vacuo resulted in 3.0 mg (57%) of a purple solid. *Anal.* Calc. for $C_{18}H_{21}N_3F_2CrCl_3$: C, 45.44; H, 4.45; N, 8.83. Found: C, 45.04; H, 4.3; N, 8.91.

### 4.6. {iso-Pr(o-$C_6H_4F$)$_2$TAC}$CrCl_3$ (6)

TAC **2** (1.8 g, 5.68 mmol) and $CrCl_3(THF)_3$ (1.6 g, 4.28 mmol) were stirred in $CH_2Cl_2$ (20 mL) for 20 h. Filtration, repeated washings with ether and drying in vacuo resulted in 0.98 g (48%) of a purple solid. *Anal.* Calc. for $C_{18}H_{21}N_3F_2CrCl_3$: C, 45.44; H, 4.45; N, 8.83. Found: C, 40.04; H, 4.58; N, 8.54%. (*Anal.* Calc. for $C_{18}H_{21}N_3F_2CrCl_3{\cdot}CH_2Cl_2$: C, 40.70; H, 4.13; N, 7.49%.)

### 4.7. {Pr(p-$C_6H_4F$)$_2$TAC}$CrCl_3$ (7)

Anhydrous $CrCl_3$ (100 mg, 0.63 mmol) and a catalytic amount of Zn powder were suspended in toluene (15 mL). A solution of **3** (180 mg, 0.57 mmol) in toluene was added and the reaction mixture was heated to reflux for 12 h. After cooling to room temperature, the resulting suspension was filtered and the precipitate washed with ether, to yield after drying 147 mg (54%) of a purple solid. *Anal.* Calc. for $C_{18}H_{21}N_3F_2CrCl_3$: C, 45.44; H, 4.45; N, 8.83. Found: C, 45.37; H, 4.10; N, 8.33%.

### 4.8. {iso-Pr(p-$C_6H_4F$)$_2$TAC}$CrCl_3$ (8)

Analogous to **7**, reaction of TAC **4** (0.45 g, 1.4 mmol) with $CrCl_3$ (0.20 g, 1.3 mmol), yielded **8** in 0.20 g (32%). *Anal.* Calc. for $C_{18}H_{21}N_3F_2CrCl_3$: C, 45.44; H, 4.45; N, 8.83. Found: C, 44.97; H, 4.80; N, 8.63%. A sample was suspended in dry dichloromethane, filtered and analysed by ESI-MS: $m/z$ 548.1157 (calc. for M + ($NC_4H_{12}$): 548.1140). The source of the ionising ammonium cation $NC_4H_{12}$ was in the spectrometer and was confirmed by the observation of the analogous cation derived from a dichloromethane solution of known (Octyl)$_3$TACCrCl$_3$ [2] at $m/z$ 654.3988 (calc. 654.3989).

### 4.9. Computational studies

All calculations have been performed with a development version of the ORCA electronic structure program version 2.7-00 [24] in combination with the split-valence (SV) and triple-$\zeta$ valence (TZV) basis sets developed by the Karlsruhe group that were supplemented with the appropriate polarization functions from the TurboMole library [25,26].[1] For the fitting basis sets in the RI-J treatment, the 'def2' fit bases optimized for the SV and TZV basis sets were used for DFT calculations, the standard integration grids of the ORCA package were used. The ORCA implementation of zero order relativistic correction (ZORA) and of a COSMO solvent model with infinite $\varepsilon$ was used for all calculations. All calculations were converged to $10^{-7}$ Eh in the total energy (ORCA keyword TightSCF). Maximum integration grid 7 was used for chromium. Grimme's van der Waals corrections were used. Minima and transition states were confirmed by numerical frequency calculations.

[1] Basis sets were obtained from the ftp server of the Karlsruhe quantum chemistry group, ftp.chemie.uni-karlsruhe.de/pub/basen.

**Table 3**
Crystal data and structure refinement parameters for **4**.

| | |
|---|---|
| Formula | $C_{18}H_{21}F_2N_3$ |
| Formula weight; $D_{calc}$ | 317.38; 1.288 |
| Crystal color and shape | colorless plate |
| Crystal size (mm) | 0.50 × 0.40 × 0.20 |
| Crystal System | orthorhombic |
| Space Group | Pcmn (62) |
| Unit cell dimensions | |
| $a$ (Å) | 6.3167(2) |
| $b$ (Å) | 13.4579(4) |
| $c$ (Å) | 19.2516(5) |
| $V$ (Å$^3$); Z | 1636.69(8); 4 |
| $D_{calc}$ (g/cm$^3$) | 1.288 |
| Absorption coefficient $\mu$ (mm$^{-1}$) | 0.093 |
| $F$(0 0 0) | 672 |
| $\theta$ (°)/completeness | 3.03–28.67/99.1% |
| Reflections collected/unique/$R_{int}$ | 20031/2172/0.0459 |
| Data/restraints/parameters | 2172/0/116 |
| Largest difference in peak and hole (e Å$^{-3}$) | 0.26 and −0.21 |
| Final $R$ indices [$I > 2\sigma(I)$][a] | $R_1$ = 0.053, w$R_2$ = 0.123 |
| $R$ indices (all data)[a] | $R_1$ = 0.064, w$R_2$ = 0.129 |
| Extinction coefficient[b] | 0.039(8) |
| Goodness-of-fit (GOF) on $F^2$ [c] | 1.109 |

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)]\}^{1/2}$.
[b] $F_c^* = kF_c[1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3 / \sin(2\theta)]^{-1/4}$ ($k$: overall sale factor).
[c] GOF = $S = \sum[w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$ ($n$: number of reflections, $p$: number of parameters).

### 4.10. X-ray diffraction studies

Intensity data were collected at 150 K on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo Kα radiation (0.71073 Å). Data were processed using the NONIUS Software [27]. Structure solution, followed by full-matrix least squares refinement was performed using the WINGX-1.70, SHELXS and SHELXL suite of programs throughout [28,29]. All non-hydrogen atoms were refined anisotropic, hydrogen atoms were refined on calculated positions using a riding model. Crystal parameters and details of the data collection, solution and refinement are summarised in Table 3.

## Acknowledgements

The authors thank the University of Bath and the Natural Sciences and Engineering Research Council of Canada for funding. S.L. was recipient of a Ph.D. stipend from the Algerian government.

## Appendix A. Supplementary data

CCDC 743924 contains the supplementary crystallographic data for **4**. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2, IEZ, UK; Fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.01. 008.

## References

[1] A.I. Kuramshin, E.V. Asafyeva, R.A. Cherkasov, Russ. J. Org. Chem. 41 (2005) 779.
[2] R.D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, Angew. Chem., Int. Ed. 39 (2000) 4337.
[3] R.D. Köhn, D. Smith, M.F. Mahon, M. Prinz, S. Mihan, G. Kociok-Köhn, J. Organomet. Chem. 683 (2003) 200.
[4] M. Haufe, R.D. Köhn, G. Kociok-Köhn, A.C. Filippou, Inorg. Chem. Commun. 1 (1998) 263.
[5] R.D. Köhn, G. Kociok-Köhn, Angew. Chem., Int. Ed. 33 (1994) 1877.
[6] R.D. Köhn, Z. Pan, G. Kociok-Köhn, M.F. Mahon, Dalton Trans. (2002) 2344.
[7] S. Latreche, R. Köhn, unpublished results.
[8] R.D. Köhn, M. Haufe, G. Kociok-Köhn, J. Am. Chem. Soc. 128 (2006) 10682.
[9] S. Latreche, A. Bouchemma, S. Bouacida, H. Mousser, A. Mousser, Acta Crystallogr., Sect. E 62 (2006) o4960.
[10] S. Latreche, A. Bouchemma, S. Bouacida, M. Bouhenguel, A. Mousser, Acta Crystallogr., Sect. E E62 (2006) o4676.
[11] S. Latreche, A. Bouchemma, S. Bouacida, M. Bouhenguel, A. Mousser, Acta Crystallogr., Sect. E 62 (2006) o4674.
[12] A. Bouchemma, P.H. McCabe, G.A. Sim, J. Chem. Soc., Perkin Trans. 2 (1989) 583.
[13] T. Dinadayalane, J. Leszczynski, Struct. Chem. 20 (2009) 11.
[14] E.C. Lee, D. Kim, P. Jurečka, P. Tarakeshwar, P. Hobza, K.S. Kim, J. Phys. Chem. A 111 (2007) 3446.
[15] S.J. Grimme, J. Comb. Chem. 27 (2006) 1787.
[16] Unpublished results.
[17] R.D. Köhn, Z. Pan, M.F. Mahon, G. Kociok-Köhn, J. Chem. Soc., Dalton Trans. (2003) 2269.
[18] S. Mihan, D. Lilge, G. Schweier, R. Köhn, G. Seifert, WO2000058369, 2000.
[19] S. Mihan, D. Lilge, G. Schweier, R. Köhn, G. Seifert, US277823, 2004.
[20] A. Flores-Parra, S.A. Sanchez-Ruiz, Heterocycles 51 (1999) 2079.
[21] E.C. Wagner, J. Org. Chem. 2 (1937) 157.
[22] M. Kobayashi, R. Iwamoto, H. Tadokoro, J. Chem. Phys. 44 (1966) 922.
[23] H. Heiss, W. Herwig, J. Org. Chem. 23 (1958) 1404.
[24] F. Neese, ORCA, an ab initio, Density Functional and Semi-empirical Program Package, University of Bonn, Germany, 2008.
[25] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571.
[26] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829.
[27] DENZO-SCALEPACK: Z. Otwinowski, W. Minor, Methods in Enzymology, in: C.W. Carter, R.M. Sweet (Eds.), Macromolecular Crystallography, vol. 276, Academic Press, 1997, p. 307.
[28] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[29] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.