The electrophilic character of tin in the new compounds **3** is manifested in reactions with nucleophiles.[14] With pyridine and with 2,2'-bipyridyl, **3a** forms the adducts **6a** and **7a**,[15] in which the tin atom is coordinatively saturated (cf. Table 1, ^{119}Sn resonance signals at high field). As in the case of **3a**, dynamic processes can also be demonstrated for **6a** and **7a** by ^{1}H- and ^{13}C-NMR spectroscopy. The structure for the intermediates **4** is based on consistent sets of NMR data (cf. Table 1 for **4b**) and is confirmed by the isolation of the final product **5**. The results suggest that the for-

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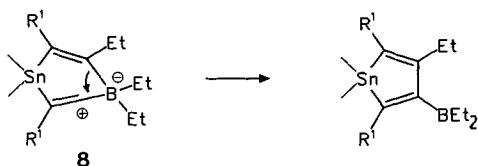
mation of compounds **4** and **5** from **3** and **4** respectively proceeds via an Sn-Substituted vinyl cation **8**.

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[2] a) N. A. Bell, I. W. Nowell, H. M. M. Shearer, *J. Chem. Soc. Chem. Commun. 1982*, 147; b) P. N. V. P. Kumar, E. D. Jemmis, *J. Am. Chem. Soc. 110* (1988) 125; c) P. Jutzi, *Adv. Organomet. Chem. 26* (1986) 217.

[3] a) B. Wrackmeyer, *Rev. Silicon Germanium Tin Lead Compd. 6* (1982) 75; b) B. Wrackmeyer in S. Hermanek (Ed.): *Boron Chemistry*, World Scientific, Singapore 1987, p. 387–415.

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[5] L. Killian, B. Wrackmeyer, *J. Organomet. Chem. 148* (1978) 137.

[6] a) Only in the case of tetra-1-propynylstannane **1a** and triethylborane **2** and upon using the pure intermediate **3a** could no well-defined products be obtained. Various solutions of **3a** [concentration between 0.5 M down to 0.001 M (in order to suppress intermolecular reactions) in CH$_2$Cl$_2$, THF, hexane or toluene at −78 °C afford elemental tin and red, highly viscous oils on warming to room temperature. The large number of broad ^{13}C- and ^{1}H-resonances point to complex mixtures with polymeric constituents. Separation into pure components could not be achieved by distillation. An analogous behavior was observed upon heating the compounds **6a** and **7a**.—b) In contrast, spiro compounds analogous to **5** are formed smoothly from tetra-1-propynylsilane or -germane and excess triethylborane: R. Köster, G. Seidel, MPI für Kohlenforschung, Mülheim a. d. Ruhr (FRG), private communication.

[7] **5b**: A solution of **1b** (3.10 g, 9.37 mmol) in toluene (20 mL) was cooled to −78 °C, treated with **2** (3.00 mL, 21.3 mmol), and the stirred mixture was slowly warmed to room temperature. After heating to 60 °C for 24 h the solvent and unchanged **2** were removed in vacuo. Kugelrohr distillation of the residue afforded 3.85 g (78 %) of **5b** (b.p. 175–180 °C/10^{-3} torr). **5c** (180–190 °C/10^{-3} torr), **5d** (b.p. 200 °C/10^{-3} torr), and **5e** (b.p. 185–190 °C/10^{-3} torr) were obtained analogously. ^{1}H- and ^{13}C-NMR data are consistent with the proposed structures. ^{119}Sn/^{11}B-NMR (111.9 MHz, CD$_2$Cl$_2$, 298 K): (^{119}Sn)/(^{11}B) = − 19.7/83.0 (**5b**), − 13.7/84.3 (**5c**), − 48.3/86.3 (**5d**), − 15.7/85.2 (**5e**).

[8] **3a**: A solution of **1a** (3.2 g, 11.6 mmol) in toluene (40 mL) was cooled to −78 °C, treated with 4 mL (28 mmol) of **2** and the stirred mixture warmed to 0 °C. After ca. 30 min the solvent and excess **2** were removed in vacuo. The remaining yellow solid was crystallized from pentane at −78 °C; 3.8 g (69 %); decomp. above − 20 °C. **3a**: ^{1}H NMR (300 MHz, C$_7$D$_8$, 243 K): δ(^{1}H)[^{n}J(^{119}Sn^{1}H)] = 0.80 m, 1.10 t (20H; BEt$_2$) 2.22 q, 0.96 t (10H; =CEt), 1.42[7.3] s(6H; ≡CMe), 1.81[107.6] s(6H; =CMe).

[9] **3b**, **3c**, **3d**, **3e**: relevant ^{1}H- and ^{13}C NMR data correspond to the values for **3a**. ^{119}Sn/^{11}B NMR (CD$_2$Cl$_2$, 298 K): δ(^{119}Sn)/δ(^{11}B) = + 207.5/ −4.9 (**3b**); + 203.1/−4.5 (**3c**); + 223.2/−4.3 (**3d**); + 202.1/−4.4 (**3e**).

[10] R. Boese, D. Bläser, *J. Appl. Crystallogr. 22* (1989) 394.

[11] X-ray structure analysis of **3a** at 115 K: $P2_1/c$, $a = 11.924(2)$, $b = 14.512(3)$, $c = 14.299(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 97.29(1)°$, $V = 2454.4(7)$ Å^3, $Z = 4$, $\varrho_{calcd} = 1.274$ g cm^3, $\mu = 1.05$ mm^{-1}, Mo$_{K\alpha}$ radiation (graphite monochromator), $\lambda = 0.71069$ Å; 3414 independent reflections. 2979 observed ($F_0 \geq 4\sigma(F)$); 2θ(max) = 45°; absorption correction: empirical, Ψ scans in the 2θ range, (°): 3 2 35 max/min. Transmission: 0.926/0.815, R_{merg} before/after the correction: 0.0303/0.0203; $R = 0.029$, $R_w = 0.026$. Further details of the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-320291, the names of the authors, and the journal citation.

[12] ^{13}C- and ^{119}Sn-CP/MAS-NMR (Bruker MSL 300). We thank Drs. *A. Sebald* and *L. H. Merwin* for recording the spectra.

[13] R. Boese, M. Bühl, P. von R. Schleyer, unpublished results.

[14] A report of the reaction of **3a** with ammonia, amines, and alcohols will be reported elsewhere.

[15] **6a**: A solution of **3a** (0.5 g, 1.1 mmol) in toluene (ca. 20 mL) was treated with pyridine (0.3 mL, 3.7 mmol) at −78 °C. After removal of solvent and excess pyridine in vacuo at 0 °C their remained 0.6 g (95%) of a colorless solid (>20 °C, decomp.). **7a** was obtained analogously as a yellow solid (>40 °C, decomp.), whereby **3a** already reacts at −78 °C.

Stable Phosphazenium Ions in Synthesis—an Easily Accessible, Extremely Reactive "Naked" Fluoride Salt **

By *Reinhard Schwesinger,* *Reinhard Link, Gerhard Thiele, Heinz Rotter, Dieter Honert, Hans-Heinrich Limbach,* and *Ferdinand Männle*

Dedicated to Professor Horst Prinzbach on the occasion of his 60th birthday
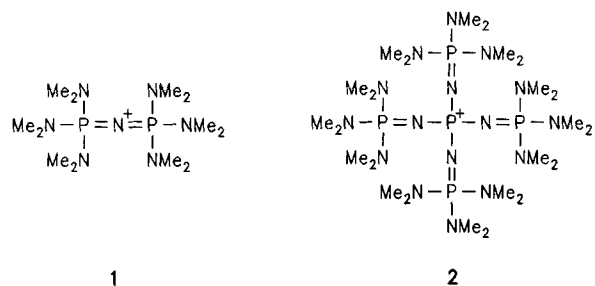
Lipophilic organic cations are of exceptional importance in preparative organic chemistry; however, their breadth of application has hitherto been limited owing to their modest stability towards bases and nucleophiles.[1] This is especially true in the case of organic fluoride salts,[2] efficient auxiliary bases and indispensable reagents in organosilicon chemistry. The only unsolvated organic ("naked") fluoride salt that has proven reliable[3] is tetramethylammonium fluoride,[6] certainly the most reactive source of fluoride known so far.[7] However, it is only sparingly soluble, and the cation is particularly unstable towards strong nucleophiles. We now report on the stable, easily accessible phosphazenium fluoride **1-F**, a source for THF solutions of naked fluoride ions.

In connection with our studies on the preparation of novel, extremely basic polyaminophosphazenes we found that peralkylated cations such as **1** and particularly **2** are many orders of magnitude more stable than conventional organic cations towards nucleophiles.[8, 9] In the meantime we have been able to simplify the synthesis of **1**[8, 10] considerably: reaction of PCl$_5$ with NH$_4$Cl and subsequently with
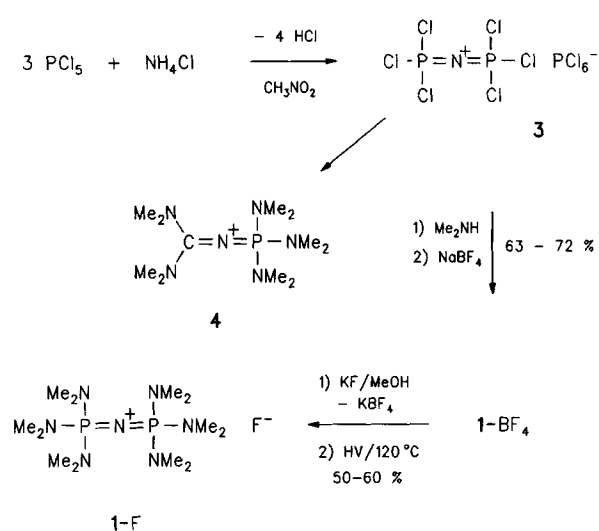
[*] Priv.-Doz. Dr. R. Schwesinger, Dipl.-Chem. R. Link
Institut für Organische Chemie und Biochemie der Universität
Albertstr. 21, W-7800 Freiburg (FRG)

Prof. Dr. G. Thiele, Dr. H. Rotter, Dr. D. Honert
Institut für Anorganische Chemie der Universität Freiburg (FRG)

Prof. Dr. H.-H. Limbach, Dipl.-Chem. F. Männle
Institut für Physikalische Chemie der Universität Freiburg (FRG)

1

Me₂N   NMe₂
 | |
Me₂N−P=N⁺=P−NMe₂
 | |
Me₂N   NMe₂

2

                NMe₂
                 |
        Me₂N−P−NMe₂
                 ||
Me₂N   N   NMe₂
 | || |
Me₂N−P=N−P⁺−N=P−NMe₂
 | || |
Me₂N   N   NMe₂
                 |
        Me₂N−P−NMe₂
                 |
                NMe₂

dimethylamine and NaBF₄ to give 1-BF₄ via 3[11] can be carried out in a one-pot process; hexamethylphosphoric triamide (HMPA) and salts of **4** are formed as by-products via complex routes from the aminolysis product of PCl_6^- and CH_3NO_2 (Scheme 1).

Scheme 1.

3 PCl₅ + NH₄Cl $\xrightarrow[CH_3NO_2]{-4\ HCl}$

        Cl   Cl
         | |
   Cl−P=N⁺=P−Cl   PCl₆⁻
         | |
        Cl   Cl

3

Me₂N   NMe₂
   \ |
    C=N⁺=P−NMe₂
   / |
Me₂N   NMe₂

4

1) Me₂NH
2) NaBF₄   63 − 72 %

Me₂N   NMe₂
 | |
Me₂N−P=N⁺=P−NMe₂   F⁻
 | |
Me₂N   NMe₂

1-F

1) KF/MeOH
   − KBF₄
                        1-BF₄
2) HV/120 °C
   50−60 %

Scheme 1. HV = high vacuum.

On attempting to obtain 1-F by double reaction of 1-BF₄ with KF in methanol/water and drying in a vacuum, partial hydrolysis of the cation and formation of 1-FHF was observed. However, on using anhydrous methanol a product was obtained from which the solvent could be largely removed at 120 °C. After washing with THF, colorless, extremely hydroscopic 1-F was obtained in 50−60% yield and could be recrystallized from THF.

According to the X-ray structure analysis,[12] the very first of an organic unsolvated fluoride salt, 1-F crystallizes with FeS₂-(in the broadest sense NaCl-)type structure, hitherto unprecedented for organic compounds, with discrete phosphazenium and fluoride ions. The cation–anion distance (6.3 Å) is the largest observed in any known solvent-free fluoride salt (KF 2.67 Å, CsF 3.01 Å, NMe₄F presumably 4.2 Å[6]), which immediately allows conclusions to be drawn about the solubilities and reactivities of the ion pairs or ion aggregates. Six P–N bonds point almost exactly (P1−N2−F = 178°) to a fluoride ion, which is surrounded approximately icosahedrally by one proton each of the twelve methyl groups. The F–H distances (2.37 and 2.57 Å), however, are in the region of the sum of the van-der-Waals radii and are too large for hydrogen bridges, i.e. the fluoride ion here (in agreement with IR data) can be regarded as "naked". The cation has crystallographic C_{3i} (S_6) symmetry,

its conformation is almost the same as that of the isoelectronic oxa compound[14] and, with respect to the linearity of the bridge, also that of the carba compound.[15] The PNP bridges in the cation of 5[8] are indeed bent (141 and 143°[16]), but in the case of 1 there is no evidence of disordered bent conformers, for example the P–N1 distance is very similar to the P–N distances in the bridges of 5 (1.55–1.58 Å), and the standard deviation is small. The dimethylamino groups are turned through about 39° from the N1–P–N2 plane, their six N atoms staggered with respect to the P–N1–P bridge and slightly pyramidal (sum of angles 358.2°).

Me₂N   HN⁺tBu NMe₂
 | || |
Me₂N−P=N−P−N=P−NMe₂   PF₆⁻   **5**
 | | |
Me₂N   NMe₂   NMe₂
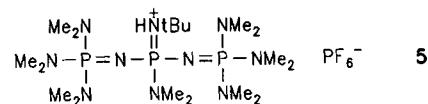
Crystalline 1-F is stable indefinitely at room temperature in the absence of moisture, and is stable to a limited extent on heating; above 144 °C, however, it melts with decomposition and formation of 1-FHF.

At 20 °C, 1-F dissolves in THF to give an approximately 2 mM solution, which rapidly becomes inactive in the absence of the corresponding solid phase, even in fired glass vessels; at boiling temperature it is markedly more soluble and, for a few hours, is stable except for the reaction with the glass surface. The solutions of 1-F are more basic than the corre-
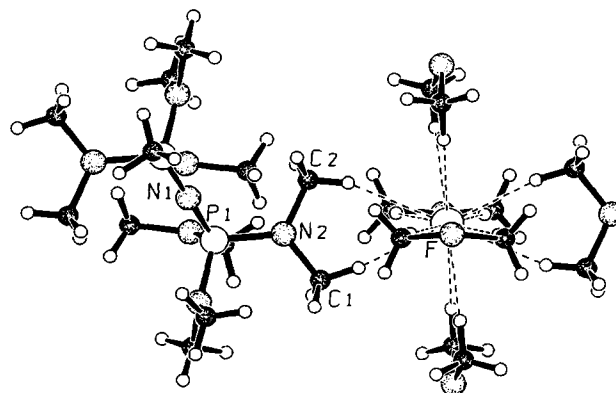

Fig. 1. Structure of 1-F in the crystal [17]. Bond lengths [Å] and angles [°]: P–N1 1.536(2), P–N2 1.644(5), N2–Cl 1.471(9), N2–C2 1.483(8); N1–P–N2 110.8(2), P–N2–Cl 122.3(4), P–N2–C2 118.9(4).

sponding solutions of previously known phosphazene bases.[8] Triphenylmethane-containing, deep-red solutions of 1-F (with solid phase) are decolorized within a minute already at − 55 °C upon treatment with an excess of tetrabutylammonium hexafluorophosphate; this suggests that "naked tetrabutylammonium fluoride" was no more than a myth.[2b]

Compared with solvated fluorides,[2a] potassium *tert*-butoxide[18] or phosphazene bases,[8] the fluoride ion in 1-F shows unique E2 reactivity (with formation of 1-FHF) with comparatively unusually low nucleophilicity, and is excellently suitable for the generation of 1-alkenes from 1-halides; e.g., three equivalents of 1-F react with 1-iodoundecane already at − 70 °C to give a 9:1 mixture of 1-undecene and 1-fluoroundecane. The benzenesulfonate of lanost-8(9)-en-3β-ol reacts in THF within 30 minutes at room temperature

to give lanosta-2,8(9)-diene exclusively, a reaction which with potassium *tert*-butoxide in dimethyl sulfoxide/THF (1:1) furnishes the diene in only 75% yield after four days at 80°C.[19]
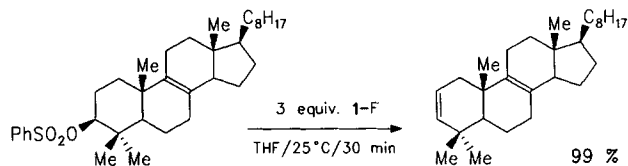
1-F enables, for the first time, the alkylation of an allyl anion species generated from allyltrimethylsilane. The addition of one equivalent of a 1:1 mixture of allyltrimethylsilane and 1-iodoundecane to 2.2 equivalents of 1-F at −78°C leads (not optimized) to 1-tetradecene in 70% yield; only the aforementioned reaction of 1-F with alkyl halide competes to any significant extent.

No extensive conversion can be achieved with one equivalent of 1-F; the difluorotrimethylsilicate monoanion[21] formed after alkyl transfer (presumably from the allyldifluorotrimethylsilicate dianion[20]) is here apparently neither sufficiently reactive as source of fluoride nor as source of methyl anions; in the absence of electrophiles, however, even the methyl groups of the silane are transferred to other compounds, as recognizable by the formation of a precipitate of
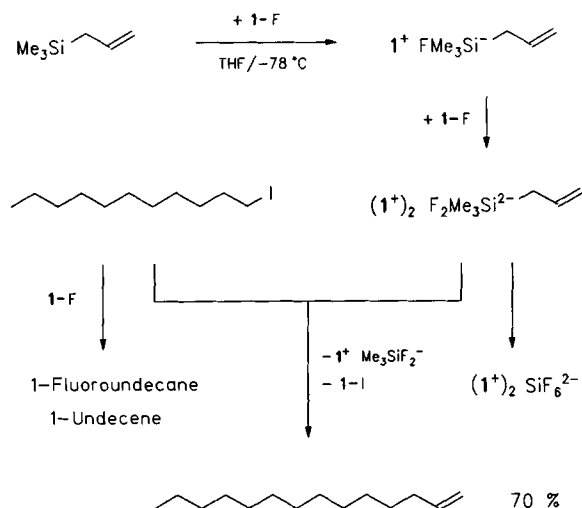
$(1)_2$-SiF_6; the supernatant orange solution decolorizes on thawing and 1 can be recovered from the mixture almost quantitatively as tetrafluoroborate by aqueous work-up. Further studies will be concerned with elucidating the mechanisms of the reactions involved ("naked" allyl anion or hypervalent Si species), exploring the scope of application of this alkylation (and analogous reactions of other silanes) particularly in cyclization reactions, and investigating, in general, the possible use of "naked" phosphazenium salts for the anion-activation of main group organometallic compounds.

Experimental

1-BF_4: A suspension of PCl_5 (208.5 g, 1.00 mol) and NH_4Cl (17.83 g, 0.333 mol) in anhydrous CH_3NO_2 (330 mL) under N_2 was slowly heated to 100°C. After evolution of HCl had ceased (ca. 1 h), the mixture was cooled to −10°C (dry-ice bath, 3 crystallized as pale yellow, robust needles). Dimethylamine

(330 g, 7.33 mol, free of primary amines) was then passed (after drying over Na_2O) into the mixture at −10°C (delivery tube above solution). After storage at 20°C for 2 d the mixture, which had turned yellow-orange, was treated with a solution of $NaBF_4$ (73 g, 0.67 mol) in water (330 mL) and stirred vigorously. The mixture was then adjusted to pH 8 by addition of H_3PO_4. The heavier, organic phase was separated off, the aqueous phase extracted once with a little CH_3NO_2, and the combined organic phases washed once with water (170 mL). The organic phase was then evaporated down in vacuo and dried in a high vacuum. The orange-brown, partly crystalline residue (Caution! contains ca. 0.2 mol HMPA) was treated with a 5% $NaBF_4$ solution (330 mL), and the mixture stirred vigorously, cooled to −5°C for 30 min, and finally filtered. The colorless crystals were then washed with ice-cooled 5% $NaBF_4$ solution (170 mL) and with a little ice-water. For the further reaction to give 1-F, the crude crystals of 1-BF_4 were recrystallized from THF (800 mL) and dried in a high vacuum. Yield 90–102 g (63–72%); m.p. 260°C (decomp). Correct elemental analysis (C,H,N). ^1HNMR (250 MHz, $CDCl_3$, 30°C, TMS): $\delta = 2.69$ (m).

1-F: A solution of 1-BF_4 (25.63 g, 60.00 mmol) in MeOH (60 mL, < 50 ppm water) was treated with a solution of KF (3.486 g, 60.00 mmol, dried for 12 h at 240°C in a high vacuum) in MeOH (40 mL) under N_2. After removal of KBF_4 by suction, the majority of MeOH was removed by evaporation in vacuo at room temperature. The residue was dried in a high vacuum for 1 h at 100°C (initially with stirring until the contents of the flask became solid, no Teflon used, vacuum apparatus with 10-mm flow cross-section) and 1–2 h at 120°C bath temperature (until constant weight, if necessary with ^1H-NMR monitoring of MeOH), and finally digested and washed with THF (distilled over Na/K/anthracene). After drying in a high vacuum at room temperature, 11–13 g (50–60%) of almost colorless crystals were obtained; according to titration (with HPF_6 salt of 1,8-bis(dimethylamino)naphthalene against N-ethyl-4-nitroaniline in THF) at least 88–93% in strongly basic fluoride; ca. 20% 1-BF_4 could still be recovered from the mother liquor. The crude product was sufficiently pure for most reactions, but could be recrystallized from THF, whereupon the titer increased. M.p. 144°C (decomp.). IR [perfluorokerosine]: $\tilde{\nu}$ [cm^{-1}] = 2978, 2910, 2886, 2850, 2798, 2478, 2386, 2340, 2214, 1866, 1806, 1736, 1464. ^{19}F-NMR (282 MHz, HMPA, 77°C, polyethylene ampule in NMR-tube, CCl_3F external): $\delta = -81$ (s, $\nu_{1/2} = 97$ Hz) [22].

1-Tetradecene from allyltrimethylsilane and 1-iodoundecane: A suspension of crude 1-F (832 mg, at least 2.05 mmol of strongly basic fluoride, see above) in anhydrous THF (3.5 mL) was degassed by removal of 0.5 mL of solvent in a high vacuum. The degassed solution was cooled to −80°C, treated dropwise with a mixture of 1-iodoundecane (296 mg, 242 μL, 1.05 mmol) and allyltrimethylsilane (120 mg, 168 μL, 1.05 mmol), and the mixture warmed to room temperature. After addition of water (10 mL), the mixture was extracted with 4 × 5 mL of pentane, the combined pentane extracts washed four times with water, dried over Na_2SO_4, and then the solvent was removed in vacuo. Yield: 208 mg of crude product, according to GC and ^1H-NMR analysis consisting of 144 mg of 1-tetradecene (70% yield), 1-iodoundecane (2%), trimethylsilanes (ca. 2%), 1-undecene (22%), and 1-fluoroundecane (2–3%).

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[3] Salts of naked fluoride ions have already been reported which apparently were obtained from acetonitrile solutions [4] or extracted into $CDCl_3$ [5]. The very high basicity already found for the tetramethylammonium fluoride, however, indicates that naked fluoride ions could not be capable of existing in such acidic solvents [6].

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[12] X-ray structure analysis: $C_{12}H_{36}N_7P_2 \cdot$ F, space group *Pa3* (No. 205), $a = 12.603(1)$ Å from 25 reflections with $19.5 < 2\theta < 39°$, $V = 2001.33$ Å^3, $Z = 4$, crystal dimensions $0.16 \times 0.1 \times 0.08$ mm^3, $\mu(Mo_{K_\alpha}) = 2.3$ cm^{-1}, 296 K, no absorption correction, ω-2θ scan, Nonius CAD4 diffractometer, 7346 measured reflections, 589 independent reflections,

471 with $F_0 > 6\sigma(F_0)$. Direct methods [13], $R = 0.0534$ ($R_w = 0.0461$), anisotropic temperature factors for all atoms except hydrogen. Weighting scheme $\omega^{-1} = \sigma^2(F_0) + 0.000024\ F_0^2$, 35 free parameters. Maximum electron density in subsequent difference Fourier synthesis $\pm\ 0.3$ eÅ^3. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-55496, the names of the authors, and the journal citation.

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[22] Because of the relatively high proportion of entrained water associated with the sparing solubility of 1-F, considerable amounts of FHF$^-$ were recognizable, in particular, in the THF spectra ($\delta = -91$) (in HMPA: $\delta = -145$ (d, ^1J(F,H) $= 120$ Hz) (so far, best F$^-$:FHF$^-$ ratio in THF $= 1:1$, in HMPA 2.3:1).
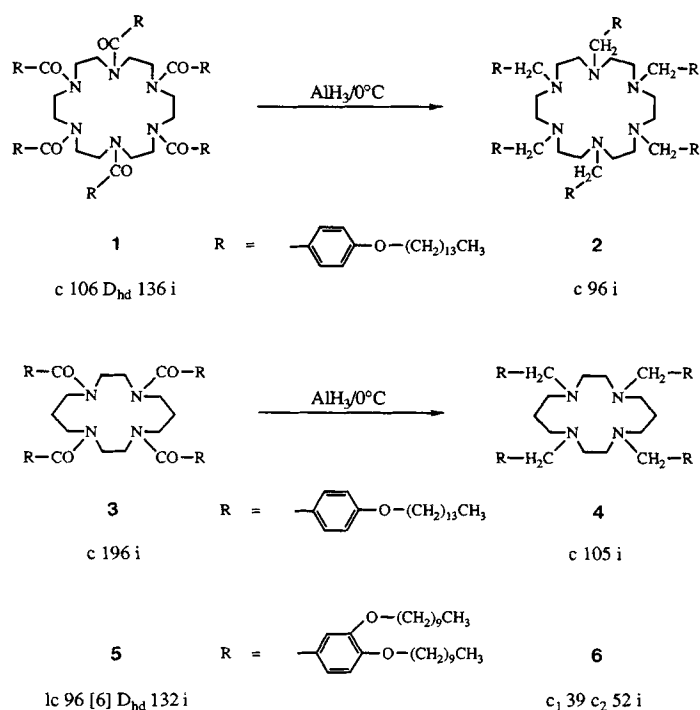
Scheme 1. Temperatures in °C.

Complexation of Transition Metal Ions with Substituted Aza Macrocycles: Induction of Columnar Mesophases by Molecular Recognition

By Andrea Liebmann, Carlo Mertesdorf, Thomas Plesnivy, Helmut Ringsdorf,* and Joachim H. Wendorff

Coronands, as for example [18]crown-6, readily complex metal ions. Whereas crown ethers can incorporate both alkali-metal ions and alkaline-earth-metal ions with high complexation constants, the nitrogen analogues show special affinity for transition metal ions.[1] Furthermore, the aza macrocycles can be converted by substitution at the nitrogen atom into discoid compounds, which in the case of acylated compounds can form discotic liquid crystal phases;[2] however, their complexing ability is only modest. The results presented in this contribution show that both of these aspects of coronand chemistry can be combined, namely the formation of host/guest complexes and their self-assembly to liquid crystalline phases.

At temperatures between 106 and 136°C, hexa(p-tetradecyloxybenzoyl)hexacyclene 1 forms a columnar discotic mesophase (D_{hd}),[3] which, owing to the central cavity in the columns, has been described by Malthête et al. as tubular.[2] With the help of gas-volumetrically calibrated solutions of AlH₃ in THF it was possible to carry out the reduction of 1 to the nonliquid crystalline amine 2 in high yields (83%) (Scheme 1).[4]

The cyclam derivatives 4 and 6[5] were prepared analogously from the acylated tetraaza macrocycles 3[3] and 5[6] respectively (Scheme 1), of which only the derivative 5 bearing eight wing groups forms a mesophase.

With exception of compound 6, complexation of transition metal salts by the highly flexible cyclic amines induces a

liquid crystalline phase which is absent for the free amines. We attribute this phenomenon in part to a stiffening of the macrocycle. This interpretation is consistent with the fact that the stiffer, structurally analogous amides can form mesophases. The phase behavior of the metal complexes is given in Table 1.

Table 1. Phase behavior of the transition metal complexes [a].

Complex	Ratio host/guest	Phase T [°C]
2 · Co(NO₃)₂	2:1 [7]	c 30 N_c 60 [b] i
2 · Ni(NO₃)₂	1:1	c 29 lc 95 i
4 · Cu(NO₃)₂	1:1	c 18 lc [c]
6 · Cu(NO₃)₂	1:1	g 67 i

[a] Abbreviations: c = crystalline; N_c = nematic-columnar; i = isotropic; lc = liquid crystalline; g = glassy. [b] First cooling curve of the DSC thermogram. [c] Decomposition above 160°C.

In the following communication we shall deal more closely with the 1:2 Co(NO₃)₂/amine 2 system, which has been characterized as liquid crystalline by polarization microscopy, differential calorimetry, and X-ray diffraction analysis. Upon heating under the polarization microscope the birefringence of the enantiotropic liquid crystal phase is visible up to a temperature of about 53°C. Initially, no specific texture is recognizable, but tempering at ca. 40°C leads after 3 h to the formation of characteristic schlieren. The texture depicted in Figure 1 shows the singularities of $s = -1/2$ and $s = -1$ typical for a nematic phase. The enthalpy for the transition between the liquid crystalline and isotropic phase, which is obtainable from the cooling curve of the DSC thermogram is of an order of magnitude that is consistent with a transition into a slightly ordered nematic phase. A macroscopic planar orientation of the mesophase can easily be achieved by mechanical shearing. Under crossed polarizers it

[*] Prof. Dr. H. Ringsdorf, Dipl.-Chem. C. Mertesdorf, T. Plesnivy
Institut für Organische Chemie der Universität
J.-J.-Becher-Weg 18–20, W-6500 Mainz (FRG)

Dipl.-Phys. A. Liebmann, Prof. Dr. J. H. Wendorff
Deutsches Kunststoff-Institut
Schlossgartenstrasse 6 R, W-6100 Darmstadt (FRG)