The Coordination Chemistry of Fluorocarbons: Difluoro-*m*-cyclophane-Based Fluorocryptands and Their Group I and II Metal Ion Complexes

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Received June 27, 1997[⊗]

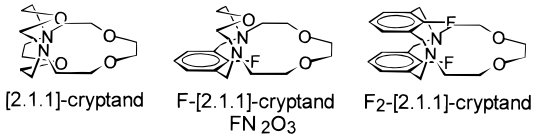
The reactions of 1,3-bis(bromomethyl)-2-fluorobenzene with the bis(trifluoroacetamides) of 1,3-bis(aminomethyl)-2-fluorobenzene and 1,3-bis(aminomethyl)benzene yield the respective 1+1-condensed [3.3]-*m*-cyclophanes, respectively termed F_2-phane (yield 39%) and HF-phane (yield 48%) without trifluoroacetamide groups. The reactions of F_2-phane with 1,8-diiodo-3,6-dioxaoctane and 1,11-diiodo-3,6,9-trioxaundecane result in the respective 1+1-addition products 1,10-diaza-25,26-difluoro-4,7-dioxatetracyclo[8.7.7.$1^{12,16}$.$1^{19,23}$]hexaeicosa-12,14,16(25),-19,21,23(26)-hexene (= F_2-[2.1.1]-cryptand) (yield 5%) and 1,13-diaza-28,29-difluoro-4,7,10-trioxatetracyclo-[11.7.7.$1^{15,19}$.$1^{22,26}$]nonaeicosa-15,17,19(28),22,24,26(29)-hexene (= F_2-[3.1.1]-cryptand) (yield 39%). Analogous reactions of the HF-phane give the related macrocycles HF-[2.1.1]-cryptand (yield 68%) and HF-[3.1.1]-cryptand (yield 76%). The coordination of alkali and alkaline earth metal ions by these fluorophane cryptands results in significant shifts of the ^{19}F NMR resonances: F_2-[2.1.1]-cryptand, δ −100.70 ppm; its Li^+ complex, δ −129.23 ppm. The $^1J_{CF}$ coupling constant for such complexes is correlated with the degree of interaction between CF units and metal ions, and the most pronounced decrease (262 Hz to 232 Hz) is found for the lithium complex of the F_2-[2.1.1]-cryptand. Competition experiments show the difluoro F_2-[3.1.1]-cryptand to form significantly stronger complexes with Na^+ than the monofluoro HF-[3.1.1]-cryptand. In the crystal structure of F_2-[2.1.1]-cryptand·$NaCF_3SO_3$, the sodium ion displays an unusual F_2O_4N coordination sphere with extremely short sodium−fluorine distances: CF···Na^+ = 229.8(3), 235.7(4) pm; O−Na^+ = 228.5(4), 242.0(4), 243.8(4), 247.6(4) pm; N−Na^+ = 285.1(7) pm. In the closely related crystal structure of HF-[3.1.1]-cryptand·$NaClO_4$, the metal has an FO_5N coordination sphere: CF···Na^+ = 236.0(4) pm; O−Na^+ = 234.8(6), 239.3(6), 240.3(12), 240.6(6), 285.7-(17) pm; N−Na^+ = 272.3(6) pm. In the crystal structure of F_2-[3.1.1]-cryptand·HCF_3SO_3, the proton is in a pseudotetrahedral environment: N−H = 84 pm; O···HN = (216 pm; CF···HN = 224, 236 pm. This, however, is not considered indicative of significant CF···HN hydrogen bonding.

Introduction

The ability of covalently bonded fluorine in fluorocarbons to act as a donor atom for metal ions is increasingly recognized to be of significance in coordination and organometallic chemistry.[1] The properties of this donor atom are determined by its hardness, and it appears that covalently bonded fluorine is best suited to ligate correspondingly hard metal ions such as those of the alkali and alkaline earth metals.[2,3] In this context it is also of significance that the homogeneous Ziegler−Natta polymerization of olefins requires highly electrophilic cationic zirconocenes as active centers,[4] and as a consequence of the increased use of fluorinated counteranions in such systems, several groups have reported examples of close CF···Zr interactions,[5] which appear to exert a very significant influence on the catalytic activity of such species.[6]

Previously we have described—among those of other fluoro macrocycles—the synthesis of the fluorocryptand FN_2O_3,[7,8] and in the crystal structure of its lithium complex, it can be easily seen that this ligand is topologically related to the [2.1.1]-cryptand (Chart 1), since the single fluorine atom in the lithium complex of the former ligand occupies the same position with respect to the metal ion as an ether oxygen in the lithium complex of the [2.1.1]-cryptand. This relationship motivated us to attempt the synthesis of ligands in which an additional ether oxygen is replaced by a CF unit and to investigate whether such ligands would still form stable complexes with metal ions. One such compound is displayed in Chart 1, and in analogy to the cryptand nomenclature, this ligand may be termed F_2-[2.1.1]-cryptand. In this respect, we are interested in promoting the

Chart 1. Topological Relations among the Different Cryptands



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⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

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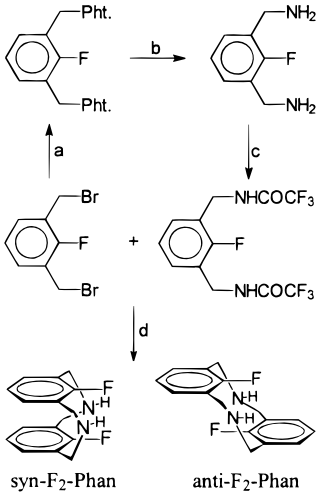
S0020-1669(97)00806-9 CCC: $14.00

Scheme 1. Synthesis of the Difluoro-*m*-cyclophane[a]



[a] Key: (a) potassium phthalimide (Pht. = phthalimide), dmf; (b) hydrazine hydrate, 5 d reflux, ethanol; (c) $(CF_3CO)_2O$, ether; (d) KOH, acetone.

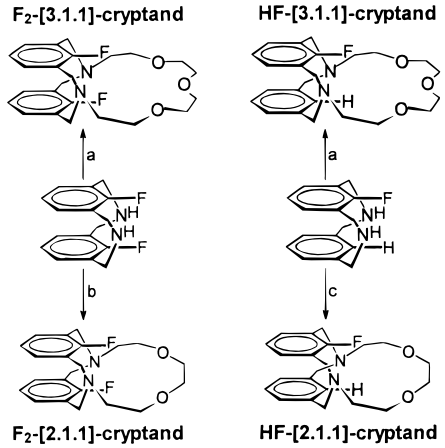
concept of CF units as efficient donors for hard metal cations, and we seek ligands in which more than one CF unit can coordinate to metal ions. Accordingly we have very recently described a cesium complex of a soccerball-like ligand in which CF coordination is more important than oxygen coordination, as evidenced by Shannon−Brown valence bond sums.[9]

Here we wish to describe the synthesis of novel fluoro-*m*-cyclophane-based cryptands with two CF donors as well as an investigation into the coordination chemistry of such ligands with alkali and alkaline earth metal ions.

Results and Discussion

Synthesis of the Ligands. The basic fluorine-containing building block for all ligands described here is 1,3-bis-(bromomethyl)-2-fluorobenzene (**1**). A Gabriel reaction of **1** with potassium phthalimide, followed by hydrazine cleavage of the resulting amide, leads in an overall yield of 75% (via two steps) to the desired 1,3-bis(aminomethyl)-2-fluorobenzene. For the synthesis of the difluoro-*m*-cyclophane, this amine was first converted into the corresponding bis(trifluoroacetamide) and was then reacted with the dibromide **1** to yield the difluoro-*m*-cyclophane F_2-phane (Scheme 1), since the trifluoroacetamide protective group is cleaved off during the synthesis of the phane. Our reaction is modeled after the procedure by Takemura et al. for the analogous fluorine-free phane.[10] However, in contrast to the synthesis of the fluorine-free product, the condensation of the two fluorine-containing molecules leads to a kinetically controlled, roughly equimolar mixture of *syn*- and *anti*-F_2-phane. It was, however, very easy to isomerize the undesired anti isomer by simply equilibrating the isomeric mixture in boiling acetonitrile for 24 h. This procedure leads to the predominant formation of the thermodynamically favored *syn*-F_2-phane (39% yield), which can be separated by chromatography from the remaining anti product (ca. 9% yield) (this anti product may be re-isomerized). The related mixed HF-phane was synthesized in the reaction of dibromide **1** and the bis(trifluoroacetamide) of 1,3-bis(aminomethyl)benzene in 48% yield (Scheme 1). The formation of significant amounts of the undesired *anti*-phane was not observed. For the synthesis of the fluorophane

Scheme 2. Synthesis of the Difluoro- and Monofluorocryptands[a]



[a] Key: (a) 1,11-diiodo-3,6,9-trioxaundecane, K_2CO_3, CH_3CN; (b) 1,8-diiodo-3,6-dioxaoctane, Et_3N, CH_3CN; (c) 1,8-diiodo-3,6-dioxaoctane, Na_2CO_3, CH_3CN.

cryptands, the respective F_2-phane and HF-phane were reacted with either 1,8-diiodo-3,6-dioxaoctane or 1,11-diiodo-3,6,9-trioxaundecane (Scheme 2). The reactions of the F_2-phane result in the formation of the respective 1+1-addition products F_2-[2.1.1]-cryptand (yield 5%) and F_2-[3.1.1]-cryptand (yield 39%). The analogous ligands HF-[2.1.1]-cryptand (yield 68%) and HF-[3.1.1]-cryptand (yield 76%) were isolated from the reactions of the mixed HF-phane. Somewhat surprisingly, the amount of the mixed HF-phane cryptands formed always exceeds that of the closely related difluorocryptands.

Metal Complexes of Fluorocryptands. The complexation of metal ions within the cavity of the fluoro macrocycles is essentially quantitative, leading to strong complexes with the difluorocryptands when the size of the cavity and the ionic radius of the metal ion are complementary. Complexation also results in large shifts of the ^{19}F NMR resonances (Table 1), and it is typical for complexes of fluoro macrocycles that addition of metal ions leads to a pronounced additional shielding of all NMR resonances.[7] In the case of the larger fluorocryptands F_2-[3.1.1]-cryptand and HF-[3.1.1]-cryptand, the largest shift differences $\Delta\delta$ are observed for the respective Na^+ complexes with $\Delta\delta = -16.0$ and -13.0 ppm. The cavities of the related macrocycles F_2-[2.1.1]-cryptand and HF-[2.1.1]-cryptand are much smaller, and only the difluoro ligand seems to be able to accommodate the smallest alkali metal cation Li^+. The $\Delta\delta$ value of -28.5 ppm observed for this complex is by far the largest ever observed for fluoro macrocycles and their respective metal complexes. In contrast, the HF-[2.1.1]-cryptand does not seem to able to form a reasonably strong complex with Li^+ or any of the larger alkali metal ions, since the shifts of the ^{19}F NMR resonances are quite small. It was shown by us that a more reliable tool indicative of CF···metal interactions is the characteristic decrease of the $^1J_{CF}$ coupling constant.[7a] The stronger the CF···metal contact, the more lone pair electron density is removed from the C−F bond, consequently leading to a corresponding decrease in the $^1J_{CF}$ coupling constant. In this respect, the complexation of Li^+ by the HF-[2.1.1]-cryptand also has to be classified as very weak, since there is only a rather small (2.5 Hz) drop in the $^1J_{CF}$ coupling constant. Quite in contrast, a very pronounced reduction of the $^1J_{CF}$ coupling constant of 30 Hz (from 262 Hz to 232 Hz) was observed for the Li^+ complex with the F_2-[2.1.1]-cryptand, which is also the strongest such effect ever observed by us. This and the large upfield shift of the ^{19}F NMR signal evidence strong CF···Li

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Table 1. Selected ^{19}F NMR Data for the Ligands F_2-[3.1.1]-cryptand, HF-[3.1.1]-cryptand, F_2-[2.1.1]-cryptand, and HF-[2.1.1]-cryptand and Their Metal Complexes[a]

	F_2-[3.1.1]-cryptand		HF-[3.1.1]-cryptand		F_2-[2.1.1]-cryptand		HF-[2.1.1]-cryptand	
	δ (ppm)	$^1J_{CF}$ (Hz)	δ (ppm)	$^1J_{CF}$ (Hz)	δ (ppm)	$^1J_{CF}$ (Hz)	δ (ppm)	$^1J_{CF}$ (Hz)
ligand	−105.8	259	−110.38	253	−100.70	262	−109.48	253.5
+ Li^+	−119.15	246	−118.38	244	−129.23	232	−111.36	251
+ Na^+	−121.80	242	−123.40	240			−111.15	
+ K^+	−111.99	247	−116.69	245			−109.95	
+ Ca^{2+}	−119.1	235	−113.81	245.5				
+ Sr^{2+}	−116.18	236	−116.25	239				
+ Ba^{2+}	*b*	240	−112.56	239.5				
+ H^+	−110.7	254	−111.20	245.5			−112.32	247
+ $2H^+$	−114.9	251	−109.14	242.5			−111.26	241

[a] The ^{19}F NMR shifts are referenced to $CFCl_3$ (0.00 ppm). $^1J_{CF}$ is the C−F coupling constant in the fluorobenzene; each value is ±0.5 Hz. [b] Several species.

interactions in solution. For the larger fluoro-*m*-cyclophane cryptands the $^1J_{CF}$ coupling constants for both ligands indicate that metal ions the size of sodium, i.e. with an ionic radius of about 100 pm, fit best into the larger macrocyclic cavity ($^1J_{CF}$ is decreased by up to 24 Hz). This interpretation is in accord with the results of the X-ray crystal structure determination of the complex F_2-[3.1.1]-cryptand·$NaCF_3SO_3$.

The mixed ligands HF-[2.1.1]-cryptand and HF-[3.1.1]-cryptand were prepared with a view to probing the effect of a decreasing number of CF donor units on the stability of metal ion complexes. As is evident from the $^1J_{CF}$ data, the monofluorocryptands do not form very strong complexes, since the decrease of the carbon−fluorine coupling constant is typically much less pronounced than in the difluoro ligand complexes (Table l). To verify this decreased stability of the metal complexes of the mixed HF cryptands by an independent experiment, we probed the relative stabilities of the complexes of F_2-[3.1.1]-cryptand and HF-[3.1.1]-cryptand with sodium salts by performing an NMR competition experiment in CD_3CN. In this experiment, the ^{19}F NMR spectrum of an equimolar mixture of both cryptands and $NaCF_3SO_3$ was determined. The outcome of this investigation leaves no doubt about the stabilizing effect of an additional CF donor unit. As evidenced by the ^{19}F NMR integrals in this mixture, virtually all of the F_2-[3.1.1]-cryptand is present as the Na^+ complex, while virtually all HF-[3.1.1]-cryptand is uncomplexed. This provides clear evidence of the Na^+ complex of the difluoro cryptand being at least 2 orders of magnitude stronger than that of the mixed HF-[3.1.1]-cryptand with the same metal ion.[11]

The fluorophane cryptands as well as their metal complexes display rather broad ($\nu_{1/2}$ = 10−50 Hz) ^{19}F NMR signals, preventing the direct determination of the $^{19}F-^{19}F$ coupling constants via the isotopomers, which is unfortunate, as variations in the coupling constants could have provided additional information on the structures of such complexes in solution, since Ernst et al. were able to show that the $^{19}F-^{19}F$ coupling constant is correlated with the distance of the two fluorine atoms.[12]

Protonation of Fluorocryptands. The two nitrogen atoms in the fluorocryptands can be protonated stepwise, which is indicative of a significant difference in the basicities of the two nitrogen atoms,[13] and this process can be monitored easily by characteristic shifts of the ^{19}F NMR resonances (Tables 1 and 2). In the case of the F_2-[2.1.1]-cryptand and the F_2-[3.1.1]-cryptand, the ^{19}F NMR resonances experience significant additional shielding, while those of the mixed HF cryptands display only fairly small up- or downfield shifts. For the smaller cryptands, the ^{19}F NMR resonances are split due to CF···HN through-space coupling on the order of J = 5−10 Hz. The coupling constants could not be determined with high accuracy because the ^1H as well as the ^{19}F NMR signals are rather broad ($\nu_{1/2}$ > 10−50 Hz). However, this through-space coupling is indicative of the ammonium protons being located within the macrocyclic cavity and not on the outside, as one might expect with a view to Coulombic repulsion of the two positive charges in the doubly protonated fluorophane cryptands. A rationale for this (fairly typical) endohedral protonation of cryptands could be the energy gain due to reduced lone pair repulsion between the other donor atoms in the constrained macrocyclic cavity.

Again—since this phenomenon is also observed for the complexation of metal ions by fluoro macrocycles—the protonation of the fluorophanes leads to a pronounced decrease of the $^1J_{CF}$ coupling constant between 5 and 7.5 Hz for the first protonation and between 8 and 12.5 Hz for the second protonation (relative to the $^1J_{CF}$ of the respective free ligand).

X-ray Crystal Structures

F_2-[3.1.1]-cryptand·$NaCF_3SO_3$. In the crystal, the sodium cation displays an unusual coordination sphere consisting of four oxygen [228.5(5)−247.6(4) pm] and two fluorine donors [229.8-(3), 235.7(3) pm], whereas only one of the two nitrogen atoms [285.1(5) pm] has a rather weak contact to the metal ion (Figure 1). The coordination sphere of Na^+ may be described as approximately pentagonal bipyramidal with the equatorial ligands O1, O2, O3, N2, and F2 being roughly in one plane (even though N2 is somewhat removed), which is capped by the two axial ligands F2 and O4 (F2−Na1−O4 164.2°). The two benzene rings of the fluorophane are roughly coplanar, with the planes being tilted by only 11.9° with respect to each other, leading to a relatively close, nonbonded approach of the two fluorine atoms of 301.2 pm. The two CF···Na^+ distances represent the second and third shortest distances within the coordination sphere of sodium and are thus shorter than three of the four Na^+−O distances. In addition, it should be mentioned that the shorter one of the two CF···Na^+ distances is the shortest CF···Na^+ distance reported so far.[l,14] There can thus be no doubt that CF···Na^+ interactions contribute significantly to the stability of the complex.

HF-[3.1.1]-cryptand·$NaClO_4$. To better understand the coordination chemistry of CF donors and to investigate the

(11) This is only a rough estimate, since NMR competition experiments are best suited to determine small differences in the stability constants. In our experiment, the ^{19}F NMR signal corresponding to the free F_2-[3.1.1]-cryptand had disappeared and the integral ratio between HF-[3.1.1]-cryptand and F_2-[3.1.1]-cryptand·Na^+ was exactly 1:2, as required by the different fluorine content of the ligands.

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Table 2. Crystal Data Summary

	F_2-[3.1.1]-cryptand·$NaCF_3SO_3$	F_2-[3.1.1]-cryptand·HCF_3SO_3	HF-[3.1.1]-cryptand·$NaClO_4$
empirical formula	$C_{25}H_{30}F_5N_2NaO_6S$	$C_{25}H_{31}F_5N_2O_6S$	$C_{24}H_{31}ClFN_2NaO_7$
fw	604.56	582.58	536.95
temp (K)	293(2)	183(2)	203(2)
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1$
unit cell dimens			
a	9.439(2)	11.840(2)	8.796(2)
b	20.388(4)	16.136(3)	14.508(3)
c	28.308(6)	13.815(3)	10.097(2)
α	90	90	90
β	90	99.21(3)	96.49(3)
γ	90	90	90
vol (A^3)	5448(2)	2605.3(9)	1280.2(5)
Z	8	4	2
density (g cm^{-3})	1.474	1.485	1.393
abs coeff (mm^{-1})	0.212	0.204	0.220
F(000)	2512	1216	564
crystal size (mm)	0.8 × 0.7 × 0.7	0.6 × 0.5 × 0.5	0.7 × 0.6 × 0.5
θ range (deg)	2.5−26.0	2.5−26.3	3.6−22.6
index range (*h*/*k*/*l*)	0,11/0,25/0,34	−14,14/0,20/−17,0	−9,9/−6,15/−10,10
no. of reflns: collected independent	5335, 5335	5514, 5295	2754, 2605
data/parameters	4458/362	4315/371	2605/325
GOF	1.103	1.068	1.063
final *R* indices [$I > 2\sigma(I)$]: *R*1, w*R*2	0.0845, 0.2428	0.0468, 0.109	0.0722, 0.1931
largest peak and hole (e $Å^{-3}$)	+0.99, −0.79	+0.27, −0.32	+0.67, −0.55

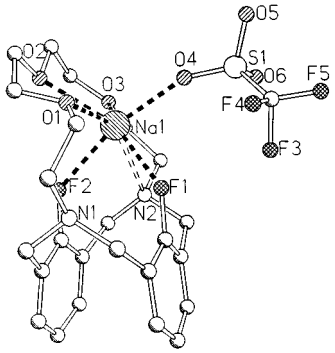

Figure 1. Crystal structure of F_2-[3.1.1l-cryptand·$NaCF_3SO_3$. Important bond lengths (pm), nonbonded distances (pm), and interplanar angle (deg): Na1−O4 228.5(4), Na1−F1 229.8(3), Na1−F2 235.7(4), Na1−O3 242.0(4), Na1−O1 243.8(4), Na1−O2 247.6(4), Na1−N2 285.1-(5), Na1−N1 369.8, F1−C1 136.8(5), F2−C9 136.6(5), F1−F2 301.2, Ph1−Ph2 11.9.

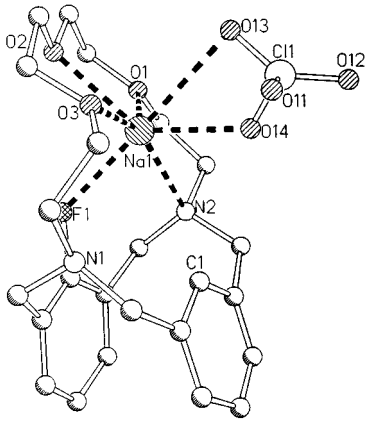

Figure 2. Crystal structure of HF-[3.1.1]-cryptand·$NaClO_4$. Important bond lengths (pm), nonbonded distances (pm), and interplanar angle (deg): Na1−O1 234.8(6), Na1−F1 236.0(4), Na1−O2 239.3(6), Na1−O14 240.3(12), Na1−O3 240.6(6), Na1−N2 272.3(6), Na1−O13 285.7-(17), Na1−H1 254, F1−H1 289, Ph1−Ph2 15.5.

changes resulting from an exchange of fluorine to hydrogen, we have determined the crystal structure of the sodium complex of the HF-[3.1.1]-cryptand (Figure 2). In the solid state, the metal ion is coordinated by four oxygen donors, one nitrogen donor, and one fluorine donor, with five short metal−ligand distances [234.8(6)−240.6(6) pm] and two longer ones [272.3-(6), and 285.7(17) pm to N2 and O13]. The overall geometry of the complex is similar to that of the difluoro complex described above. The only important changes result from the "missing" CF donor in the HF-[3.1.1]-cryptand. As can be seen in Figures 1 and 2, in the difluoro complex the counterion ($CF_3SO_3^-$) is bonded to Na^+ only by one oxygen, while in the monofluoro complex the counterion (ClO_4^-) acts as a bidentate ligand. In this way, two perchlorate oxygen atoms fill the void created by the absence of one CF donor unit.

F_2-[3.1.1]-cryptand·HCF_3SO_3. In the crystal structure (Figure 3), the proton was localized at N1. This endohedral position of the proton in the difluoro-*m*-cyclophane cryptand leads to an inequality in the oxyethylene chain linking the two nitrogen atoms. The orientation of the oxygen atom O1 is such that its lone pairs are pointing toward the inside of the cavity. Hence the resulting short oxygen−proton contact of 216 pm may be indicative of stabilizing NH^+−O hydrogen bonding, which also is a typical structural pattern observed in crystal structures of other protonated cryptands.[15,17] In contrast the other two oxygen atoms O2 and O3 are on the periphery of the cavity with their

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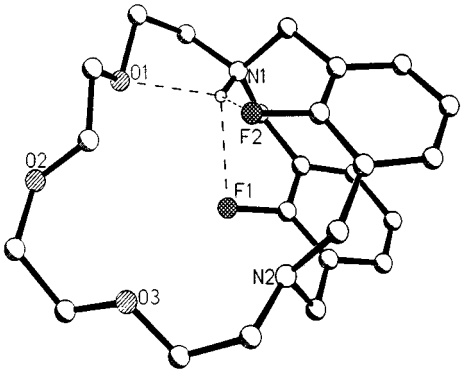

Figure 3. Crystal structure of F_2-[3.1.1]-cryptand·HCF_3SO_3. Important bond lengths (pm), nonbonded distances (pm), and interplanar angle (deg): N1−H100 84, H100−F1 224, H100−F2 236, H100−O1 216, N1−O1 266.7, N1−F1 286.0, N1−F2 292.9, N2−O3 306.4, N2−F1 287.5, N1−F2 300.9, F1−F2 280.7, Ph1−Ph2 16.8.

lone pairs oriented such that they point toward the outside in order to minimize lone pair repulsion. In other words, only the donor atoms close to the ammonium proton are "collapsing" in the direction of the excess positive charge. This effect is more clearly visible when one compares the nonbonded nitrogen−oxygen and −fluorine distances of the protonated and unprotonated nitrogen atoms N1 and N2. For N1, the average of the three distances is 282 pm while the related average of 298 pm for N2 is much larger (for individual values, see the caption of Figure 2).

In addition to the short hydrogen−O1 contacts, there are also two fairly short fluorine−hydrogen distances (F1−H 224 = pm, F2−H = 236 pm) which lead to a pseudotetrahedral environment of the proton as indicated by dashed lines in Figure 2. It can thus be speculated whether these distances are due to attractive $CF\cdots HN^+$ interactions.[16] However, we recently investigated and discussed in great detail the possibility of attractive $CF\cdots HN^+$ contacts in an experimental study with related fluorocryptands and their protonation products and came to the following conclusion: Should an interaction between $CF\cdots HN^+$ exist, it is certainly going to be of a very weak nature.[17] This interpretation of our experimental results is in accord with recent theoretical studies by Dunitz and Taylor[18] and by Glusker et al.,[19] while on the other hand high-level ab-initio calculations by Glusker et al. reveal weak interactions between NH_4^+ and CH_nF_{4-n} in the gas phase.[20] Thus we conclude that the short $CF\cdots HN^+$ contacts found here are not the result of significant attractive interactions but rather result from the constrained geometry of the difluoro-*m*-cyclophane.

In the protonated difluoro-*m*-cyclophane, the tilt of the two benzene rings is slightly larger (16.8°) than that in the Na^+ complex, which leads to a shorter inter-fluorine distance of 280.7 pm.

Summary and Conclusions

We have described the synthesis of several fluoro-[3.3]-*m*-cyclophane cryptands topologically related to the [2.1.1]- or [3.1.1]-cryptand and investigated whether this relationship also extends to the coordination behavior of such fluorine-containing ligands. In the structurally characterized complex of the F_2-[3.1.1]-cryptand with $NaCF_3SO_3$, the metal ion displays an unusual coordination sphere, consisting of two fluorine and four oxygen donor atoms and the shortness of the two $CF\cdots Na^+$ [229.8(3), 235.7(4) pm] distances provides clear evidence in favor of strong fluorine−metal interactions. The $^1J_{CF}$ coupling constants as well as the results of a competition experiment between the F_2-[3.1.1]-cryptand and the closely related HF-[3.1.1]-cryptand show that the replacement of one fluorine donor by a hydrogen atom leads to a substantial decrease in the stability of the corresponding metal complex. On the basis of NMR data, the F_2-[2.1.1]-cryptand provides an excellent fit for the lithium ion, since upon complexation the ^{19}F NMR signal is shifted by −28.5 ppm (−100.7 to −129.2 ppm) and the $^1J_{CF}$ coupling constant is reduced by 30 Hz (from 262 to 232 Hz).

In conclusion, there is ample evidence in favor of a close relationship between fluoro and conventional cryptands and both display the preference for the same metal ions. Furthermore the number of fluorine atoms in the coordination sphere of metal ions can be increased without sacrificing stability of the resulting complexes, and it remains to be shown whether it will be possible to realize complexes in which a metal ion is exclusively coordinated by CF donor units.

Experimental Section

Commercially available solvents and reagents were purified according to literature procedures. Chromatography was carried out with silica MN 60. NMR spectra were recorded at 300 K with a Bruker Avance 200 (^1H NMR 200 MHz, ^{13}C NMR 50.3 MHz, ^{19}F NMR 188.2 MHz, ^{23}Na 52.9 MHz) or a Varian Unity 300 (^1H NMR 300 MHz, ^6Li 44.1 MHz, ^7Li 116.6 MHz, ^{13}C NMR 75.4 MHz). ^1H NMR spectra were referenced to residual H impurities in the solvent and ^{13}C NMR spectra to the respective solvent signals: $CDCl_3$ (7.26, 77.0 ppm) and CD_3CN (1.93, 1.30 ppm). ^{13}C NMR spectra were accumulated in 32K data fields in both the time and frequency domains with a digital resolution of 0.8 Hz/point. ^{19}F NMR spectra were referenced to internal $CFCl_3$ (0 ppm). Melting points were determined with a Meltemp melting point apparatus in sealed capillaries. Starting materials were available commercially or were prepared according to literature procedures: 1,3-dimethyl-2-fluorobenzene,[21] 1,3-bis(bromomethyl)-2-fluorobenzene,[22] diaza-12-crown-4,[23] various triflate salts,[24] 1,8-diiodo-3,6-dioxaoctane,[25] 1,11-diiodo-3,6,9-trioxaundecane.[25]

1,3-Bis(phthalimidomethyl)-2-fluorobenzene. Potassium phthalimide (7.0 g, 37.8 mmol) and 1,3-bis(dibromomethyl)-2-fluorobenzene (5.0 g, 17.7 mmol) in dimethylformamide (100 mL) were heated to 80 °C for 10 h. After addition of water (100 mL), a white solid precipitated, which was filtered off and washed with water and ethanol. Yield: 6.83 g (16.5 mmol), 93%. Mp: 178 °C. ^1H NMR ($CDCl_3$): δ 4.94 (s, 4H, $ArCH_2$), 6.97−7.05 (m, 1H, Ar), 7.20−7.26 (m, 2H, Ar), 7.70−7.77 (m, 4H, Ar), 7.82−7.88 (m, 4H, Ar).

1,3-Bis(aminomethyl)-2-fluorobenzene. A mixture of 1,3-bis(phthalimidomethyl)-2-fluorobenzene (6.83 g, 16.5 mmol)

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and hydrazine hydrate (2.8 mL, 45.0 mmol) in ethanol (200 mL) was refluxed for 5 d. After cooling, concentrated HC1 (20 mL) was added and the mixture refluxed for another 45 min. The cold solution was filtered, the filtrate was washed with water (40 mL) three times, and the solvent was evaporated. The oily residue was titrated with concentrated aqueous KOH up to pH 14. The mixture was washed four times with CH_2Cl_2 (40 mL). The organic layer was separated, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo to yield 1,3-bis(aminomethyl)-2-fluorobenzene as a pale yellow oil. Yield: 2.06 g (13.4 mmol), 81%. ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 4H, NH_2), 3.89 (s, 4H, $ArCH_2$), 7.03−7.11 (m, 1H, Ar), 7.18−7.30 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 40.41 (d, J_{CF} = 0.7 Hz, $ArCH_2$), 123.98 (d, J_{CF} = 4.8 Hz, Ar), 127.62 (d, J_{CF} = 5.1 Hz, Ar), 130.15 (d, J_{CF} = 14.4 Hz, Ar), 158.90 (d, $^1J_{CF}$ = 244.8 Hz, Ar). ^{19}F NMR ($CDCl_3$): δ −127.82.

1,3-Bis((trifluoroacetamido)methyl)-2-fluorobenzene. To a solution of 1,3-bis(aminomethyl)-2-fluorobenzene (2.06 g, 13.4 mmol) in diethyl ether (15 mL) at 0 °C was rapidly added dropwise trifluoroacetanhydride (3.25 g, 13.4 mmol) in ether (5 mL). After 20 min at 0 °C, the solvent was removed and the colorless residue dried in vacuo. Yield: 4.20 g (13.1 mmol), 91%. Mp: 177 °C. ^{1}H NMR (dmso-d_6): δ 4.44 (d, J = 5.6 Hz, 4H, $ArCH_2$), 7.18−7.25 (m, 3H, Ar), 9.99 (br s, 2H, NH). ^{13}C NMR (dmso-d_6): δ 36.64 (d, J_{CF} = 5.3 Hz, $ArCH_2$), 115.89 (q, $^1J_{CF}$ = 287.7 Hz, CF_3), 124.06 (d, J_{CF} = 8.0 Hz, Ar), 124.25 (d, J_{CF} = 2.2 Hz, Ar), 128.99 (d, J_{CF} = 4.1 Hz), 156.36 (q, $^2J_{CF}$ = 36.3 Hz, OCN), 157.95 (d, $^1J_{CF}$ = 247.3 Hz, Ar). ^{19}F NMR (dmso-d_6): δ −73.58 (s, CF_3), −123.13 (s, ArF).

***syn*-F_2-phane and *anti*-F_2-phane.** To a mixture of 1,3-bis-(bromomethyl)-2-fluorobenzene (2.55 g, 9.04 mmol) and 1,3-bis((trifluoroacetamido)methyl)-2-fluorobenzene (3.11 g, 9.04 mmol) in boiling acetone (1500 mL) was added KOH powder in four portions (4 × 1.0 g) every 15 min. After an additional 2 h under reflux and 10 h at room temperature, the solvent was removed under reduced pressure. To the residue was added HCl (150 mL, 20% aqueous), and the impurities were extracted with CH_2Cl_2 (3 × 50 mL). The aqueous solution was basified with KOH to pH 14, and the resulting solution was extracted with CH_2Cl_2 (4 × 50 mL). The organic layer was separated from the mixture, dried over $MgSO_4$, and filtered, and the filtrate was evaporated. The residue was filtered off over silica and dried, , leading to the isolation of an equimolar mixture of the two isomers. This mixture was dissolved in CH_3CN, and the solution was heated under reflux for 24 h to produce an isomeric mixture which now contained approximately 80% of the syn isomer and approximately 20% of the anti isomer. The remaining solid was chromatographed on silica (cyclohexane/diethylamine, 5/1), resulting in *syn*-F_2-phane (R_f = 0.26) and *anti*-F_2-phane (R_f = 0.10).

Experimental data for *syn*-F_2-phane are as follows. Yield: 482 mg (1.76 mmol), 39%. Mp: 170−174 °C. MS *m*/*z*: 274 (M^+, 100%). ^{1}H NMR ($CDC1_3$): δ 3.58 (d, J = 15.1 Hz, 4H, $ArCH_2$), 4.44 (d, J = 15.2 Hz, 4H, $ArCH_2$), 6.59 (br s, 6H, Ar). ^{13}C NMR ($CDC1_3$): δ 49.09 (br s, $ArCH_2$), 124.10 (t, J = 2.0 Hz, Ar), 127.18−127.61 (m, Ar), 129.50 (t, J = 2.8 Hz, Ar), 160.45 (br d, J = 251 Hz, Ar). ^{19}F NMR ($CDCl_3$): δ −121.15 (br s).

Experimental data for *anti*-F_2-phane are as follows. Yield: 110 mg (0.41 mmol), 9%. Chromatography of the product mixture prior to thermal equilibration in acetonitrile allowed the isolation of the *anti*-phane in up to 20% yield. Mp: 186 °C. MS: *m*/*z* 274 (M^+, 100%). ^{1}H NMR ($CDCl_3$): δ 3.66 (dd, J = 14.2 Hz, J = 1.7 Hz, 4H, $ArCH_2$), 3.86 (d, J = 14.2 Hz, 4H, $ArCH_2$), 7.06−7.25 (m, 6H, Ar). ^{13}C NMR ($CDCl_3$): δ 43.26 ($ArCH_2$), 124.10 (Ar), 126.02 (d, J_{CF} = 16.1 Hz, Ar), 130.03 (Ar), 160.34 (d, $^1J_{CF}$ = 246.4 Hz, Ar). ^{13}C NMR (CD_3CN): δ 48.61, 125.25 (t, J_{CF} = 1.9 Hz, Ar), 128.99 (m, Ar), 130.76 (t, J_{CF} = 2.7 Hz, Ar), 161.41 (dd, $^1J_{CF}$ = 250.2 Hz, J = 7.4 Hz, Ar). ^{19}F NMR ($CDCl_3$): δ −121.96 (t, J = 6 Hz).

***syn*-HF-phane.** To a mixture of 1,3-bis(bromomethyl)-2-fluorobenzene (3.0 g, 10.6 mmol) and 1,3-bis((trifluoroacetamido)methyl)benzene (3.48 g, 10.6 mmol) in boiling acetone (1500 mL) was added KOH powder in four portions (4 × 1.0 g) every 15 min. After an additional 2 h under reflux and 10 h at room temperature, the solvent was removed under reduced pressure. To the residue was added HCl (150 mL, 20% aqueous), and the impurities were extracted with CH_2Cl_2 (3 × 50 mL). The aqueous solution was basified with KOH to pH 14, and the resulting solution was extracted with CH_2Cl_2 (4 × 50 mL). The organic layer was separated from the mixture, dried over $MgSO_4$, and filtered, and the filtrate was evaporated. The remaining solid was chromatographed on silica gel (cyclohexane/diethylamine, 5/1), resulting in *syn*-F_2-phane (R_f = 0.22). Yield: 1.3 g (5.1 mmol), 48%. Mp: 126 °C. MS: *m*/*z* 256 (M^+, 100%). ^{1}H NMR ($CDCl_3$): δ 1.96 (br, NH), 3.64 (dd, J = 14.2 Hz, 1 Hz, 2H, CH_2), 3.81−4.01 (m, 4H), 4.32 (d, J = 14.4 Hz), 6.53−6.71 (m, 5H, Ar), 6.88 (t, J = 7.2 Hz, 1H, Ar), 7.31 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$): 48.12, 54.15, 124.02 (d, J_{CF} = 16 Hz), 126.12, 126.70, 127.27, 128.56 (d, J_{CF} = 7.7 Hz), 129.53 (d, J_{CF} = 7.5 Hz), 139.85, 159.80 (d, $^1J_{CF}$ = 243 Hz). ^{19}F ($CDCl_3$): δ −119.36 ppm.

F_2-[2.1.1]-cryptand. A mixture of *syn*-F_2-phane (90 mg, 0.328 mmol), 1,8-diiodo-3,6-dioxaoctane (121 mg, 0.328 mmol), and triethylamine (1.14 mL) in acetonitrile (220 mL) was refluxed for 5 d. The cold reaction mixture was filtered, the solid was washed with acetonitrile (25 mL), and the solvent was evaporated in vacuo. The residue was subjected to silica gel column chromatography with chloroform to give F_2-[2.1.1l-cryptand (R_f = 0.10−0.16) as a colorless solid. Yield: 6.5 mg (16 μmol), 5%. ^{1}H NMR ($CDCl_3$): δ 3.51 (t, J = 4.2 Hz, 4H, NCH_2), 3.40 (d, ^2J = 13.8 Hz, 4H, $ArCH_2$), 3.70 (t, J = 4.2 Hz, 4H, OCH_2), 3.81 (s, 4H, OC_2H_4O), 4.25 (d, ^2J = 13.8 Hz, 4H, $ArCH_2$), 6.42−6.47 (m, 6H, Ar). ^{19}F NMR ($CDCl_3$): δ −102.66 (s). ^{1}H NMR (CD_3CN): δ 2.91 (t, J = 4.2 Hz, 4H, NCH_2), 3.38 (d, ^2J = 13.8 Hz, 4H, $ArCH_2$), 3.62 (t, J = 4.2 Hz, 4H, OCH_2), 3.68 (s, 4H, OC_2H_4O), 4.16 (d, ^2J = 13.8 Hz, 4H, $ArCH_2$), 6.36−6.52 (m, 6H, Ar). ^{19}F NMR (CD_3CN): δ −100.70 (s).

Experimental data for F_2-[2.1.1]-cryptand·$LiSO_3CF_3$ are as follows. ^{1}H NMR (CD_3CN): δ 3.08 (t, J = 4.8 Hz, 4H, NCH_2), 3.47 (td, ^2J = 15.8 Hz, J = 1.9 Hz, 4H, $ArCH_2$), 3.88 (t, J = 4.8 Hz, 4H, OCH_2), 3.93 (s, 4H, OC_2H_4O), 4.24 (d, ^2J = 14.2 Hz, 4H, $ArCH_2$), 6.74−6.77 (m, 6H, ArH). ^{19}F NMR ($CDCl_3$): δ −129.23 (s br).

HF-[2.1.1]-cryptand. A mixture of *syn*-HF-phane (200 mg, 0.78 mmol), 1,8-diiodo-3,6-dioxaoctane (289 mg, 0.78 mmol), and Na_2CO_3 (0.5 g) in acetonitrile (500 mL) was refluxed for 3 d. The cold reaction mixture was filtered, the solid was washed with acetonitrile (25 mL), and the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (25 mL), and the solution was washed with aqueous KOH (5%). The organic layer was separated form the mixture, dried over $MgSO_4$, filtered, and the volatiles were evaporated. The residue was subjected to silica gel column chromatography with cyclohexane/diethylamine (10/1) to give HF-[2.1.1]-cryptand (R_f = 0.25) as a colorless solid. Yield: 196 mg (0.53 mmol), 68%. Mp: 123 °C. MS: *m*/*z* 370 (M^+, 50%). ^{1}H NMR (CD_3CN): δ 2.78−3.06 (m, 2H, NCH_2), 3.03−3.17 (m, 2H, NCH_2), 3.26−

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for F_2-[3.1.1]-cryptand·$NaCF_3SO_3$

	x	*y*	*z*	*U*(eq)[a]
Na1	949(2)	6188(1)	892(1)	48(1)
F1	400(3)	6671(1)	1602(1)	56(1)
F2	2022(3)	7219(1)	775(1)	51(1)
O1	3284(3)	5853(2)	1169(1)	55(1)
O2	2543(4)	5917(2)	226(1)	58(1)
O3	−219(4)	6161(2)	131(1)	71(1)
N1	3332(4)	7099(2)	1695(1)	51(1)
N2	−1080(4)	7208(2)	765(1)	61(1)
C1	156(5)	7291(2)	1768(2)	46(1)
C2	−1001(5)	7626(3)	1601(2)	55(1)
C3	−1255(6)	8240(3)	1807(2)	67(2)
C4	−369(7)	8486(3)	2143(2)	71(2)
C5	855(6)	8151(2)	2266(2)	60(1)
C6	1160(5)	7546(2)	2069(2)	47(1)
C7	2561(6)	7214(3)	2143(2)	57(1)
C8	−1877(5)	7352(3)	1204(2)	71(2)
C9	1823(4)	7844(2)	935(2)	43(1)
C10	622(5)	8165(2)	787(2)	55(1)
C11	518(7)	8819(3)	904(2)	73(2)
C12	1541(9)	9111(2)	1157(2)	81(2)
C13	2686(7)	8760(3)	1338(2)	72(2)
C14	2809(5)	8098(2)	1239(2)	50(1)
C15	3929(5)	7684(3)	1469(2)	63(1)
C16	−550(6)	7797(3)	527(2)	71(2)
C17	4393(5)	6578(3)	1755(2)	63(1)
C18	3781(6)	5920(2)	1648(2)	60(1)
C19	4313(6)	5906(3)	822(2)	67(1)
C20	3795(7)	5582(3)	381(2)	77(2)
C21	1792(7)	5572(3)	−120(2)	82(2)
C22	600(7)	5989(4)	−269(2)	86(2)
C23	−1378(7)	6566(4)	10(2)	90(2)
C24	−2039(5)	6822(4)	453(2)	84(2)
C25	−1434(9)	5181(4)	1999(2)	98(2)
S1	−1459(2)	5017(1)	1392(1)	72(1)
F3	−1811(12)	5830(3)	2058(3)	224(5)
F4	−323(8)	5205(7)	2195(2)	255(6)
F5	−2389(8)	4910(3)	2252(2)	165(3)
O4	−259(6)	5316(2)	1200(2)	99(2)
O5	−1263(8)	4307(3)	1402(3)	157(3)
O6	−2711(8)	5153(8)	1237(3)	272(7)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

3.32 (m, 3H), 3.40−3.50 (m, 3H), 3.55−3.88 (m, 8H), 4.00 (d, 2H, J = 16.5 Hz), 4.27 (d, 2H, J = 12.6 Hz), 6.21 (t, 1H, J = 7.4 Hz), 6.39−6.54 (m, 4H, Ar), 6.66 (t, 1H, J = 7.4 Hz), 8.01 (s, 1H, Ar). ^{13}C NMR (CD_3CN): δ 58.52, 61.17, 62.19, 70.70 (m), 72.44, 123.00 (d, J_{CF} = 5 Hz), 123.16, 126.28, 128.76 (d, J = 1.4 Hz), 129.15, 130.7 (d, J = 5.3 Hz), 142.14, 162.90 (d, $^1J_{CF}$ = 253.5 Hz). ^{19}F NMR (CD_3CN): δ −109.49.

F_2-[3.1.1]-cryptand. A mixture of *syn*-F_2-phane (400 mg, 1.46 mmol), 1,11-diiodo-3,6,9-trioxaundecane (604 mg, 1.46 mmol), and K_2CO_3 (1 g) in acetonitrile (400 mL) was refluxed for 3 d. The cold reaction mixture was filtered, the solid was washed with acetonitrile (25 mL), and the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (100 mL), and the solution was washed with aqueous KOH (5%). The organic layer was separated from the mixture, dried over $MgSO_4$, and filtered, and the volatiles were evaporated. The residue was subjected to silica gel column chromatography with cyclohexane/diethylamine (15/1) to give F_2-[3.1.1]-cryptand (R_f = 0.27) as a colorless solid. Yield: 245 mg (0.57 mmol), 39%. Mp: 108 °C. MS: *m*/*z* 432 (M^+, 100%). ^{1}H NMR (CD_3CN): δ 2.78 (t, J = 4.9 Hz, 4H, NCH_2), 3.14 (d, ^2J = 13.6 Hz, 4H, $ArCH_2$), 3.72−3.81 (m, 12H, OCH_2), 4.26 (d, ^2J = 13.6 Hz, 4H, $ArCH_2$), 6.46−6.55 (m, 6H, Ar). ^{19}F NMR (CD_3CN): δ −105.13 (s).

Table 4. Selected (Cationic Part) Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for F_2-[3.1.1]-cryptand·HCF_3SO_3

	x	*y*	*z*	*U*(eq)[a]
F2	−1561(1)	7909(1)	−1823(1)	36(1)
C1	1156(2)	7714(2)	−885(2)	32(1)
C2	1558(2)	7174(2)	−1515(2)	36(1)
C3	2116(2)	6476(2)	−1094(2)	46(1)
C4	2217(2)	6320(2)	−94(2)	48(1)
C5	1689(2)	6835(2)	483(2)	43(1)
C6	1126(2)	7544(2)	98(2)	35(1)
C7	495(3)	8097(2)	697(2)	42(1)
C8	1403(2)	7318(2)	−2617(2)	42(1)
C9	−1260(2)	7117(2)	−1557(2)	31(1)
F1	693(1)	8457(1)	−1230(1)	39(1)
C10	−858(2)	6610(2)	−2222(2)	37(1)
C11	−640(3)	5791(2)	−1924(2)	47(1)
C12	−771(3)	5532(2)	−999(3)	54(1)
C13	−1056(3)	6084(2)	−325(2)	45(1)
C14	−1290(2)	6906(2)	−586(2)	34(1)
C15	−1534(2)	7536(2)	147(2)	40(1)
C16	−606(3)	6932(2)	−3185(2)	41(1)
N1	−729(2)	8269(2)	246(2)	37(1)
C17a	−1067(4)	8995(3)	845(3)	25(1)
C18a	−1968(4)	9486(3)	169(3)	27(1)
C17b	−1643(10)	8856(6)	649(7)	37(3)
C18b	−1335(9)	9715(6)	423(7)	40(3)
O1	−1382(2)	9696(1)	−649(1)	44(1)
C19	−2250(2)	9820(2)	−1468(2)	41(1)
C20	−1726(2)	9817(2)	−2374(2)	35(1)
O2	−1119(2)	10571(1)	−2415(1)	50(1)
C21	−771(3)	10721(2)	−3344(2)	55(1)
C22	214(3)	10214(2)	−3546(2)	54(1)
O3	−136(2)	9388(1)	−3775(1)	40(1)
C23	767(3)	8859(2)	−3926(2)	51(1)
C24	331(3)	7980(2)	−4024(2)	45(1)
N2	256(2)	7595(2)	−3073(2)	35(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Experimental data for F_2-[3.1.1]-cryptand·$LiSO_3CF_3$ are as follows. ^{1}H NMR (CD_3CN): δ 2.85 (t, J = 9.9 Hz, 4H), 3.21 (d, ^2J = 13.9 Hz, 4H, $ArCH_2$), 3.78−3.84 (m, 12H, OCH_2), 4.32 (d, J = 13.9 Hz, 4H, $ArCH_2$), 6.64 (br s, 6H, Ar). ^{19}F NMR (CD_3CN): δ −119.73 (s).

Experimental data for F_2-[3.1.1]-cryptand·$NaSO_3CF_3$ are as follows. ^{1}H NMR (CD_3CN): δ 2.86 (t, J = 4.7 Hz, 4H, NCH_2), 3.18 (td, ^2J = 14.3 Hz, 4H, $ArCH_2$), 3.73 (s, 8H, OC_2H_4O), 3.80 (t, J = 4.7 Hz, 4H, OCH_2), 4.28 (d, ^2J = 14.1 Hz, 4H, $ArCH_2$), 6.63−6.66 (m, 6H, Ar). ^{19}F NMR (CD_3CN; 240 K): δ −121.52 (br s).

HF-[3.1.1]-cryptand. A mixture of *syn*-HF-phane (400 mg, 1.56 mmol), 1,11-diiodo-3,6,9-trioxaundecane (646 mg, 1.56 mmol), and K_2CO_3 (1.5 g) in acetonitrile (500 mL) was refluxed for 3 d. The cold reaction mixture was filtered, the solid was washed with acetonitrile (25 mL), and the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (25 mL), and the solution was washed with aqueous KOH (5%). The organic layer was separated from the mixture, dried over $MgSO_4$, and filtered, and the volatiles were evaporated. The residue was subjected to silica gel column chromatography with cyclohexane/diethylamine (5/1) to give HF-[3.1.1]-cryptand (R_f = 0.22) as a colorless solid. Yield: 494 mg (1.12 mmol), 76%. Mp: 69 °C. MS: *m*/*z* 414 (M^+, 100%). ^{1}H NMR (CD_3CN): δ 2.69−2.79 (m, 2H, NCH_2), 2.89−3.29 (m, 6H), 3.58−3.80 (m, 12H), 4.10 (d, 2H, J = 15.8 Hz), 4.32 (d, 2H, J = 12.2 Hz), 6.26 (t, 1H, J = 7.4 Hz), 6.42−6.72 (m, 5H, Ar), 7.75 (s, 1H, ArH). ^{13}C NMR (CD_3CN): δ 59.44, 59.88, 61.59, 69.77, 70.46, 70.80, 71.24, 72.13, 123.15 (d, J = 5 Hz), 123.82, 126.26, 127.45 (d, J = 2 Hz), 127.92 (d, J = 12 Hz), 130.77 (d, J =

Table 5. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for HF-[3.1.1]-cryptand·$NaClO_4$

	x	*y*	*z*	*U*(eq)[a]
Na	3454(3)	3973(2)	2759(2)	79(1)
N1	3672(6)	5048(4)	−573(6)	42(1)
C1	730(6)	4430(5)	183(6)	37(2)
C2	2241(8)	5470(6)	−1116(8)	53(2)
C3	832(7)	4887(5)	−992(7)	40(2)
C4	−326(9)	4773(6)	−2006(7)	52(2)
C5	−1572(8)	4188(7)	−1828(7)	57(2)
C6	−1575(7)	3722(6)	−672(9)	56(2)
C7	−451(7)	3805(5)	354(7)	45(2)
C8	−341(7)	3203(6)	1593(8)	51(2)
C9	3039(7)	3036(5)	−399(5)	32(1)
F1	3985(4)	3262(3)	759(3)	44(1)
C10	4264(7)	4361(5)	−1429(7)	45(2)
C11	3291(7)	3496(5)	−1528(6)	39(2)
C12	2437(7)	3230(5)	−2702(6)	41(2)
C13	1349(8)	2528(6)	−2687(7)	51(2)
C14	1044(8)	2143(5)	−1488(7)	43(2)
C15	1898(7)	2408(5)	−293(6)	38(2)
C16	1537(10)	2051(6)	1045(7)	49(2)
N2	1142(6)	2775(4)	1980(5)	39(1)
C17	1056(8)	2342(5)	3305(7)	46(2)
C18	2507(9)	1944(6)	3953(8)	56(2)
O1	3605(6)	2657(4)	4120(4)	52(1)
C19	5117(10)	2305(7)	4583(9)	69(2)
C20	6086(9)	3145(7)	4842(9)	71(3)
O2	6042(6)	3691(4)	3674(5)	59(2)
C21	6833(9)	4539(6)	3860(9)	60(2)
C22	6604(9)	5069(7)	2579(10)	67(2)
O3	5018(5)	5266(4)	2285(5)	52(1)
C23	4678(10)	6011(6)	1388(8)	58(2)
C24	4833(9)	5743(5)	−62(8)	54(2)
Cl	1609(2)	5485(1)	4333(2)	12(1)
O11	1947(11)	6228(10)	3600(2)	200(7)
O12	205(12)	5531(10)	4839(11)	154(4)
O13	2963(11)	5096(11)	4995(12)	186(7)
O14	1439(12)	4980(13)	3290(15)	220(9)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

5.5 Hz), 140.98 (d, $J = 0.5$ Hz), 162.98 (d, $^1J_{CF} = 253$ Hz). ^{19}F NMR (CD_3CN): δ −110.38.

Production of the Single Crystals. F_2-[3.1.1]-cryptand·$NaCF_3SO_3$ was synthesized by mixing stoichiometric amounts of ligand and $NaCF_3SO_3$ in acetonitrile. HF-[3.1.1]-cryptand·$NaClO_4$ was synthesized by mixing stoichiometric amounts of ligand and $NaClO_4$ in acetonitrile. Single crystals of both complexes were obtained by allowing ether to slowly diffuse into an acetonitrile solution of the respective complex. F_2-[3.1.1-cryptand·HCF_3SO_3 was synthesized by adding 1 equiv of HCF_3SO_3 to an acetonitrile solution of the ligand; single crystals were obtained by allowing ether to slowly diffuse into an acetonitrile solution.

X-ray Crystal Structure Determinations (Table 2). Suitable crystals were mounted on top of a glass fiber. X-ray data were collected on a Siemens AED diffractometer using Mo Kα) radiation (71.069 pm) and a graphite monochromator. All structures were solved (SHELXS-86, SHELX-97)[26,27] and refined (SHELXL-93, SHELX-97)[28] against F_2. In the structures described, all non-hydrogen atoms were refined using anisotropic temperature coefficients (Tables 3−5). Hydrogen atoms were refined with fixed isotropic temperature coefficients (riding model); only the hydrogen atom attached to the nitrogen atom was localized and refined freely. An empirical absorption correction (ψ scans) was applied. In the crystal structure of F_2-[3.1.1]-cryptand·HCF_3SO_3, one C_2H_4 unit (C17a, C18a) is disordered and was refined in two alternative orientations. Definitions of *R* factors: $wR2 = \{\sum 2\sigma(I)[w(F_o^2 - F_c^2)^2]/\sum 2\sigma(I)[w(F_o^2)^2]\}^{1/2}$, $R1 = \sum 2\sigma(I)||F_o| - |F_c||\sum 2\sigma(I)|F_o|$. The goodness of fit is based on F^2: $\mathrm{GOF} = \{\sum 2\sigma(I)[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where *n is* the number of reflections and *p* is the total number of parameters refined.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Grants DFG Pl 178/3-1 and DFG Pl 178/3-2), the Institut für Anorganische und Analytische Chemie, the Fonds der Chemischen Industrie, the Freiburger Wissenchaftliche Gesellschaft, and a Heisenberg fellowship to H.P. We wish to thank Dipl.-Chem. B. Müller and H. G. Schmidt for the collection of the X-ray data sets.

Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

IC9708069

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