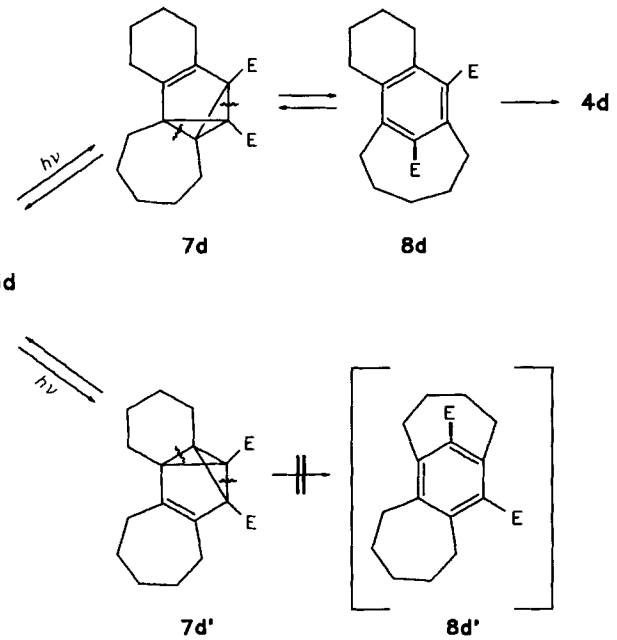
which in turn isomerizes immediately to **4b**. This was corroborated by the fact that irradiation of **5b** did not give rise to any of its precursors but afforded exclusively **4b**. A similar argument can be considered for the decomposition of **7b**. The C–C bond linking the carbomethoxy groups in the bicyclobutane moiety is destabilized for the same reason as above (in this case the interaction is with two vicinal groups), so cleavage of this bond leading to [5]metacyclophane **8b** is kinetically favored over the back reaction, which affords the thermodynamically more stable **3b**.

The postulated intermediates **7b**, **8b**, and **9b** have not yet been detected. We attribute this both to their low equilibrium concentrations and their increased reactivity. As already mentioned, **3a** did not undergo this rearrangement. Even with extended irradiation times and shorter wavelengths (254 nm) only a slow polymerization was observed, probably because the potential [4]metacyclophane **9a** does not exist under the given conditions. All efforts to isolate a [4]metacyclophane derivative have failed so far because of its enormous strain energy.[8, 9] In our case we assume that the path leading to **4a** is interrupted at the second step (**7a** → **8a**). Further evidence for benzvalene **7d** and [6]metacyclophane **8c** was obtained from the fact that **3c** and **3d** did afford their respective terephthalic ester isomers **4c** and **4d**. However, under identical conditions as those used for **4b**,[10] the yields of both **4c** (30% after 12 h) and **4d** (24% after 12 h) were considerably smaller. Because the equilibrium concentration was lower, **5c** could only be identified in the reaction mixture by the typical δ value for the protons of the methoxy groups in the ^{1}H NMR spectrum. In the case of **4d**, none of the intermediates could be fully characterized for the same reason. The reduced rate in both cases can be explained



Scheme 4.

by the postulated intermediates. Firstly, [6]metacyclophane **8c** is distinctly more stable[11] than the lower homologue **8b**, and the strain releasing steps (**8c** → **5c** → **4c**) are thus less forceful. Secondly, it is noteworthy that the conversion of **3d** to **4d** occurred at about half the rate of that of **3b** to **4b** (52% after 12 h). A plausible explanation is given in Scheme 4.

Whereas in the case of **3b** two identical benzvalene intermediates afford **8b**, only the path via **7d** is possible for **3d**, since the path via **7d'** would lead to a highly strained [4]metacyclophane **8d'**. A steric factor (tethering of neighboring centers) is necessary, because irradiation of unsubstituted phthalic ester does not yield terephthalic ester. In conclusion, a tuned interplay of steric and electronic effects is responsible for the creation of doubly bridged prismanes with C_2 symmetry from tricyclic phthalic ester derivatives. Experiments in which the ester groups are substituted by different functions are currently in progress to substantiate the electronic argument.

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1a, 141634-78-8; **1b**, 130434-04-7; **1c**, 130434-06-9; **1d**, 141634-79-9; **3a**, 51037-17-3; **3b**, 130434-08-1; **3c**, 130434-09-2; **3d**, 141634-80-2; **4b**, 141634-81-3; **4c**, 141634-82-4; **4d**, 141663-42-5; **5b**, 141663-43-6; **5c**, 141663-44-7; **5d**, 141663-45-8; **6b**, 141634-83-5; **6c**, 141634-84-6; **6d**, 141634-85-7.

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Template-Controlled Organization of a Fluoride Surface—An Analogue of a Crown Ether in the Reaction of $[\{(\eta^5\text{-}C_5Me_5)TiF_3\}_2]$ with Sodium Fluoride**

By *Herbert W. Roesky,* Mansoreh Sotoodeh,* and *Mathias Noltemeyer*

Dedicated to Professor Klaus Weissermel on the occasion of his 70th birthday

So far in studies concerning molecular recognition, host molecules were applied whose receptor surface comprises almost exclusively oxygen, sulfur, nitrogen, and/or phospho-

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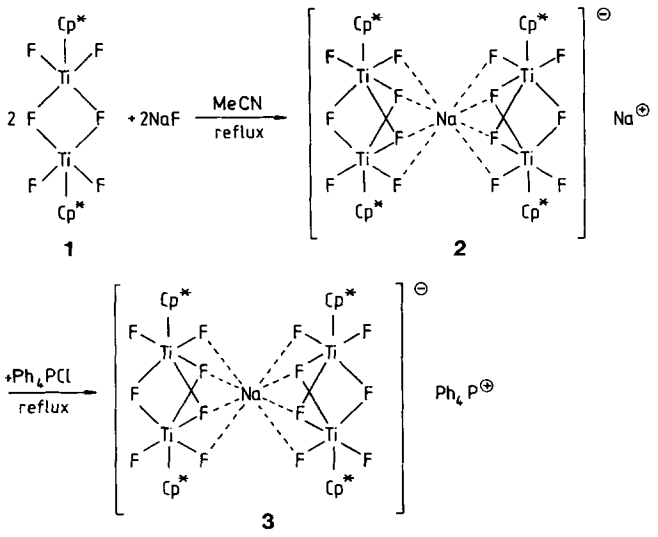
rus atoms.[1-3] For this, the receptor structures were predetermined and could be open, half-open, or closed. We report here a new class of nucleophilic host systems with a "fluoride surface", which forms in a template-controlled manner.

The reaction of $[Cp^*TiCl_3]$ ($Cp^* = \eta^5$-C_5Me_5)[4] with AsF_3 leads to the dimer $[(Cp^*TiF_3)_2]$[5] **1** by chlorine–fluorine exchange. Compound **1** reacts with NaF in MeCN to give **2**.



A third fluoride bridge is formed between the titanium atoms by the incorporation of a fluoride ion in **1**. In the salt **2**, one of the two sodium ions is complexed by two $[(Cp^*TiF_3)_2F]^-$ fragments in such a way that a fluoride surface forms at this sodium ion. By this complexation the two sodium ions become distinguishable. With tetraphenylphosphonium chloride only one sodium ion can be exchanged, and thus $Ph_4P[\{(Cp^*TiF_3)_4F_2\}Na]$ (**3**) is obtained. The nature of the wrapping of the Na^+ ion by two $[(Cp^*TiF_3)_4F_2]^-$ fragments is similar to that in $[Na([12]crown\text{-}4)_2]^+$.[6]

In order to find out whether the starting compound can differentiate between different cations, the corresponding reactions were carried out. We observed that LiF did not react, CsF led to insoluble polymeric products, and KF[7] behaved like NaF.

Indications of the stoichiometric composition of **3** were obtained from the elemental analysis and the ^1H NMR spectrum. Whereas the FD mass spectrum only shows the $[Ph_4P]^+$ fragment [*m/z* 339 with 100% intensity],[8] in the ^1H NMR spectrum the Ph and the Cp* protons are observed in the integration ratio 1:3.

The details of the structure of compound **3** were obtained from a single-crystal X-ray structure analysis (Fig. 1).[9] The Ti atoms are coordinated in a distorted octahedral fashion. The Na atom is surrounded by eight F atoms, and the Na–F distances [237.8(4) to 253.1(5) pm] lie within the values for ionic compounds[10] (ionic radii: Na^+ 116 pm for coordination number (CN) 8; F^- 128 pm for CN 2, 131 pm for CN 4). The Ti1–Ti2 distance [308.4(2) pm] within the dimeric fragment is ca. 20 pm shorter than the Ti–Ti distance in **1** [329.9(3) pm]. The deviations from the average plane of the four F atoms are ±48 and ±49 pm (the angle between the planes is 7.3°).

The selective cationic exchange in the reactions **1** → **3** allows the conclusion that corresponding reactions occur more frequently in organometallic or even inorganic fluorides.

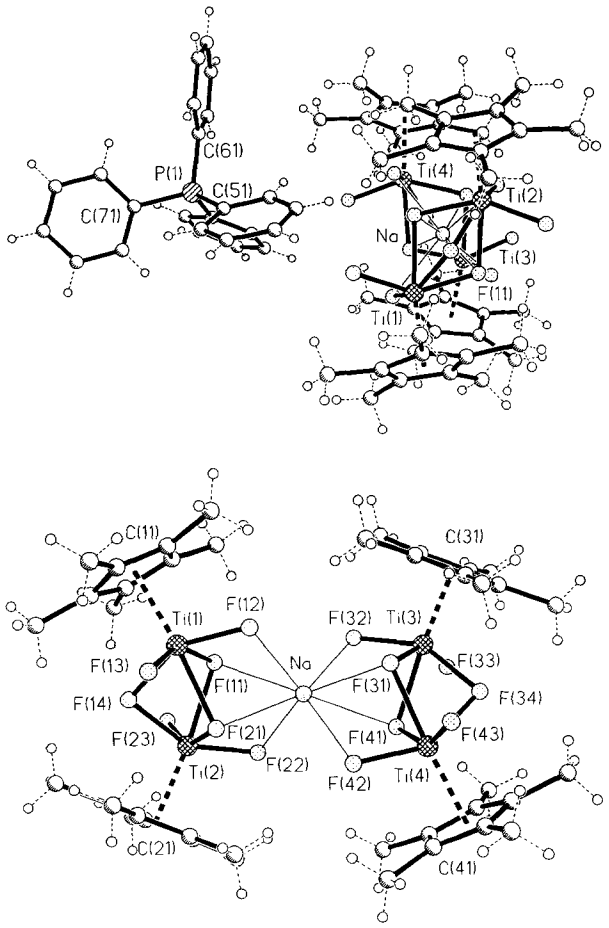


Fig. 1. Crystal structure of **3**. Above: total molecule, below: structure of anion. Selected distances [pm] and angles [°]: Ti(1)-F(12) 186.3(3), Ti(1)-F(21) 221.0(3), Ti(1)-F(11) 199.7(4), Ti(1)-F(13) 183.6(4), Ti(1)-F(14) 202.0(4), Ti(2)-F(11) 221.3(3), Ti(2)-F(22) 186.5(4) Ti(2)-F(23) 184.0(4), Ti(2)-F(14) 202.0(4), Ti(2)-F(21) 199.3(3), Ti(1)-Ti(2) 308.4(2); Ti(1)-F(11)-Ti(2) 94.1(1), Ti(1)-F(14)-Ti(2) 99.4(1), Ti(1)-F(21)-Ti(2) 94.3(1), F(11)-Ti(1)-F(14) 74.1(1), F(11)-Ti(2)-F(14) 69.6(1).

Experimental Procedure

1 (0.5 g, 2.1 mmol) and NaF (0.1 g, 2.1 mmol) were heated to reflux in MeCN (30 mL). After 3 h an orange suspension was formed. For the completion of the reaction it was stirred for a further 3 h at the same temperature. The mixture was allowed to cool and then solid Ph_4PCl (0.2 g,0.6 mmol) was added. The resultant suspension was refluxed and after 30 min the orange solid dissolved. The reflux was continued for a further 3 h, and the reaction mixture was then allowed to cool. The precipitated NaCl was then removed by filtration.

After concentration of the solution to 10 mL and cooling to −5 °C **3** was obtained as orange crystals. Yield 0.4 g, m.p. 230 °C. ^1H NMR($CDCl_3$): δ = 1.96 (s), 7.4–8.0 (m); ^{19}F NMR($CDCl_3$): δ = 100 (s), FD–MS(70 eV): *m/z* 339 (Ph_4P, 100%); correct elemental analysis (C, H, P, Na).

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1, 141585-08-2; **2**, 141585-09-3; **3**, 141585-11-7; **3** · 3 MeCN, 141585-12-8; NaF, 7681-49-4; KF, 7789-23-3; $[(EtMe_4C_5)TiF_3]_2$, 141585-13-9; $[\{[(EtMe_4C_5)TiF_3]_4F_2\}K]Ph_4P$, 141585-15-1; LiF, 7789-24-4; CsF, 13400-13-0.

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  0570-0833/92/0707-0865 $ 3.50+.25/0

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[7] $Ph_4P[\{[(\eta^5\text{-}EtMe_4C_5)TiF_3]_4F_2\}K]$ is obtained from KF, $[(\eta^5\text{-}EtMe_4C_5)TiF_3]$, and Ph_4PCl. The quality of the crystals was not sufficient for a refinement of the structure.
[8] FD and FAB mass spectra gave no indication of the $[\{(Cp^*TiF_3)_4F_2\}Na]^-$ fragment.
[9] Crystallographic data of **3**·3MeCN (M_r=1484.0): triclinic, space group $P\bar{1}$; $a = 1257.9(1)$, $b = 1690.2(2)$, $c = 1838.4(3)$ pm, $\alpha = 90.46(1)$, $\beta = 90.67(2)$, $\gamma = 98.40(1)°$, $V = 3.8662(8)$ nm^3, $Z = 2$, $\rho_{calcd} = 1.275$ g cm^{-3}, crystal size $0.6 \times 0.8 \times 0.8$ mm^3, Siemens-Stoe-AED2 four-circle diffractometer, 11296 reflections of $2\theta = 7.0°$ to $45.0°$ ($Mo_{K\alpha}$; $\lambda = 71.073$ pm), 10066 independent reflections and 7209 with ($F > 3.0\,\sigma(F)$) for the refinement (SHELXTL Plus, PC version): $R = 0.069$, $R_w = 0.079$, $w^{-1} = \sigma^2(F) + 0.0008\,F^2$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-56295, the names of the authors, and the journal citation.
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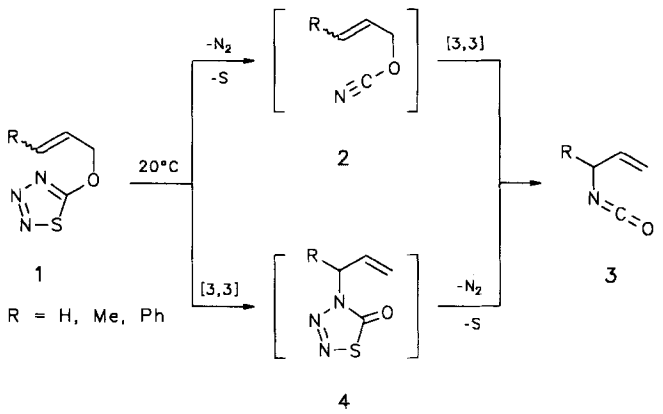
Synthesis of Isocyanate-Substituted Allenes and 1,3-Butadienes by [3,3] Sigmatropic Rearrangements**

By *Klaus Banert** and *Stefan Groth*

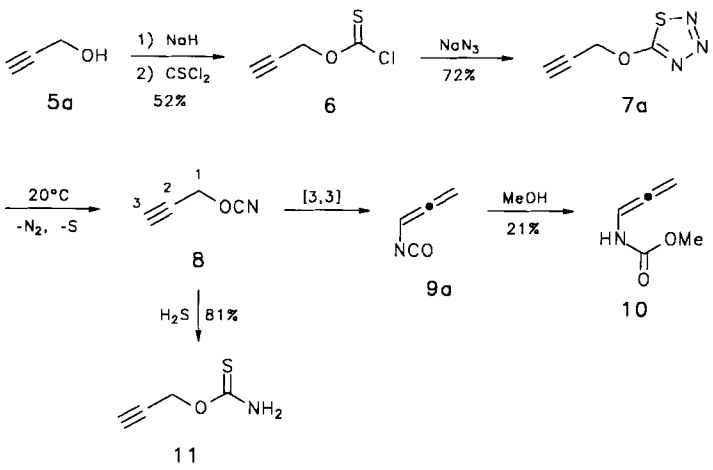
In honor of the 100th birthday of Walter Reppe

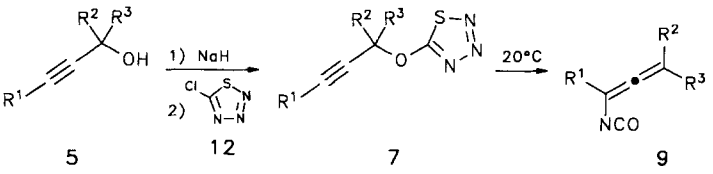
Allyl cyanates of type **2** are considered possible intermediates in the thermal decomposition of thiatriazoles **1** to isocyanates **3**.[1] However, since intermediates **2** have not yet been proved, a reaction path via heterocycles **4** cannot be discounted.[2]



We report here the first direct, spectroscopic observation of a [3,3] sigmatropic cyanate → isocyanate rearrangement; the reactions provide the novel allenyl isocyanates **9** (Scheme 1), the isocyanate-substituted 1,3-butadienes **23** and **27**, as well as the previously unknown thiatriazolones **13** and **15**.

The carbonic acid derivative **6**, readily available from propargyl alcohol **5a**, was treated with sodium azide furnishing heterocycle **7a**. This compound can be isolated and sublimed (**safety shield!**), but it decomposes in solution even at room temperature almost quantitatively to allenylisocyanate **9a**. The decomposition of **7a** in the presence of H_2S led to





Scheme 1. **a**, $R^1 = R^2 = R^3 = H$; **b**, $R^1 = R^2 = H$, $R^3 = Me$ (yield **7b** 61%, **9b** 56%); **c**, $R^1 = R^2 = H$, $R^3 = n\text{-}C_5H_{11}$ (**7c** 69%, **9c** 67%); **d**, $R^1 = H$, $R^2 = R^3 = Me$ (**7d** 34%, **9d** 47%); **e**, $R^1 = Me$, $R^2 = R^3 = H$ (**7e** 67%, **9e** 38%).

the trapping product **11**. When the conversion **7a** → **9a** was followed by NMR spectroscopy, signals of the intermediate **8** were observed (Table 1). The maximum proportion of the short-lived, quasi-stationary intermediate **8** in the reaction mixture was only 5%.

Thiatriazoles **7** can be prepared in a new one-step procedure from the propargyl alcohols **5b–e** by treatment with sodium hydride followed by chlorothiatriazole **12**.[3] The allenyl isocyanates resulting from the decomposition of **7** are not all equally stable: **9a** can only be handled in solution, whereas **9c** can be isolated and distilled under vacuum. Compounds **9** undergo reactions typical of isocyanates such as the nucleophilic addition **9a** → **10**.[4] Thus the allenyl isocyanates are distinguished from the allenyl isothiocyanates prepared only recently,[5] which react with nucleophiles to form heterocyclic products.

The decomposition of **7d** gives not only the main product **9d**, but from a parallel reaction also thiatriazolone **13**, which is less volatile than **9d** and thus easy to separate. Because compound **13** is stable at room temperature it cannot be a precursor for **9d**. Another novel thiatriazolone, **15**, can be synthesized in one step from allyl alcohol **14** by successive treatment with sodium hydride and **12**. The structural assignment was also supported by ^{15}N NMR spectroscopy (Table 1). Product **15** is a distillable liquid, which upon prolonged heating at 100 °C can be decomposed into carbonyl sulfide and an equilibrium mixture of the azides[6] **16** and **17**, as well as nitrogen, sulfur, and isocyanate **18**.[7] The high thermal stability of **15** makes the reaction path **1** → **4** → **3** seem unlikely, and together with the direct proof of **8** lends support to the sequence **1** → **2** → **3**.

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[**] Rearrangement Reactions, Part 2. This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. – Part 1: [5].