Reactions of Dichloroperfluorocycloalkenes with Triazamacrocyclic Amines

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1,2-Dichlorotetrafluorocyclobutene (**A**) and 1,2-dichlorohexafluorocylopentene-1 (**B**) were reacted with triazamacrocyclic amines (1,4,8-triazacycloundecane (**1**) and 1,5,9-triazacyclo-dodecane (**2**)) at 80 °C in the presence of stoichiometric amounts of triethylamine in benzene. Cycloalkene **A** formed a 2:1 product **3** with **1** and a 3:1 product **4** with **2**. Cycloalkene **B** formed only 2:1 products **5** and **6** with **1** and **2**, respectively. The crystal structures of **3** and **4** were determined by single-crystal X-ray diffraction.

Introduction

The field of macrocyclic complexes has expanded tremendously during the past three decades. Tailor-made macrocyclic ligands can now be prepared by an astonishing variety of powerful synthetic methods.[1−17] Complexes with predetermined stabilities and spectroscopic, magnetic, and redox properties can be prepared by altering variables such as steric and electronic factors. Historically, tetrazamacrocycles of varying ring size and degrees of unsaturation were among the first azamacrocycles synthesized. Cyclam (1,4,8,11-tetrazacyclotetradecane) has played an important role in many different areas of inorganic chemistry. Numerous complexes have been prepared and structurally characterized, and their properties have been extensively studied. It is rather surprising that until 1978 only a limited number of tridentate macrocycles were known and their coordination chemistry[15,18] had received comparatively little attention. Tridentate macrocyclic ligands coordinate readily to metal ions producing stable complexes, many of which have unusual chemical and physical properties. In recent years it was shown that by introducing additional ligating groups into a macrocycle, its properties were modified and often more stable complexes could be formed. N-functionalized derivatives of azamacrocycles were readily synthesized and their coordination chemistry has been actively investigated.[8]

The series of cyclic triamines presents a nearly ideal system to study the properties of metal complexes which contain ligands with similar coordinative tendencies yet which progressively distort the stereochemical environment of the metal. Several investigations of metal complexes of cyclic triamines have appeared in the literature,[19−28] and the interest in these and similar cyclic compounds where one or more nitrogen atoms are replaced by other heteroatoms continued to grow. The extra stability of [9]aneN_3 complexes has been well documented,[20−22] and the work with the remaining congeners suggested that these cyclic amines behave similarly.

The tridentate macrocycle, 1,4,7-triazacyclononane, has become a common ligand in coordination chemistry owing to its selective facial coordination, high affinity for transition and main group metals, and its chemical stability and that of its complexes.[29] A large number of N-functionalized derivatives[29] have been prepared from the free triamine including sulfonates (e.g., $-CH_2CH_2SO_3H$), alcohols ($-CH_2CH_2OH$), phosphates ($-CH_2PO_3H_2$), amines ($-CH_2CH_2NH_2$ and $-CH_2Pyr$), and acetates ($-CH_2COOH$). Recently, the metal binding ligand **1** has been functionalized with three amino acids ($-CH_2CONHCH(CH_2Ph)CO_2Me)_2$ in order to construct a three-helix peptide bundle (3, R = 10−15 amino acid sequence).[29a]

One of the areas of study in this laboratory[30−33] and in others[34−37] is the synthesis and characterization of heterocyclic compounds with fluorine-containing substituents. Trifluoro-

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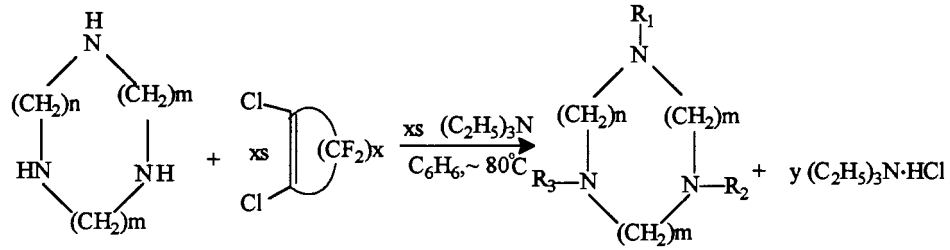
Scheme 1



1 (n = 2; m = 3)
2 (n = m =3)

A(x = 2)
B(x = 3)
(XS = excess)

	n	m	R_1	R_2	R_3	y
3	2	3	A*	A*	H	3
4	3	3	A*	A*	A*	3
5	2	3	B*	B*	H	2
6	3	3	B*	B*	H	2

A* = c-C_4F_4Cl
B* = c- C_5F_6Cl

methylsulfonyl, trifluoromethylsulfenyl, and trifluoromethylsulfinyl derivatives of some tetrazamacrocyclic amines and other heterocyclic amines are known,[38] and recently the reactivity of dichloroperfluorocycloalkenes with secondary amines has been studied.[39] Some of these compounds are used in applications such as blood substitutes,[36] antistatic coatings,[40] and inert fluids.[31] Heterocyclic compounds that contain one or two fluorine atoms or a trifluoromethyl group are frequently biologically active materials.[37,41,42] Metalloheterocycles have been synthesized and studied extensively in the preparation of conducting polymers.[43−45] We report here the functionalization of 1,4,8-triazacycloundecane (**1**) and 1,4,9-triazacyclododecane (**2**) with dichlorotetrafluorocylobutene-1 (**A)** and dichlorohexafluorocyclopentene-1 (**B)**. These triazamacrocyclic amines reacted smoothly in the presence of an organic base to give the N-substituted products. Despite the polyfunctionality of the heterocyclic amines and of the alkenes, only monomeric products formed under the conditions used. The new compounds were isolated and characterized. X-ray diffraction methods have been also used to determine two of the structures.

Results and Discussion

A review has covered the literature dealing with nucleophilic attack on per- and polyfluorinated acyclic and cyclic olefins.[46] Although reactions of polyfluorinated olefins usually proceed by addition with concomitant β-elimination, this phenomenon was not observed in our reactions. Our current interest is in the reactivity of dichloroperfluorocycloalkenes with secondary amines. We report here a variety of triazamacrocycles that contain monochloroperfluorocycloalkenes as substituents.

It is well established that fluorinated cyclic or vinyl olefins undergo nucleophilic substitution reactions, e.g., the reactions of 1,2-dichloro(hexafluoro)cyclopentene-1 (**B**) with secondary aliphatic amines or pyrrolidine and 3,3,4,4,-tetrafluoropyrrolidine, to give singly substituted products and bicyclic amines with secondary acyclic diamines.[47−49] Displacement of both chlorine atoms from the cycloolefin rings occurred only when a strong nucleophilic reagent such as trialkyl phosphite, polyfluorinated sulfonamide, or mercaptide anion were employed in the metathesis reaction. Our study showed that the reactions of triazamacrocyclic secondary amines **1** and **2** with cyclic olefins were consistent with single substitution reactions with no evidence for disubstitution occurring on the cyclic olefins (Scheme 1).

The triazamacrocyclic amines **1** and **2** reacted smoothly with 1,2-dichlorohexafluorocyclopentene-1 (**B**) to form the 2:1 substituted triazamacrocyclic amines **5** and **6**, respectively. Longer reaction times (∼48 h) and higher temperatures (∼80 °C) were required than with acyclic amines. When the reactions were run with both **1** and **2** for 2.5 days in attempts to obtain 3:1 products, unreacted cyclic alkene **B** was recovered and only the 2:1 substituted monochlorohexafluorocyclopentenyl triazamacrocyclic amines were formed. All attempts to obtain the 1:1 derivatives of **1** and **2** with **B,** even when the reaction stoichiometry was reversed, failed.

Nucleophilic substitution reactions were also studied between **1** and **2** and **A** to form a 2:1 product with the former and a 3:1 product with the latter. It is surprising that **1** formed only 2:1 products with **A** and **B** and that all attempts to obtain the 3:1 derivative even when a large excess of cyclic alkene was used and the reaction time was increased failed. **A** reacted more rapidly with **1** and **2** than did **B**. This is typical of the reactions with the tetraazomacrocycles as well.[39] All attempts to obtain

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Table 1. Crystal Data and Structure Refinement for **3** and **4**

	3	**4**
empirical formula	$C_{16}H_{17}Cl_2F_8N_3$	$C_{21}H_{18}Cl_3F_{12}N_3$
fw	474.23	646.73
temperature	293(2) K	293(2) K
wavelength	0.710 73 Å	0.710 73 Å
crystal system	orthorhombic	triclinic
space group	*Pbca*	*P*1
unit cell dimension	$a = 15.4170$ (14) Å, $\alpha = 90°$	$a = 7.856$ (5) Å, $\alpha = 81.57°$
	$b = 13.5446$ (12) Å, $\beta = 90°$	$b = 9.361$ (6) Å, $\beta = 80.08(6)°$
	$c = 18.711$ (2) Å, $\gamma = 90°$	$c = 17.504$ (6) Å, $\gamma = 89.07(4)°$
volume, *z*	3907.1 (6) Å^3, 8	1254.3 (12) Å^3, 2
density (calc)	1.612 g/cm^3	1.712 g/cm^3
absorption coefficient	0.414 mm^{-1}	0.473 mm^{-1}
F(000)	1920	648
crystal size	0.1 × 0.2 × 0.2 mm	0.05 × 0.15 × 0.15 mm
θ range for data collection	2.18−19.99^o	1.19−20.00^o
no. of reflcns collcd	9066	3664
no. of indep reflcns	1819 ($R_{int} = 0.0949$)	2256 ($R_{int} = 0.0415$)
absorption correction	semiempirical from ψ scans	semiempirical from ψ scans
max. and min. transm	0.9934 and 0.8767	0.9208 and 0.8055
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	1818/0/280	2256/36/408
goodness-of-fit on F^2	1.102	1.282
final *R* indices [$I > 2\alpha(I)$][a]	R1 = 0.0677, wR2 = 0.0956	R1 = 0.0755, wR2 = 0.1268
R indices (all data)[a]	R1 = 0.1157, wR2 = 0.1104	R1 = 0.1011, wR2 = 0.1383
largest diff. peak and hole	0.263 and −0.213 e Å^{-3}	0.212 and 0.219 e Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

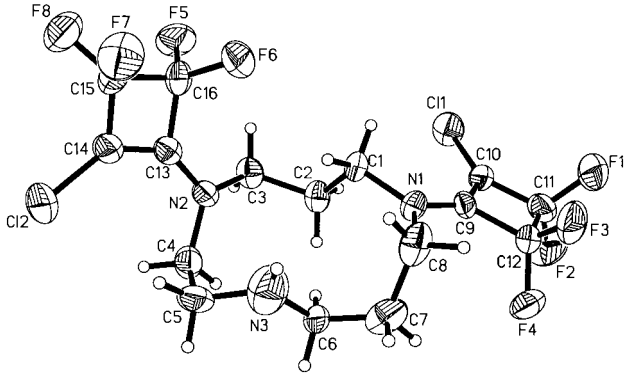

Figure 1. X-ray structure of **3**.

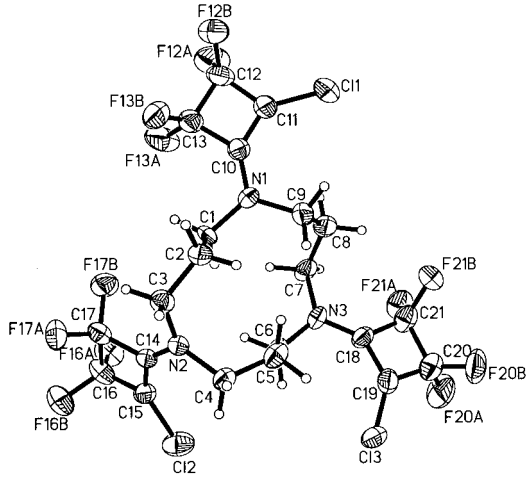

Figure 2. X-ray structure of **4**.

1:1 derivatives of these cyclicamines with **A** failed regardless of the stoichiometry used. It appears that steric reasons may be responsible for the inability of three moles of **A** or **B** to react with **1**. Nitrogen atoms separated by only two methylene groups preclude the attack of a third molecule of either **A** or **B**.

The mass spectra of the new compounds **3**−**6** have intense M^+ ions. Compounds **3** and **4** were crystallized from an ether−hexane (75:25) solvent mixture and these crystals were used for X-ray crystal structure determination. No change occurred when each of these products was stored under vacuum at 25 °C for long periods. The X-ray crystal structures of compounds **3** and **4** are given in Figures 1 and 2, respectively, with the crystallographic data summarized in Table 1. Selected bond distances and bond angles are in Tables 2 and 3.

Experimental Section

All reactions and manipulations were carried out under nitrogen. Solvents were dried using standard procedures and distilled under nitrogen. Glassware was oven-dried prior to use. Reagents and solvents were obtained from Aldrich and used as received unless specifically noted. 1,4,7-Triazacycloundecane (**1**) and 1,5,9-triazacyclododecane (**2**) were prepared by literature methods or received as gifts (3M Co.). 1,2-Dichlorotetrafluorocyclobutene-1 (**A**) and 1,2-dichlorohexafluorocylopentene (**B**) were obtained from PCR Inc. and used as received. Infrared spectra were recorded on a Perkin-Elmer model 1710 FTIR spectrometer. Chemical ionization mass spectrometric analysis (CI MS) were obtained by using a VG 7070HS mass spectrometer. Correct chlorine isotope ratios were observed. All NMR spectra were recorded on a Bruker AC-200 NMR spectrometer unless indicated otherwise. ^{1}H NMR spectra were obtained in $CDCl_3$ with Me_4Si as internal reference. ^{19}F NMR spectra were recorded with $CFCl_3$ as an external reference. Chemical shifts upfield from $CFCl_3$ are assigned negative values. Melting points are determined with a Thomas−Hoover apparatus. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium (Göttingen, Germany). The structures of reactants may be found in ref 39.

X-ray Structural Determination. To obtain single crystals of **3** and **4**, a solvent mixture composed of ether/hexane was used. The X-ray diffraction data for these compounds were collected on a Syntex P21 diffractometer upgraded to a Siemens P4 at 293(2)K using graphite monochromated MoK (λ = 0.710 73 Å). The cell constants were determined initially from the Hemispherical Search (xSCANS) from six and nine reflections of $9 < 2\theta < 20°$ for **3** and **4**, respectively. The precise unit cell dimensions were determined by least-squares refinement of an additional 27 (**3**) and 23 (**4**) computer centered reflections from their shell search routine with $25 < 2\theta < 30°$.

Table 2. Bond Lengths [Å] and Angles [deg] for **3**

C(1)−C(10)	1.698(8)	Cl(2)−C(14)	1.687(8)
F(1)−C(11)	1.340(8)	F(5)−C(16)	1.359(8)
N(1)−C(9)	1.334(8)	N(1)−C(1)	1.467(7)
N(1)−C(8)	1.479(8)	N(2)−C(13)	1.329(8)
N(2)−C(4)	1.462(8)	N(2)−C(3)	1.479(8)
N(3)−C(6)	1.397(9)	N(3)−C(5)	1.549(10)
C(4)−C(5)	1.519(9)	C(6)−C(7)	1.465(10)
C(9)−C(12)	1.489(10)	C(9)−C(10)	1.356(9)
C(13)−C(14)	1.363(9)	C(11)−C(12)	1.536(11)
C(15)−C(16)	1.519(10)	C(13)−C(16)	1.488(10)
C(1)−N(1)−C(8)	119.4(6)	N(2)−C(13)−C(14)	138.6(8)
C(6)−N(3)−C(5)	109.9(9)	C(13)−C(14)−Cl(2)	136.4(7)
C(1)−C(2)−C(3)	113.1(6)	Cl(2)−C(14)−C(16)	174.7(6)
N(2)−C(4)−C(5)	114.7(7)	C(4)−N(2)−C(3)	118.0(7)
N(1)−C(8)−C(7)	114.8(7)	C(4)−C(5)−N(3)	114.6(7)
N(1)−C(9)−C(12)	130.3(8)	N(1)−C(9)−C(10)	138.4(7)
F(1)−C(11)−F(2)	105.4(7)	N(2)−C(13)−C(16)	130.3(7)
F(4)−C(12)−F(3)	105.3(7)	C(13)−C(14)−C(15)	95.0(7)
F(3)−C(12)−C(9)	115.8(7)	C(15)−C(14)−Cl(16)	48.2(4)
F(3)−C(12)−C(11)	114.2(7)	C(13)−C(16)−C(14)	42.0(4)

Table 3. Bond Lengths [Å] and Angles [deg] for **4**

N(1)−C(1)	1.459 (9)	N(1)−C(10)	1.332 (10)
N(2)−C(14)	1.347 (9)	N(2)−C(4)	1.465 (9)
N(2)−C(3)	1.478 (9)	N(3)−C(18)	1.353 (10)
C(1)−C(2)	1.506 (11)	N(3)−C(6)	1.472 (10)
C(4)−C(5)	1.518 (11)	C(2)−C(3)	1.512 (10)
C(10)−C(11)	1.374 (12)	C(5)−C(6)	1.508 (11)
C(12)−F(12A)	1.354 (10)	C(8)−C(9)	1.503 (11)
C(14)−C(15)	1.348 (11)	C(10)−C(13)	1.461 (12)
C(15)−C(16)	1.438 (11)	C(14)−C(17)	1.484 (11)
C(16)−C(17)	1.516 (12)	C(18)−C(19)	1.369 (12)
C(10)−N(1)−C(1)	121.8 (6)	C(4)−N(2)−C(3)	119.7 (7)
C(1)−N(1)−C(9)	120.0 (6)	C(18)−N(3)−C(6)	118.3 (7)
C(14)−N(2)−C(3)	119.4 (6)	C(6)−C(5)−C(4)	114.3 (7)
C(7)−N(3)−C(6)	121.5 (6)	N(3)−C(7)−C(8)	115.2 (7)
C(1)−C(2)−C(3)	112.8 (7)	N(1)−C(9)−C(8)	116.0 (7)
N(3)−C(6)−C(5)	114.1 (7)	N(1)−C(10)−C(13)	131.9 (8)
C(11)−C(10)−C(13)	90.0 (8)	C(10)−C(11)−C(12)	94.9 (8)
C(10)−C(11)−Cl(1)	135.3 (8)	C(10)- C(11)−F(11D)	113.5 (12)
C(10)−N(1)−C(9)	118.1 (7)	C(12)−C(11)−Cl(1)	129.2 (8)
C(14)−N(2)−C(4)	120.2 (7)	C(11)−C(12)−C(13)	85.8 (8)

General Procedures. The reactions were run on a 0.5−1.0 mmol scale in dilute solutions under an inert atmosphere in a 250 mL round-bottomed Pyrex flask equipped with a 14/20 ground glass joint and magnetic stirring bar. The macrocyclic amine **1** or **2** was weighed and dissolved in 150−200 mL dry benzene and a stoichiometric amount of triethylamine was added to the flask. The required amount of dichloroperfluorocycloalkene **A** or **B** was weighed and dissolved in 5.0 mL dry benzene and added to the flask slowly with stirring. A water condenser was attached to the flask. The reaction mixture was stirred under nitrogen for 0.5 h at 25 °C and then continued at ∼80 °C. The reaction mixture was cooled and filtered to remove the solid triethylamine hydrochloride that formed. The filtrate was concentrated by distilling off the benzene and was dried under vacuum. A solid or a viscous oil was obtained, and any residual triethylamine hydrochloride was removed from products by using a silica gel-G column with C_6H_6 as eluent.

Synthesis: 1,5-Bis(chlorotetrafluorocyclobutenyl)-1,5,8-triazacycloundecane (3) was prepared as described above. A white crystalline solid was obtained in 60% yield (mp 110 °C). Spectral data obtained are as follows. IR (KBr pellet): 3425 w, 2957 m, 1628 vs, 1459 m, 1420 m, 1366 m, 1334 s, 1273 s, 1191 m, 1125 s, 1026 m, 985 s, 869 s, 751 ms, 642 w, 625 cm^{-1}. NMR: ^{19}F, δ −110.5 p (4 F), −112.96 (4 F); ^1H, δ 3.94 (s, 4 H), 3.88 (t, 8 H), 2.66 (m, 4 H), 2.20 (s, br, 1 H); MS (CI^+) [*m*/*z* (species) intensity]: 477 (M^+) 38.7.

1,5,9-Tris(chlorotetrafluorocyclobutenyl)-1,5,9-triazacyclododecane (4) was prepared as described. A white crystalline solid was obtained in 70% yield (mp 135 °C). Spectral data obtained are as follows. IR (KBr pellet): 2935 s, 2852 m, 1660 vs, 1449 s, 1362 m, 1319 s, 1279 m, 1168 m, 1679 w, 1030 w, 969 m, 827 w, 758 s, 707 s, cm^{-1}. NMR: ^{19}F, δ 3.74 (t, 12 H), 2.90 (m, 6 H), 2.21 (s, br, 1 H); MS (CI^+) [*m*/*z* (species) intensity]: 645 (M^+) 21.5.

1,5-Bis(chlorohexafluorocyclopentenyl)-1,5,8-triazacycloundecane (5) was prepared as described earlier. Dry benzene was used as solvent, and the reaction was carried out at 80 °C for 24 h. A colorless oil was obtained in 55% yield. Spectral data obtained are as follows. IR (KBr disk): 3425 w, 2957 m, 1628 vs, 1459 m, 1420 m, 1366 m, 1334 s, 1272 s, 1191 m, 1125 s, 1026 m, 985 s, 869 s, 751 s, 842 w, 625 w, cm^{-1}. NMR: ^{19}F, δ −106.31 (4 F), −108.52 (4 F), −129.34 (4 F); ^1H, δ 3.96 (s, 4 H), 3.87 (t, 8 H), 2.66 (m, 4 H), 2.22 (s, Br, 1 H). MS (CI^+) [*m*/*z* (species) intensity]: 574 (M^+) 54.0. Anal. Calcd for $C_{18}H_{17}N_3F_{12}Cl_2$: C, 37.63; H, 2.96; N, 7.31. Found: C, 37.57; H, 3.02; N, 6.90.

1,5-Bis(chlorohexafluorocyclopentenyl)-1,5,9-triazacyclododecane (6) was prepared as described by using dry benzene as solvent and the reaction was carried out for 24 h. A thick colorless oil was obtained in 60% yield. Spectral data obtained are as follows. IR (KBr disk): 3320 m, 2950 vs, 2810 vs, 1640 vs, 1472 s, 1424 s, 1260 vs, 1192 s, 1126 s, 992 s, 860 m, 702 m, 627 m, cm^{-1}. NMR: ^{19}F δ −107.71 (4 F), −109.40 (4 F), −129.42 (4 F); ^1H δ 3.79 (t, 12 H), 2.66 m, 6 H), 2.35 (s, br, 1 H). MS (CI^+) [*m*/*e* (species) intensity]: 587(M^+) 30.2. Anal. Calcd for $C_{19}H_{19}N_3F_{12}Cl_2$: C, 38.77. Found: C, 40.16.

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Supporting Information Available: For compounds **3** and **4**, complete bond lengths and bond angles, tables of data collection and processing parameters, atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients are available (12 pages). Ordering information is available on any current masthead page.

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