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[1] a) D. J. Berrisford, C. Bolm, K. B. Sharpless, *Angew. Chem.* **1995**, *107*, 1159–1171; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1059–1070; b) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**; c) A. Pfaltz, *Acc. Chem. Res.* **1993**, *26*, 339–345; d) *Chirality in Industry: The Commercial Manufacture and Applications of Optically Active Compounds* (Eds.: A. N. Collins, G. N. Sheldrake, J. Crosby), Wiley, Chichester, **1992**; e) *Chirality in Industry II: Developments in the Commercial Manufacture and Applications of Optically Active Compounds* (Eds.: A. N. Collins, G. N. Sheldrake, J. Crosby), Wiley, Chichester, **1997**; f) A. Persidis, *Nat. Biotechnol.* **1997**, *15*, 594–595; g) R. A. Sheldon, *Chirotechnology: Industrial Synthesis of Optically Active Compounds*, Dekker, New York, **1993**; h) *Industrial Enzymology* (Eds.: T. Godfrey, S. West), 2nd ed., Macmillan, London, **1996**.

[2] a) F. Balkenhohl, C. von dem Bussche-Hünnefeld, A. Lansky, C. Zechel, *Angew. Chem.* **1996**, *108*, 2436–2488; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2288–2337; b) J. S. Früchtel, G. Jung, *Angew. Chem.* **1996**, *108*, 19–46; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 17–42; c) *Chem. Rev.* **1997**, *97* (2), 347–510 (Special Issue on Combinatorial Chemistry); d) S. R. Wilson, A. W. Czarnick, *Combinatorial Chemistry: Synthesis and Application*, Wiley, New York, **1997**.

[3] a) G. Liu, J. A. Ellman, *J. Org. Chem.* **1995**, *60*, 7712–7713; b) K. Burgess, H.-J. Lim, A. M. Porte, G. A. Sulikowski, *Angew. Chem.* **1996**, *108*, 192–194; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 220–222; c) B. M. Cole, K. D. Shimizu, C. A. Krueger, J. P. A. Harrity, M. L. Snapper, A. H. Hoveyda, *Angew. Chem.* **1996**, *108*, 1776–1779 *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1668–1671; d) C. Gennari, H. P. Nestler, U. Piarulli, B. Salom, *Liebigs Ann.* **1997**, 637–647.

[4] M. T. Reetz, A. Zonta, K. Schimossek, K. Liebeton, K.-E. Jaeger, *Angew. Chem.* **1997**, *109*, 2961–2963; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2830.

[5] For an alternative quick photometer test of ester hydrolysis see: L. E. Janes, R. J. Kazlauskas, *J. Org. Chem.* **1997**, *62*, 4560–4561.

[6] Application of IR cameras in the thermographic detection of chemical processes based on heterogeneous catalysis: a) G. Georgiades, V. A. Self, P. A. Sermon, *Angew. Chem.* **1987**, *99*, 1050–1052; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1042–1043; b) P. C. Pawlicki, R. A. Schmitz, *Chem. Eng. Prog.* **1987**, *83* (2), 40–45; c) L. Lobban, G. Philippou, D. Luss, *J. Phys. Chem.* **1989**, *93*, 733–736; d) F. C. Moates, M. Somani, J. Annamalai, J. T. Richardson, D. Luss, R. C. Willson, *Ind. Eng. Chem. Res.* **1996**, *35*, 4801–4803; e) D. E. Bergbreiter, *Chemtracts: Org. Chem.* **1997**, *10*, 683–686; f) S. J. Taylor, J. P. Morken, *Science* **1998**, *280*, 267–270.

[7] In our system we used an AIM-256^2 IR camera (AIM, Heilbronn, Germany) with a PtSi-FPA detector and a germanium lens. This detection system is sensitive to IR radiation in the wavelength range 3–5 µm and to temperature changes of 10–100 mK, depending upon the conditions.

[8] A. Holzwarth, H. W. Schmidt, W. F. Maier, *Angew. Chem.* **1998**, *110*, 2788–2792; *Angew. Chem. Int. Ed.* **1998**, *37*, 2644–2647.

[9] A commercially available Eppendorf-Thermomixer was modified such that the top was replaced by an aluminum plate. Holes were drilled into the plate and cylindrical glass reaction vessels about 8 mm in diameter and 35 mm in height placed therein.

[10] a) A. L. E. Larsson, B. A. Persson, J.-E. Bäckvall, *Angew. Chem.* **1997**, *109*, 1256–1258; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1211–1212; b) M. T. Reetz, A. Zonta, J. Simpelkamp, *Angew. Chem.* **1995**, *107*, 373–376 *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 301–303.

[11] In the experiment equimolar solutions of 100 µL of (*R*)-**1**, (*S*)-**1** and *rac*-**1** in toluene were mixed correspondingly with 100 µL vinyl acetate in toluene. Three different concentrations were used: 0.5 M, 1 M and 2 M.

[12] a) J. F. Larrow, S. E. Schaus, E. N. Jacobsen, *J. Am. Chem. Soc.* **1996**, *118*, 7420–7421; b) S. E. Schaus, E. N. Jacobsen, *Tetrahedron Lett.* **1996**, *37*, 7937–7940; c) E. N. Jacobsen, F. Kakiuchi, R. G. Konsler, J. F. Larrow, M. Tokunaga, *Tetrahedron Lett.* **1997**, *38*, 773–776.

[13] M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *277*, 936–938.

[14] For the catalyst screening in the hydrolysis of epichlorohydrin **3c** a mixture of (*S*,*S*)-**5a**, (*S*,*S*)-**5b**, and (*S*,*S*)-**5c** (each 60.0 µmol) in toluene (1.00 mL) and acetic acid (120 µmol, 7.21 mg, 6.86 mL) was stirred in an open flask for 1 h. After removal of the solvent the three residues were dried in vacuum. Each of these activated catalysts (*S*,*S*)-**5a–c** was dissolved in toluene (300 µL) and distributed in three reaction vessels. Epichlorohydrin **3c** (1.00 mmol, 92.5 mg, 78.4 mL) was added. As described before the temperature was calibrated in the range of 24–39 °C. The reaction was initiated by the addition of water (0.55 equiv, 0.55 mmol, 9.9 µL) at 27 °C. Screening was performed similar to the first experiments, except that the detection time was prolonged, averaging 500 recordings in 10 s.

[15] For the substrate activity screening the cobalt catalyst (*S*,*S*)-**5c** was activated as described before. Nine aliquots each containing 2.00 µmol of the catalyst in toluene (100 µL) were distributed in the wells of the microtiter plate. The three different epoxides **3a–c** in the (*R*)-, (*S*)-, and *rac*-form were added to the catalyst, resulting in the arrangement shown in Figure 3. The reaction mixtures contained the epoxides at a concentration of 3.95 M in toluene and a final volume of 253 µL. Detection of the reactions was performed for 10 s, resulting in 500 recordings which were averaged.

[16] Substrate **3a** was not included in the studies carried out by Jacobsen et al.[12, 13]

Molecular Model for Aluminophosphates Containing Fluoride as a Structure-Directing and Mineralizing Agent**

Yu Yang, Jiri Pinkas, Martina Schäfer, and
Herbert W. Roesky*

*Dedicated to Professor Ernst Otto Fischer
on the occasion of his 80th birthday*

Microporous materials such as zeolites, alumino- and gallophosphates, and their transition metal substituted analogues are currently targets of a very active research effort. Their traditional uses as size- and shape-selective catalysts,[1] molecular sieves, adsorbents, and ion exchangers are complemented by new applications as reaction vessels of molecular dimensions,[2] highly ordered matrices for fabrication of optoelectronic nanodevices[3] and sensors,[4] and molds for the preparation of carbon molecular sieves.[5] Their syntheses rely mainly on hydrothermal methods in aqueous and recently also in nonaqueous media.[6, 7] Important developments in the synthetic methodology were achieved by introduction of HF in the reaction mixture. Fluoride acts as a mineralizer and a structure-directing agent,[8] and its presence promotes growth of large crystals of molecular sieves.[9] Fluoride itself is in many cases not retained in the resulting structure. However, in some frameworks fluoride ions coordinate to the metal center, as has been reported for aluminophosphates (AFI,[8]

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LTA,[10] AST,[11] GIS,[12] and CHA[13]), for gallophosphates (LTA,[8] CLO,[14] CHA,[15] and ULM-*n* compounds[16]), and recently also for indium phosphates.[17] Other such examples include transition metal doped aluminophosphates (CrAPO-5,[18] CoAPO-34[19]) as well as microporous oxyfluorinated metallophosphates of vanadium[20] and iron.[21] Interestingly, fluoride can also coordinate to the phosphorus center and form fluorophosphate (Zn[22]).

There has been increasing interest in developing rational syntheses of alumino- and gallophosphates. To reach this goal, we and others followed the building-block strategy in which preformed clusters of alumino- or gallophosphate that possess reactive groups and are soluble in organic solvents are expected to condense and form extended three-dimensional structures. Pore size, shape, and dimensionality would be governed by the characteristics of the building blocks. We extended the "library" of known molecular models of alumino- and gallophosphate secondary building units (SBUs) found in extended three-dimensional structures of these materials.[23] To the previously known model compounds, mimicking a single four-ring[24–28] (4R or 4) and a double four-ring[28–31] (D4R or 4–4), we added a double six-ring[32] (D6R or 6–6) and a single six-ring[33] (6R or 6). Herein we report on the synthesis and the structural and spectroscopic characterization of aluminophosphonate cluster **1**, which contains two tricyclic capped six-ring moieties (C6R or 6≡1) and a central cube-like unit (D4R) incorporating terminal and bridging fluoride ions (FAl(μ-F)$_2$AlF).

$[Cs_3(thf)_3F(i\mathrm{BuAl})_3(t\mathrm{BuPO}_3)_4]_2[(i\mathrm{BuAl})_2Al_2(\mu\text{-}F)_2(t\mathrm{BuPO}_3)_4]$ **1**

Reaction of equimolar amounts of Cs(iBu$_3$AlF)[34] and *tert*-butylphosphonic acid in THF provides **1** as colorless block crystals in 25% yield. The reaction solution contains several other by-products, one of which was identified by ^{31}P NMR spectra as cubic [iBuAlO$_3$PtBu]$_4$ (**2**).[29] The molecular structure of **1** in the solid state was established by single-crystal X-ray crystallography (Figure 1).[35] The cluster consists of a central cube-like Al$_4$P$_4$O$_{12}$(μ-F)$_2$F$_2$ core and two peripheral tricyclic Al$_3$P$_4$O$_{12}$ units. These two capped six-rings are related by a crystallographically imposed C_2 axis passing through the bridging F1 and F2 atoms; **1** possesses pseudo-C_{2v} symmetry. The capped six-rings are isoelectronic with the [Al$_3$P$_4$O$_{16}$]$^{3-}$ structural motif found in a host of layered aluminophosphates,[7b] and the C6R building unit was also found in three-dimensional frameworks of BPH[36] and AFS[23] types. The central cube is connected to the two capped six-rings through "sandwiched" triangles of cesium atoms. These cesium atoms interact with the three terminal phosphonate oxygen atoms of the C6R units along with the terminal fluorine atoms F3 and four bridging oxygen atoms of the central core. Recently, we reported similar interactions of gallophosphonates with Li, Na, and K ions.[37] The coordination sphere of each cesium center is completed by one oxygen atom of a THF molecule. There are two additional THF half-molecules of crystallization in the asymmetric unit. Compound **1** contains Al atoms in two different coordination environments: two octahedral *mer*-Al1O$_3$F$_3$ and eight tetrahedral AlO$_3$C units. A prominent feature of **1** is the FAl(μ-F)$_2$AlF unit formed from two edge-sharing octahedra. This unit can serve as a molecular model for analogous units observed in GIS- and CHA-type AlPO$_4$ phases. The Al1–F1 and Al1–F2 bridging distances (1.863(3) and 1.909(3) Å, respectively) closely match the corresponding distances in AlPO$_4$-CHA (1.854(2) and 1.894(2) Å).[13b] The short Al1–F3 distance (1.724(3) Å) is the same as in bioctahedral [Al$_2$F$_8$(H$_2$O)$_2$]$^{2-}$ (1.729(2) Å).[38] The F3 atoms are four-coordinated and reside 0.95 Å above the triangle of the three cesium atoms (Cs–F3 2.835(3)–2.970(4) Å).

The ^{13}C DEPT NMR spectra display two singlets (ratio ca. 3:1) for iBuAl methyl groups and four doublets (3:2:2:2) for tBuP methyl groups, which is in agreement with the solid-state structure. Furthermore, four signals in the ^{31}P NMR spectrum of **1** suggest that the structure is retained in solution. A single resonance at $\delta = 14.7$ for the three crystallographically inequivalent phosphorus atoms P3, P4, and P5 hints at a rotation of the capped six-ring units about the Al1-F1-P6 axes that is fast on the NMR time scale. In fact, on lowering the temperature below −20°C, this signal decoalesces to two peaks ($\delta = 14.3$, 13.8 at −60°C). This attests to the slow rotation of the C6R units. Owing to its lower intensity, the high-field signal is assigned to P4, and the stronger signal at low field to P3 and P5. These two phosphorus centers are rendered equivalent in a racemization process by which **1** is interconverted between left- and right-handed C_2-symmetric propellerlike enantiomeric forms via a C_{2v}-symmetric transition state. A signal at $\delta = 16.5$ is very close to the ^{31}P NMR chemical shift of **2** ($\delta = 16.9$), and it was assigned to P6 of the capping phosphonate groups. The remaining two signals of equal intensity show coupling to fluorine and must therefore belong to the central D4R unit. A triplet ($\delta = 18.8$) and a broad quartet ($\delta = 30.3$) were assigned to P2 and P1, respectively; there is a correlation between the ^{31}P NMR shift and the mean P-O-Al bond angle in AlPO$_4$ polymorphs.[39] The phosphorus center is more strongly shielded as the average P-O-Al angle widens. We found that this correlation is also valid for the phosphonate groups in **1** and **2** ($r = 0.9902$) as well as [MeAl-O$_3$PtBu]$_6$ (**3**)[32] (Table 1). The ^{19}F NMR spectrum

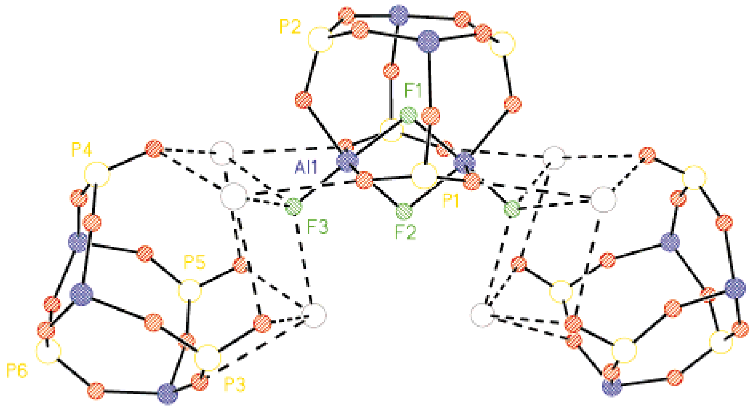

Figure 1. Molecular structure of **1**. The carbon atoms of all *i*BuAl and *t*BuP groups and THF molecules are omitted for clarity; Al: blue, P: yellow, O: red, F: green, Cs: gray. Selected bond distances [Å] and angles [°]: Al1–F1 1.863(3), Al1–F2 1.909(3), Al1–F3 1.724(3); Al1-F1-Al1′ 101.9(2), Al1-F2-Al1′ 98.5(2).

Table 1. Correlation between the ^{31}P NMR chemical shift and the mean P-O-Al bond angle in **1**, **2**, and **3**.

Compd, atom	$\delta(^{31}\mathrm{P})$[a]	P-O-Al [°]
1, P1	30.2	128.7
1, P2	19.0	143.6
1, P6	17.2	147.5
2	16.9	150.5
3	13.4	154.6

[a] In C_6D_6.

features two broad singlets of equal intensity ($\delta = -96.8$ and -131.5). We assigned them to the bridging and terminal fluorine atoms, respectively, in analogy to $\mathrm{AlPO_4}$-CJ2[40] and in accord with an empirical rule that higher coordination causes higher shielding.[20b]

Compound **1** features several interesting structural motifs that are closely related to those of zeolitic frameworks. Moreover, the strong Al–F bonds in the starting material are retained in the product, which provides a lead for the investigation of the mineralizing action and structure-directing role of fluoride in the microporous materials by ^{19}F NMR spectroscopy. Most importantly, this molecule contains several reactive centers, which may be employed in the transformation of this precursor to porous materials.

Experimental Section

1: A solution of *tert*-butylphosphonic acid (0.23 g, 1.7 mmol) in THF (20 mL) was added dropwise to an equimolar solution of Cs($i\mathrm{Bu_3AlF}$) in THF (5 mL) at 0°C. The resulting solution was stirred overnight at room temperature and then concentrated to 15 mL. A white precipitate was removed by filtration, and the clear solution was allowed to stand at room temperature for 10 d. Colorless block crystals of **1** (0.13 g) formed in 25% yield; m.p. > 350°C. ^{1}H NMR (250 MHz, [D_8]THF): $\delta = -0.18$ (d, $J = 6.9$ Hz, 4H; $\mathrm{Al(D4R)CH_2}$), -0.09 (d, $J = 7.0$ Hz, 12H; $\mathrm{Al(C6R)CH_2}$), 0.91–1.29 (m, 156H; $\mathrm{CH_3}$), 1.77 (m; THF), 1.89 (sept, $J = 6.6$ Hz, 8H; CH), 3.64 (m; THF); ^{13}C DEPT NMR (100 MHz, [D_8]THF): $\delta = 68.2$ (s; $\mathrm{CH_2O}$, THF), 28.8 (s; $\mathrm{Al(C6R)CH_2CH(\mathit{CH}_3)_2}$), 28.5 (s; $\mathrm{Al(D4R)CH_2CH(\mathit{CH}_3)_2}$), 27.0 (s; $\mathrm{Al(D4R)CH_2\mathit{CH}(CH_3)_2}$), 26.9 (s; $\mathrm{Al(C6R)CH_2\mathit{CH}(CH_3)_2}$), 26.4 (s; CH_2, THF), 26.1 (d, $J = 1.5$ Hz; $\mathrm{P(3,\ 4,\ 5)C(\mathit{CH}_3)_3}$), 26.0 (d, $J = 1.8$ Hz; $\mathrm{PC(\mathit{CH}_3)_3}$), 25.9 (d, $J = 2.1$ Hz; $\mathrm{PC(\mathit{CH}_3)_3}$), 24.9 (d, $J = 1.7$ Hz; $\mathrm{P(1)C(\mathit{CH}_3)_3}$); ^{19}F NMR (188 MHz, [D_8]THF): $\delta = -96.8$ (s, $\Delta\tilde{\nu}_{1/2} = 100$ Hz; F1, F2), -131.5 (s, $\Delta\tilde{\nu}_{1/2} = 100$ Hz; 2F3); ^{31}P NMR (162 MHz, [D_8]THF): $\delta = 30.3$ (br q, J(PF) = 9 Hz, 2P; P1), 18.8 (t, J(PF) = 11.5 Hz, 2P; P2), 16.5 (s, 2P; P6), 14.7 (s, 6P; P3, P4, P5); IR (KBr): $\tilde{\nu} = 2952$, 2926, 2871, 1481, 1464, 1425, 1363, 1263, 1187, 1148, 1047, 946, 878, 836, 813, 698, 671, 541, 504, 466 cm^{-1}; MS (EI): *m/z* (%): 832 (87) [$\mathrm{Bu_6P_4Al_4O_{12}F_3}$], 785 (100) [$\mathrm{Bu_6P_4Al_4O_{12}F}$]; elemental analyses (THF removed by drying under vacuum) calcd for $\mathrm{C_{80}H_{180}Al_{10}Cs_6F_4O_{36}P_{12}}$ (3233.48): C 29.72, H 5.61; found: C 29.8, H 6.1.

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[1] a) J. M. Thomas, *Angew. Chem.* **1994**, *106*, 963; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 913; b) N. Herron, W. E. Farneth, *Adv. Mater.* **1996**, *8*, 959; c) I. W. C. E. Arends, R. A. Sheldon, M. Wallau, U. Schuchardt, *Angew. Chem.* **1997**, *109*, 1190; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1144; d) M. E. Davis, *Chem. Eur. J.* **1997**, *3*, 1745.

[2] a) G. A. Ozin, C. Gil, *Chem. Rev.* **1989**, *89*, 1749; b) *Inclusion Chemistry with Zeolites: Nanoscale Materials by Design* (Eds.: N. Herron, D. R. Corbin), Kluwer, Dodrecht, **1995**; c) G. Sundarababu, M. Leibovitch, D. R. Corbin, J. R. Scheffer, V. Ramamurthy, *Chem. Commun.* **1996**, 2159; d) S. B. Ogunwumi, T. Bein, *Chem. Commun.* **1997**, 901; e) M. J. Sabater, A. Corma, A. Domenech, V. Fornes, H. Garcia, *Chem. Commun.* **1997**, 1285; f) B.-Z. Zhang, X.-Y. Li, *Chem. Commun.* **1998**, 349.

[3] a) G. A. Ozin, A. Kuperman, A. Stein, *Angew. Chem.* **1989**, *101*, 373; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 359; b) G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612; c) G. A. Ozin, S. Ozkar, *Adv. Mater.* **1992**, *4*, 11.

[4] a) K. J. Balkus, L. J. Ball, B. E. Gnade, J. M. Anthony, *Chem. Mater.* **1997**, *9*, 380. b) T. Bein, *Chem. Mater.* **1996**, *8*, 1636.

[5] J. Rodriguez-Mirasol, T. Cordero, L. R. Radovic, J. J. Rodriguez, *Chem. Mater.* **1998**, *10*, 550.

[6] a) Q. Huo, R. Xu, *J. Chem. Soc. Chem. Commun.* **1990**, 783; b) R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, Y. Xu, A. K. Cheetham, D. Bieber, *J. Chem. Soc. Chem. Commun.* **1990**, 1170.

[7] a) R. E. Morris, S. J. Weigel, *Chem. Soc. Rev.* **1997**, 309; b) S. Oliver, A. Kuperman, G. A. Ozin, *Angew. Chem.* **1998**, *110*, 48; *Angew. Chem. Int. Ed.* **1998**, *37*, 46.

[8] H. Kessler, J. Patarin, C. Schott-Darie in *Advanced Zeolite Science and Application*, (Eds.: J. C. Jansen, M. Stöcker, H. G. Krage, J. Weitkamp), Elsevier, Amsterdam (*Stud. Surf. Sci. Catal.* **1994**, *85*, 75).

[9] a) A. Kuperman, S. Nadimi, S. Oliver, G. A. Ozin, J. M. Garces, M. M. Olken, *Nature* **1993**, *365*, 239; b) S. Nadimi, S. Oliver, A. Kuperman, A. Lough, G. A. Ozin, J. M. Garcés, M. M. Olken, P. Rudolf in *Zeolites and Related Microporous Materials: State of the Art 1994* (Eds.: J. Weitkamp, H. G. Karge, H. Pfeifer, W. Hölderich), Elsevier, Amsterdam (*Stud. Surf. Sci. Catal.* **1994**, *84*, 93).

[10] a) L. Sierra, C. Deroche, H. Gies, J. L. Guth, *Microporous Mater.* **1994**, *3*, 29; b) L. Schreyeck, F. D'agosto, J. Stumbe, P. Caullet, J. C. Mougenel, *Chem. Commun.* **1997**, 1241.

[11] C. Schott-Darie, J. Patarin, P. Y. Le Goff, H. Kessler, E. Benazzi, *Microporous Mater.* **1994**, *3*, 123.

[12] J.-L. Paillaud, B. Marler, H. Kessler, *Chem. Commun.* **1996**, 1293.

[13] a) M. M. Harding, B. M. Kariuki, *Acta Crystallogr. Sect. C* **1994**, *50*, 852; b) S. Oliver, A. Kuperman, A. Lough, G. A. Ozin, *J. Mater. Chem.* **1997**, *7*, 807.

[14] M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, *Nature* **1991**, *352*, 320.

[15] C. Schott-Darie, H. Kessler, M. Soulard, V. Gramlich, E. Benazzi in *Zeolites and Related Microporous Materials: State of the Art 1994* (Eds.: J. Weitkamp, H. G. Karge, H. Pfeifer, W. Hölderich), Elsevier, Amsterdam (*Stud. Surf. Sci. Catal.* **1994**, *84*, 101).

[16] a) G. Ferey, *J. Fluorine Chem.* **1995**, *72*, 187; b) T. Loiseau, G. Ferey, *J. Mater. Chem.* **1996**, *6*, 1073; c) S. J. Weigel, S. C. Weston, A. K. Cheetham, G. D. Stucky, *Chem. Mater.* **1997**, *9*, 1293.

[17] H. Du, J. Chen, W. Pang, J. Yu, I. D. Williams, *Chem. Commun.* **1997**, 781.

[18] S. F. Radaev, W. Joswig, W. H. Baur, *J. Mater. Chem.* **1996**, *6*, 1413.

[19] N. Rajic, A. Ristic, A. Tuel, V. Kaucic, *Zeolites* **1997**, *18*, 115.

[20] a) D. Riou, G. Ferey, *J. Solid State Chem.* **1994**, *111*, 422; b) D. Riou, F. Taulelle, G. Ferey, *Inorg. Chem.* **1996**, *35*, 6392.

[21] a) M. Cavellec, D. Riou, J.-M. Greneche, G. Ferey, *Inorg. Chem.* **1997**, *36*, 2187. b) M. Cavellec, C. Egger, J. Linares, M. Nogues, F. Varret, G. Ferey, *J. Solid State Chem.* **1997**, *134*, 349.

[22] P. S. Halasyamani, M. J. Drewitt, D. O'Hare, *Chem. Commun.* **1997**, 867.

[23] W. M. Meier, D. H. Olson, *Atlas of Zeolite Structure Types*, 3rd revised ed., Butterworth-Heinemann, London, **1992**.

[24] S. A. Sangokoya, W. T. Pennington, G. H. Robinson, D. C. Hrncir, *J. Organomet. Chem.* **1990**, *385*, 23.

[25] F. E. Hahn, B. Schneider, F.-W. Reier, *Z. Naturforsch. B* **1990**, *45*, 134.

[26] a) C. C. Landry, A. Hynes, A. R. Barron, I. Haiduc, C. Silvestru, *Polyhedron* **1996**, *15*, 391; b) A. Keys, S. Bott, A. R. Barron, *Chem. Commun.* **1996**, 2339.

[27] a) D. J. Browning, J. M. Corker, M. Webster, *Acta Crystallogr. Sect. C* **1996**, *52*, 882; b) J. M. Corker, D. J. Browning, M. Webster, *Acta Crystallogr. Sect. C* **1996**, *52*, 583.

[28] a) M. R. Mason, R. M. Matthews, M. S. Mashuta, J. F. Richardson, *Inorg. Chem.* **1996**, *35*, 5756; b) M. R. Mason, M. S. Mashuta, J. F. Richardson, *Angew. Chem.* **1997**, *109*, 249; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 239.

[29] a) Y. Yang, H.-G. Schmidt, M. Noltemeyer, J. Pinkas, H. W. Roesky, *J. Chem. Soc. Dalton Trans.* **1996**, 3609.

[30] J. E. Cassidy, J. A. Jarvis, R. N. Rothon, *J. Chem. Soc. Dalton Trans.* **1975**, 1497.

[31] M. G. Walawalkar, R. Murugavel, H. W. Roesky, H.-G. Schmidt, *Inorg. Chem.* **1997**, *36*, 4202.

[32] Y. Yang, M. G. Walawalkar, J. Pinkas, H. W. Roesky, H.-G. Schmidt, *Angew. Chem.* **1998**, *110*, 101; *Angew. Chem. Int. Ed.* **1998**, *37*, 96.

[33] Y. Yang, J. Pinkas, M. Noltemeyer, M. Schäfer, H. W. Roesky, *Inorg. Chem.*, submitted.

[34] Cs(iBu$_3$AlF) was prepared according to a modified procedure of B. Werner, B. Neumüller, *Chem. Ber.* **1996**, *129*, 355.

[35] Crystal data for **1**: $C_{104}H_{228}Al_{10}Cs_6F_4O_{42}P_{12}+2 \times 1/2\,C_4H_8O$, $M_r = 3738.23$, monoclinic, space group $C2/c$, $a = 28.890(4)$, $b = 27.177(3)$, $c = 25.096(4)$ Å, $\beta = 117.17(1)^\circ$, $V = 17530(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.441$ g cm^{-3}, $F(000) = 7776$, $\lambda = 0.71073$ Å, $T = 133$ K, $\mu(Mo_{K\alpha}) = 14.63$ cm^{-1}, min./max. transmission: 0.6284/0.6679, crystal size $0.35 \times 0.30 \times 0.30$ mm, $2.18^\circ \leq 2\Theta \leq 48.00^\circ$; of 196896 data collected, 13762 were independent ($R_{int} = 0.0802$). For the final refinement of the 1114 parameters, 2190 restraints were used. $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0464$ for $I > 2\sigma(I)$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2} = 0.1198$ for all data; min./max. residual electron density: $-0.599/0.896$ e · Å^{-3}. One of the cesium atoms is disordered over two positions (occupancies 0.9:0.1). One iBu group is disordered over two (occupancies 0.35:0.65), and one tBu group over three positions (occupancies 0.5:0.25:0.25). In one of the THF molecules, one carbon atom is disordered over two positions (occupancies 0.2:0.8), whereas the carbon atoms of another THF molecule are disordered over three positions (occupancies 0.45:0.35:0.20). The two THF half-molecules of crystallization in the asymmetric unit are disordered over the two different inversion centers in space group $C2/c$. The data were collected on a Stoe-Siemens-Huber four-circle diffractometer with a Siemens CCD area detector using φ scans. The crystal was transferred in an inert oil and then flash-cooled in a nitrogen stream.[41] For the integration of intensities, the program SAINT[42] was used. A semiempirical absorption correction was employed for all data. The structure was solved with direct methods (SHELXS-96)[43] and refined against F^2.[44] All non hydrogen atoms were refined anisotropically. For the hydrogen atoms, the riding model was used. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101366. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[36] G. Harvey, C. Baerlocher, T. Wroblewski, *Z. Kristall.* **1992**, *201*, 113.

[37] a) M. G. Walawalkar, R. Murugavel, A. Voigt, H. W. Roesky, H.-G. Schmidt, *J. Am. Chem. Soc.* **1997**, *119*, 4656; b) M. G. Walawalkar, R. Murugavel, H. W. Roesky, I. Uson, R. Kraetzner, *Inorg. Chem.* **1998**, *37*, 473.

[38] N. Herron, R. L. Harlow, D. L. Thorn, *Inorg. Chem.* **1993**, *32*, 2985.

[39] D. Müller, E. Jahn, G. Ladwig, U. Haubenreisser, *Chem. Phys. Lett.* **1984**, *109*, 332.

[40] F. Taulelle, T. Loiseau, J. Maquet, J. Livage, G. Ferey, *J. Solid State Chem.* **1993**, *105*, 191.

[41] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[42] SAINT, *Program for Reduction and Integration of Diffraction Data*, V.4.050, AXS, **1997**.

[43] G. M. Sheldrick, SHELXS-96, *Program for Structure Solution*, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[44] G. M. Sheldrick, SHELXL-96, *Program for Structure Refinement*, Universität Göttingen, **1996**.

Zirconocene-Catalyzed Silylation of Alkenes with Chlorosilanes**

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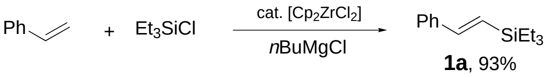
Organosilanes play an important role in organic synthesis as useful intermediates in a number of synthetic transformations.[1] To date, a variety of procedures have been developed for the introduction of silyl functionalities into organic molecules. The most straightforward and practical methodology for C–Si bond formation involves electrophilic trapping of the corresponding organometallic reagents of main group metals with chlorosilanes. An attractive alternative is the transition metal catalyzed silylation of unsaturated compounds,[1, 2] as exemplified by the hydrosilylation of alkenes and alkynes.[2a, 3] The reactions in this category proceed not only with silanes containing one or more hydrogen atoms, but also with various silylating reagents such as disilanes,[2c, d] silacyclobutanes or silacyclopropanes,[4] silyl cyanides,[5] silylgermanes,[6] silylstannanes,[7] silylselenides,[6] and iodosilanes.[8]

Although chlorosilanes are the most readily available silylating reagents, their use in catalytic silylation has not yet been achieved. This is probably due to the difficulty of the oxidative addition of the Si–Cl bonds to transition metal centers.[9] We report herein the first example of the transition metal catalyzed silylation of alkenes with chlorosilanes as well as silylsulfides, silylselenides, and silyltellurides. This reaction proceeds under mild conditions with a catalytic amount of a zirconocene complex[10] in the presence of a Grignard reagent to give alkenylsilanes and/or allylsilanes.

For example, styrene reacted with chlorotriethylsilane in refluxing THF in the presence of nBuMgCl and a catalytic amount of zirconocene dichloride (conditions A) to give the *E* isomer of alkenylsilane **1a** in 93 % yield and with greater than 99 % regio- and stereoselectivities [Eq. (1)]. In this reaction,



1a, 93% (1)

only a trace amount of Et$_3$SinBu (< 5 %) was formed as a byproduct, probably through the direct reaction of Et$_3$SiCl with nBuMgCl.

Table 1 summarizes the results of the silylation of styrene using different reagents and catalysts. When [Cp$_2$TiCl$_2$] was

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