

Chemistry with WCAs - a short Introduction

What is a WCA ?

Weakly coordinating anions (WCAs)^[1] allow us to study highly electrophilic cations or complex cations that are held together by extremely weak interactions. These can often be observed in the gas phase in a mass spectrometer, in a solid argon matrix, or predicted in ab-initio calculations. Some prominent examples include the $C(CH_3)_3^+$ cation^[2-4] and the halocarbonium ions CX_3^+ ^[5-8] which are well known in the gas phase^[9-11] and could recently be fully characterized in solution by NMR and in the solid state by xray diffraction with the help of weakly coordinating anions. An example for a weakly bound Lewis-acid-Lewis-base complex cation is $[Ag(P_4)_2]^+$. This ion has been characterized in 1995 through mass spectrometry and subsequent calculations predicted a minimum geometry with η^1 coordination of the P_4 units.^[12] However, this is not true in the solid state, as could be shown by the crystal structure of a salt of the same cation, in which P_4 is η^2 -coordinated.^[13, 14] This example shows that conclusions drawn from gas phase studies should be validated in the solid state if possible. Further spectacular results, many of which have found their way into modern textbooks, include the stabilizations of cations like Xe_2^+ ,^[15] N^5+ ^[16] and HC_{60}^+ ^[17].

It becomes clear that such cations must be partnered with a suitable anion that is ideally non-coordinating and not distorting the cation's geometry. True non-coordination is of course not possible; everybody intuitively understands that opposed charges interact with each other. But it is possible to find anions which help to replace few strong cation-anion interactions by many very weak ones, placing the cation in a field of weak interactions that mostly cancel each other out. These "weakly coordinating" anions (or "spectator anions") ideally play no role in reactions of their partner cation. To be weakly coordinating, an anion must possess a very low nucleophilicity and basicity. A high stability versus oxidation and strong electrophiles is necessary to prevent degradation, thus the WCA should be formed of chemically robust moieties. Finally, its negative charge should be delocalized over a large surface area, because sites that offer a significantly higher charge concentration than the rest of the surface would be primary locations of electrophilic attack.

WCAs used in the group

Many classes of weakly coordinating anions are known.^[1] Our group concentrates on alkoxy- and aryloxymetallates (mainly alkoxyaluminates) of the general formula $[M(OR^F)_n]^-$ (Fig. 1, R^F = poly- or perfluorinated alkyl or aryl group, $M = Al^{III}, Nb^V, Ta^V, Y^{III}, La^{III}$).^[18-23]

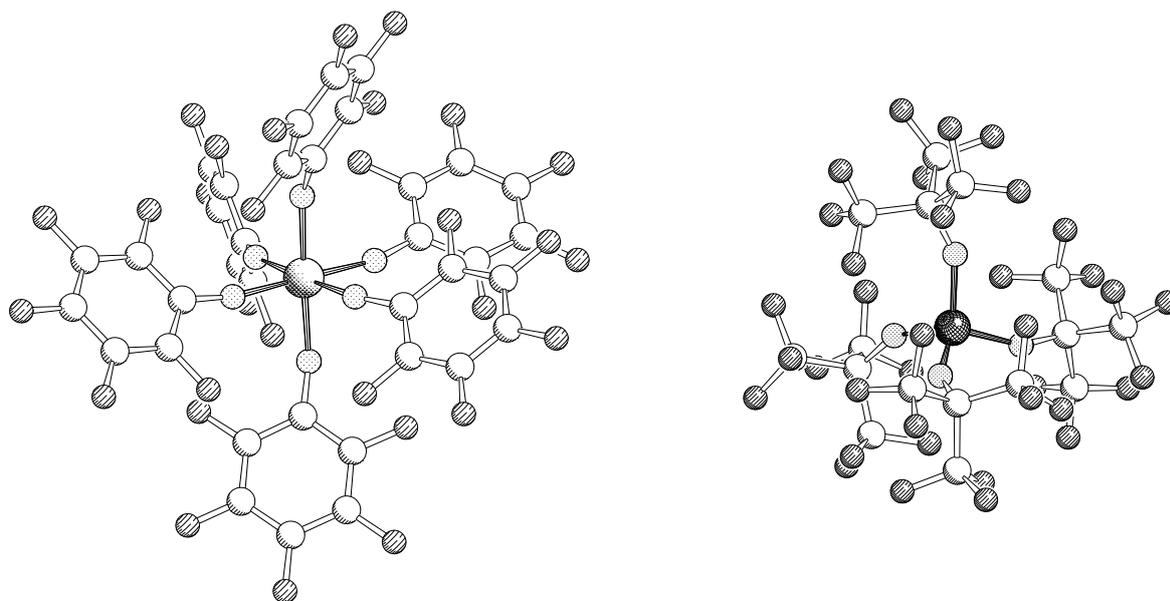


Fig. 1: Structures of $[Nb(OC_6F_5)_6]^-$ (left) and $[Al(OC(CF_3)_3)_4]^-$ (right).

Salts of $[M(OR^F)_n]^-$ are easily accessible even in larger scales. Some of these anions have successfully been tested e.g. as counterions in cationic polymerization reactions.^[24-26] Especially the introduction of sterically demanding ligands like $OC(CF_3)_3$, $OC(CH_3)(CF_3)_2$ or $OCH(CF_3)_2$ has led to alkoxyaluminate anions that are well suited for many purposes.^[20, 21] $[Al(OC(CF_3)_3)_4]^-$ is among the most weakly coordinating anions currently known (due to the high number of peripheral C-F bonds), comparable with the carboranate $[CB_{11}(CF_3)_{12}]^-$, which suffers from an extremely tedious synthetic route with low yields^[27] and has the disadvantage of being explosive. The Li^+ salt of the aluminate is available in 100g scale with over 95% yield from commercially available starting materials and is even stable in water and boiling aqueous nitric acid.^[20] This high stability arises from the steric shielding of the basic oxygen atoms by the bulky ligands with perfectly interlocking $-CF_3$ groups and the electronic stabilization resulting from perfluorination. Consequently, the $[Al(OC(CF_3)_3)_4]^-$ can be used to stabilize very reactive cations like $[H(OEt_2)_2]^+$,^[28] Cl_3^+ ,^[5] $[Ag(P_4)_2]^+$,^[13] PX_4^+ , $P_2X_5^+$, $P_5X_2^+$ ($X = Br, I$),^[29, 30] $AsBr_4^+$ ^[31] and many more. The stability is further improved in the fluoride-

bridged $[F\{Al(OC(CF_3)_3)_3\}_2]^-$ anion (Fig. 2), in which the negative charge is distributed across 54 peripheral C-F bonds.^[32]

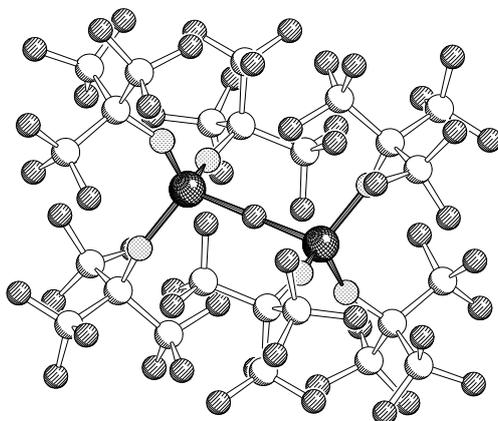


Fig. 2: Structure of the fluoride-bridged $[F\{Al(OC(CF_3)_3)_3\}_2]^-$ anion.

Size matters !

Comparing the sizes of WCA, one notices that over time, in many applications the focus has shifted towards bigger anions. But why is a larger size desirable if one wants to minimize ionic interactions? This is due to the fact that the coulombic force is inversely proportional to the square distance of two separated charges. The coulomb attractive energy for a 1:1 ion pair in a vacuum is

$$E = \int_{\infty}^d F dr = -\frac{1}{4\pi\epsilon_0} \frac{z^2 \cdot e^2}{d}$$

(Eq. 1)

z = ion charge; d = contact distance between cation and anion; ϵ_0 = vacuum permittivity.

This yields a rather drastic effect on the strength of cation-anion interactions as can be depicted for the simplified case of singly charged anions paired with Li^+ in a vacuum (**Fig. 3**):

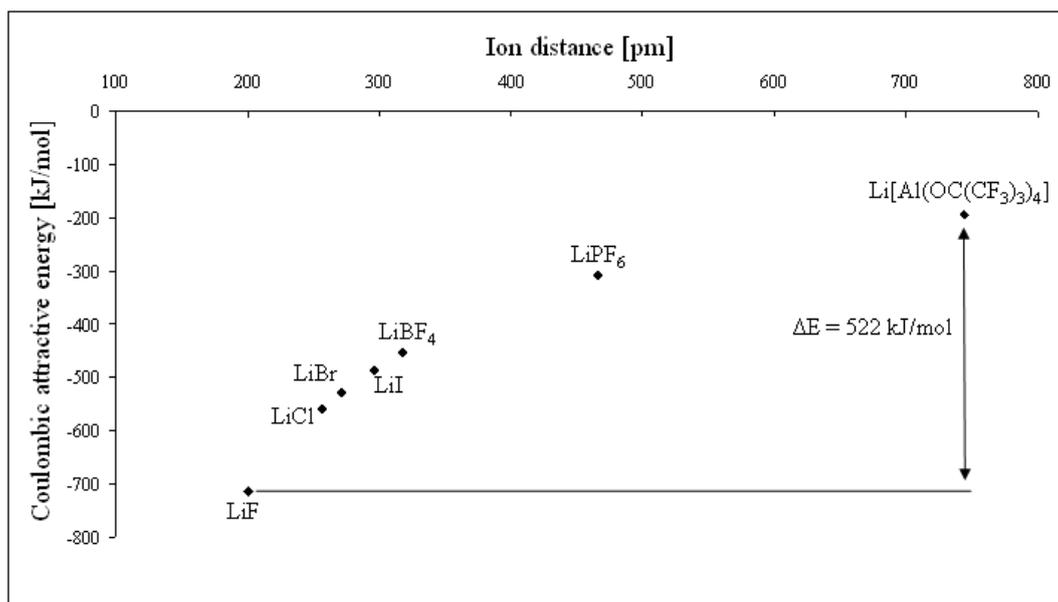


Fig. 3: Calculated dependence of coulomb attraction energy on anion size for ion pairs in the gas phase.

Large WCA approach diameters in the nanometer scale ($[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$: 1.25 nm^[20], $[\text{Sb}(\text{OTeF}_5)_6]^-$: 1.20 nm^[33]). Comparing $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ with the much smaller BF_4^- , which can be considered a “classic” WCA, this corresponds to a reduction in coulomb attraction by 258 kJ/mol. This difference becomes more than twice as large (522 kJ/mol) in comparison with the strongly coordinating fluoride anion. This is oversimplified, because the model completely neglects all condensed phase interactions, but it clarifies why size is a major factor in the design of new anions.

Gas phase conditions in the solid state ?

In the solid state, when charges are forced into close contact, strong electrostatic fields influence the interactions of matter. The quantity that describes these interactions is called the lattice potential energy. For a long time, the simple Kapustinskii equation (Eq. 2) has successfully been used to approximate values of the lattice energy for inorganic salts of varying complexity based on thermochemical radii.^[34, 35]

$$U_L = -120250 \frac{v \cdot |z^+| \cdot |z^-|}{r^+ + r^-} \left(1 - \frac{34.5}{r^+ + r^-} \right) \text{kJ} \cdot \text{mol}^{-1}$$

(Eq. 2)

U_L = lattice energy; r^+ , r^- = cation and anion radii in pm; v = number of ions in the unit cell; z^+ , z^- = cation and anion charges.

The lattice energy is a major structure-determining factor in the solid state that is at least one order of magnitude stronger than dispersive van der Waals or dipole-dipole interactions. Many WCAs have poly- or perfluorinated surfaces, which further diminishes dispersive interactions because fluorine atoms and element-fluorine bonds show a very low polarizability. From eq. 2 it becomes clear that an increase in the size of the anion leads to a decrease in lattice energy. For a large weakly coordinating anion, the lattice energy can approach the sublimation enthalpy of a molecular solid of comparable atomic weight. This indicates that the environment of the cation in the WCA's proximity more closely resembles gas phase conditions or conditions in a molecular solid than the situation in the strong electrostatic field usually found in typical ionic compounds (Tab. 1). Comparing for example the calculated lattice energy of the WCA salt $\text{Ag}(\text{S}_8)_2^+[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^{-[36]}$ ($M = 1588 \text{ g mol}^{-1}$) of 326 kJ mol^{-1} with that of C_{60} or C_{70} as representatives of molecular solids with large molecular weights, this effect becomes very clear: the fullerenes have lattice energies in the same order of magnitude, namely 175 and $200 \text{ kJ mol}^{-1[37-39]}$ ($M = 721$ (C_{60}) and 841 (C_{70}) g mol^{-1}).

Tab. 1: Thermochemical volumes and lattice potential energies of several 1:1 salts.

Compound	$V_{\text{therm}} [\text{\AA}^3]$	$U_{\text{L}} [\text{kJ mol}^{-1}]$
Li^+F^-	27	$1036^{\text{[a]}}$
Cs^+F^-	43	$740^{\text{[a]}}$
$\text{Cs}^+[\text{AsF}_6]^-$	128	$568^{\text{[b]}}$
$\text{Li}^+[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$	760	$361^{\text{[b]}}$
$\text{Cs}^+[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$	776	$362^{\text{[b]}}$
$\text{Ag}(\text{S}_8)_2^+[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^{-[36]}$	1169	$326^{\text{[b]}}$

[a] experimental values;^[37-39] [b] calculated from the thermochemical volumes.^[40]

Generally, large and possibly highly fluorinated weakly coordinating anions provide environments in the solid state that resemble the gas phase closely enough that they can be called “pseudo gas-phase conditions”.^[36]

The high solubility of WCAs also results from their decreased lattice energy. A salt is soluble if the sum of Gibbs free energies of solvation for both the cation and anion exceeds the lattice enthalpy of the salt A^+X^- , as can be depicted by a simple Born-Haber-Fajans cycle (Fig. 4).

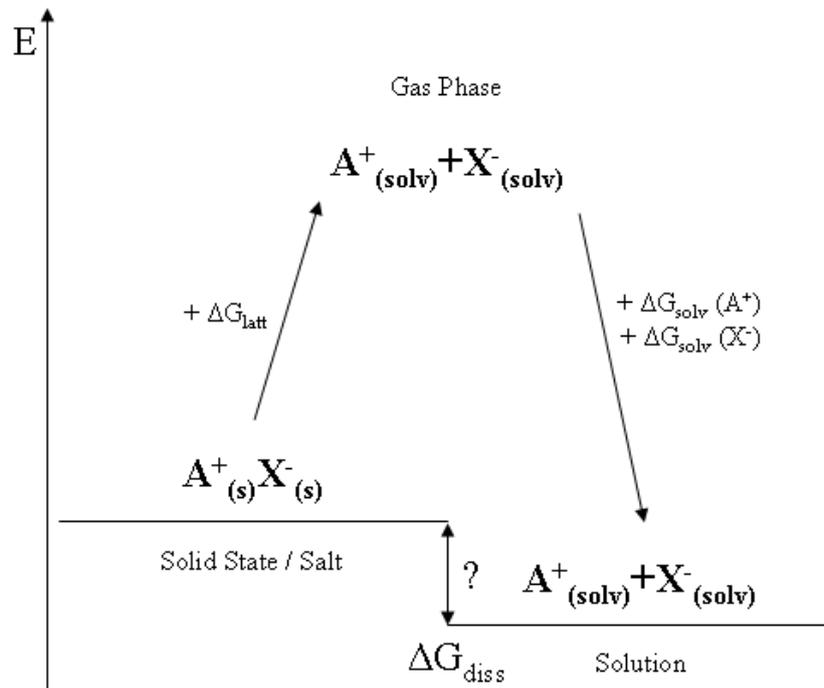


Fig. 4: Born-Haber-Fajans cycle for the dissolution of a soluble salt A^+X^- .

A very large WCA A^- yields a lattice enthalpy that is smaller than the negative sum of Gibbs solvation energies, hence the WCA salt is soluble.

Applications of WCAs ?

- Fundamental chemistry (stabilization of reactive cationic species)^[5-8, 12, 15-17, 28-31]
- Homogenous catalysis (e.g. electrocyclic organic reactions, 1,4-conjugate additions, pericyclic rearrangements, olefin polymerizations, hydrogenations)^[18, 41-47]
- Ionic liquids (ILs), salts that are liquid below 100°C (electrochemistry, electrical deposition, sensor technology, reaction media)^[48-55]
- Electrochemistry (supporting electrolytes)^[56, 57]
- Lithium ion batteries (electrolytes or ionic liquids with lithium cations)^[58-63]

- [1] I. Krossing, I. Raabe, *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 2066.
- [2] S. Hollenstein, T. Laube, *J. Am. Chem. Soc.* **1993**, *115*, 7240.
- [3] T. Kato, C. A. Reed, *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 2908.
- [4] G. A. Olah, A. M. White, D. H. O'Brien, *Chem. Rev.* **1970**, *70*, 561.
- [5] I. Krossing, A. Bihlmeier, I. Raabe, N. Trapp, *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 1531.
- [6] G. J. Schrobilgen, H. P. A. Mercier, M. D. Moran, *ACS Symposium Series* **2007**, *965*, 394.
- [7] G. J. Schrobilgen, H. P. A. Mercier, M. D. Moran, C. Steinberg, R. J. Suontamo, *J. Am. Chem. Soc.* **2004**, *126*, 5533.
- [8] G. A. Olah, L. Heiliger, G. K. S. Prakash, *J. Am. Chem. Soc.* **1989**, *111*, 8020.
- [9] A. E. P. M. Sorrilha, L. S. Santos, F. C. Gozzo, R. Sparrapan, R. Augusti, M. N. Eberlin, *J. Phys. Chem. A* **2004**, *108*, 7009.
- [10] E. Marotta, C. Paradisi, *J. Mass Spectr.* **2001**, *36*, 1195.
- [11] J. Dyke, N. Jonathan, E. Lee, A. Morris, M. Winter, *Phys. Scripta* **1977**, *16*, 197.
- [12] M. Lin, C. Liu, L. Zheng, *Wuli Huaxue Xuebao* **1995**, *11*, 266.
- [13] I. Krossing, *J. Am. Chem. Soc.* **2001**, *123*, 4603.
- [14] I. Krossing, L. Van Wullen, *Chemistry--A European Journal* **2002**, *8*, 700.
- [15] T. Drews, K. Seppelt, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 273.
- [16] A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy, K. O. Christe, *J. Am. Chem. Soc.* **2001**, *123*, 6308.
- [17] C. A. Reed, K. C. Kim, R. D. Bolskar, L. J. Mueller, *Science* **2000**, *289*, 101.
- [18] T. J. Barbarich, S. M. Miller, O. P. Anderson, S. H. Strauss, *J. Mol. Cat. A* **1998**, *128*, 289.
- [19] I. Krossing, H. Brands, R. Feuerhake, S. Koenig, *J. Fluor. Chem.* **2001**, *112*, 83.
- [20] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490.
- [21] S. M. Ivanova, B. G. Nolan, Y. Kobayashi, S. M. Miller, O. P. Anderson, S. H. Strauss, *Chem. Eur. J.* **2001**, *7*, 503.
- [22] T. J. Barbarich, S. T. Handy, S. M. Miller, O. P. Anderson, P. A. Grieco, S. H. Strauss, *Organomet.* **1996**, *15*, 3776.
- [23] S. H. Strauss, S. V. Ivanov, (Colorado State University Research Foundation, USA). Application: US 2000-704252, **2002**, p. 20 pp.
- [24] F. A. R. Kaul, G. T. Puchta, H. Schneider, M. Grosche, D. Mihalios, W. A. Herrmann, *J. Organomet. Chem.* **2001**, *621*, 177.

- [25] M. V. Metz, Y. Sun, C. L. Stern, T. J. Marks, *Organomet.* **2002**, *21*, 3691.
- [26] Y. Sun, M. V. Metz, C. L. Stern, T. J. Marks, *Organomet.* **2000**, *19*, 1625.
- [27] B. T. King, J. Michl, *J. Am. Chem. Soc.* **2000**, *122*, 10255.
- [28] I. Krossing, A. Reisinger, *Eur. J. Inorg. Chem.* **2005**, 1979.
- [29] M. Gonsior, I. Krossing, L. Muller, I. Raabe, M. Jansen, L. Van Wullen, *Chem. Eur. J.* **2002**, *8*, 4475.
- [30] I. Krossing, I. Raabe, *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4406.
- [31] M. Gonsior, I. Krossing, *Dalton Trans.* **2005**, 1203.
- [32] A. Bihlmeier, M. Gonsior, I. Raabe, N. Trapp, I. Krossing, *Chem. Eur. J.* **2004**, *10*, 5041.
- [33] D. M. Van Seggen, P. K. Hurlburt, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1995**, *34*, 3453.
- [34] A. Kapustinskii, *Z. Phys. Chem.* **1933**, *B22*, 257.
- [35] A. F. Kapustinskii, *Quart. Revs. (London)* **1956**, *10*, 283.
- [36] T. S. Cameron, A. Decken, I. Dionne, M. Fang, I. Krossing, J. Passmore, *Chem. Eur. J.* **2002**, *8*, 3386.
- [37] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2, 392 pp.
- [38] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*, 861 pp.
- [39] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, **2002**.
- [40] H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609.
- [41] K. Fujiki, J. Ichikawa, H. Kobayashi, A. Sonoda, T. Sonoda, *J. Fluor. Chem.* **2000**, *102*, 293.
- [42] N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost, A. S. Weller, *Chem. Eur. J.* **2002**, *8*, 2088.
- [43] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169.
- [44] W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345.
- [45] W. E. Piers, G. J. Irvine, V. C. Williams, *Eur. J. Inorg. Chem.* **2000**, 2131.
- [46] G. Erker, *Acc. Chem. R.* **2001**, *34*, 309.
- [47] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391.
- [48] P. Wasserscheid, *Chemie in Unserer Zeit* **2003**, *37*, 52.
- [49] P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3772.

- [50] T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
- [51] D. Wei, A. Ivaska, *Anal. Chim. Acta* **2008**, *607*, 126.
- [52] A. Hengstenberg, P. Tschuncky, (Draegerwerk AG, Germany). Application: 2005-102005020719, **2006**, p. 11pp.
- [53] K. Ding, Z. Miao, Z. Liu, Z. Zhang, B. Han, G. An, S. Miao, Y. Xie, *J. Am. Chem. Soc.* **2007**, *129*, 6362.
- [54] G. Buhler, C. Feldmann, *Angewandte Chemie (International ed. in English)* **2006**, *45*, 4864.
- [55] Y.-J. Zhu, W.-W. Wang, R.-J. Qi, X.-L. Hu, *Angewandte Chemie (International ed. in English)* **2004**, *43*, 1410.
- [56] N. J. Stone, D. A. Sweigart, A. M. Bond, *Organomet.* **1986**, *5*, 2553.
- [57] C. G. Zoski, D. A. Sweigart, N. J. Stone, P. H. Rieger, E. Mocellin, T. F. Mann, D. R. Mann, D. K. Gosser, M. M. Doeff, A. M. Bond, *J. Am. Chem. Soc.* **1988**, *110*, 2109.
- [58] J. O. Besenhard, *Handbook of Battery Materials*, Wiley-VCH, **1998**.
- [59] M. Schmidt, A. Kuehner, K.-D. Franz, G.-V. Roesenthaler, G. Bissky, (Merck Patent G.m.b.H., Germany). Application: 2001-10103189, **2002**, p. 10 pp.
- [60] N. Ignat'ev, P. Sartori, *J. Fluor. Chem.* **2000**, *101*, 203.
- [61] F. Kita, H. Sakata, S. Sinomoto, A. Kawakami, H. Kamizori, T. Sonoda, H. Nagashima, J. Nie, N. V. Pavlenko, Y. L. Yagupolskii, *J. Power Sources* **2000**, *90*, 27.
- [62] L. M. Yagupolskii, Y. L. Yagupolskii, *J. Fluor. Chem.* **1995**, *72*, 225.
- [63] W. Xu, C. A. Angell, *Electrochem. Sol. St. Lett.* **2000**, *3*, 366.