ITSC-IC 2019/2020
Seminar „Scientific Writing"

Ammonia Synthesis   Hot Paper

The Formation of Surface Lithium–Iron Ternary Hydride and its Function on Catalytic Ammonia Synthesis at Low Temperatures

Peikun Wang+, Hua Xie+, Jianping Guo, Zhi Zhao, Xiangtao Kong, Wenbo Gao, Fei Chang, Teng He, Guotao Wu, Mingshu Chen, Ling Jiang,* and Ping Chen*

Abstract: Lithium hydride (LiH) has a strong effect on iron leading to an approximately 3 orders of magnitude increase in catalytic ammonia synthesis. The existence of lithium–iron ternary hydride species at the surface/interface of the catalyst were identified and characterized for the first time by gas-phase optical spectroscopy coupled with mass spectrometry and quantum chemical calculations. The ternary hydride species may serve as centers that readily activate and hydrogenate dinitrogen, forming Fe-(NH₂)-Li and LiNH₂ moieties—possibly through a redox reaction of dinitrogen and hydridic hydrogen (LiH) that is mediated by iron—showing distinct differences from ammonia formation mediated by conventional iron or ruthenium-based catalysts. Hydrogen-associated activation and conversion of dinitrogen are discussed.

Ammonia is one of the most important synthetic chemicals for the sustainable growth of human society because it is the nitrogen (N) source of manmade fertilizer and a promising energy carrier in the upcoming renewable energy era.[1] The activation and transformation of dinitrogen (N₂) under mild conditions is thus one of the grand challenges in chemistry and has been pursued actively for a century.[1a,2] Advanced surface-science investigations and theoretical calculations have demonstrated that the dissociative activation of N₂ on

active sites made of multiple transition metal atoms (for example, the C7 site of Fe catalysts) is the slow elementary step.[3] Alkali metals (except Li), in their oxidative form, are electronic promoters that enhance the catalytic activity of Fe through electron donation or electrostatic effect.[3a,4] Since both the activation energies and adsorption energies of reacting adspecies are dominated by the electronic properties of transition metals and obey the scaling relations, efficient ammonia synthesis at low temperatures can hardly be achieved.[2a,5]

Recently, ammonia synthesis at low temperatures (such as, 150 °C) was recorded upon employing TM-LiH (transition metal (TM) = Cr, Mn, Fe, Co) composites as catalyst.[6] Kinetic analyses show that these catalysts have smaller apparent activation energies (45–65 kJ mol⁻¹) and lower reaction orders of N₂ (ca. 0.5), implying that the rate-determining step is unlikely to be the dissociation of N₂. To determine the mechanistic foundation of this new TM-LiH catalytic system for the multielectron and multihydrogen process, a number of imperative questions should be addressed: 1) the nature of the active site; 2) the manner in which N₂ is activated; 3) the site of NH₃ formation, and so forth. These issues are crucial for a molecular-level understanding of ammonia synthesis over the TM-LiH composite catalyst and directive for the design and optimization of catalytic material, but difficult to completely elucidate solely with conventional condensed-phase characterization techniques. Gas-phase clusters, bombarded from the surface of a catalyst and efficiently cooled by supersonic expansion of pulsed carrier gas, contains compositional and structural information of the surface and may represent the most active or least coordinated site on the surface.[7] The reaction between those clusters and gaseous reactants can thus provide structural and energetic information for mechanistic understanding of a catalytic process.[7,8] Combined with the condensed-phase approaches, herein, the gas-phase optical spectroscopy coupled with mass spectrometry (GOS-MS) supplemented with density functional theory (DFT) calculations was employed to characterize the active site, reactive surface species, and intermediates of the Fe-LiH catalyst, and to provide detailed insights into the microscopic mechanism of the activation and transformation of N₂ on that catalyst surface.

We first tested the effect of LiH content on the catalytic performance of the Fe-LiH composite (Figure 1). The activity of neat polycrystalline Fe is negligible, which is about 2 to 3 orders of magnitude lower than that of the Fe-xLiH (x = 1–693) catalysts. The Fe-LiH, Fe-3LiH, Fe-5LiH, and Fe-10LiH catalysts show similar ammonia synthesis rates in terms of the

[*] P. K. Wang,[+] Dr. H. Xie,[+] Dr. J. P. Guo, Z. Zhao, X. T. Kong, W. B. Gao, F. Chang, Dr. T. He, Prof. G. T. Wu, Prof. Dr. L. Jiang, Prof. Dr. P. Chen
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Dalian 116023 (China)
E-mail: ljiang@dicp.ac.cn
pchen@dicp.ac.cn
P. K. Wang,[+] X. T. Kong, W. B. Gao, F. Chang
University of Chinese Academy of Sciences
Beijing 100049 (China)
Dr. H. Xie,[+] Z. Zhao, X. T. Kong, Dr. L. Jiang
State Key Laboratory of Molecular Reaction Dynamics, Dalian
Institute of Chemical Physics, Chinese Academy of Sciences
Dalian 116023 (China)
Dr. J. P. Guo, Prof. Dr. L. Jiang, Prof. Dr. P. Chen
Collaborative Innovation Center of Chemistry for Energy Materials
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Dalian 116023 (China)
Prof. Dr. M. S. Chen
State Key Laboratory of Physical Chemistry of Solid Surfaces
Department of Chemistry, Xiamen University
Xiamen 361005 (China)
[+] These authors contributed equally to this work.
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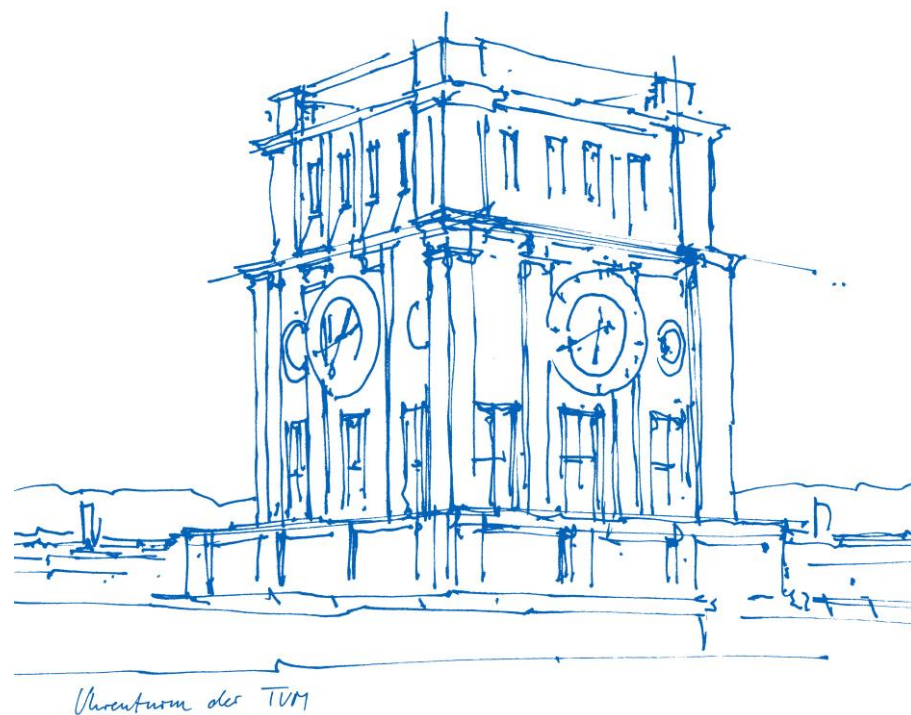
Uhrenturm der TUM

Kontakt: christian.gemel@tum.de
annette.schier@lrz.tum.de

Der Aufbau einer „Kurzmitteilung"

„Short Communication"

…in der Regel nicht als solche ausgewiesen!

- **Titel**   Title
- **Zusammenfassung**   Abstract
- **Einführung**   Introduction
- **Methoden/Experimentelles**   Methods/Experimental
- **Ergebnisse und Diskussion**   Results and Discussion
- **Fazit**   Conclusions
- **Literatur**   References

Der Aufbau einer „Kurzmitteilung"

Gesamtumfang 6 – 10 Seiten (≡ 4 – 6 „Druckseiten")

- Titel
- Zusammenfassung → ca. 10 Zeilen (Text)
- Einführung
- Methoden/Experimentelles ⎫
- Ergebnisse und Diskussion ⎭ bis zu 4 Abbildungen / Tabellen
- Fazit
- Literatur → ca. 15 – 25 Zitate

Der Titel

„Aufmacher" eines jeden Papers

- Möglichst kurz und prägnant

- Möglichst viele Informationen zum Inhalt

- Der Inhalt „muss halten, was der Titel verspricht"

Achtung: hüten Sie sich vor „Sensationen"…

„The largest…"

„The first…"

„novel…"

… und „Bewertungen"

„interesting…"

„fascinating…"

REPORTS

reaction in S_1 (model A) or by a multi–step-wise recovery of the bR_{570} ground state within S_0 (model B). Indications for model A were given from the observation of a biphasic decay of the excited electronic state with time constants of 0.24 and 0.75 ps (5). These authors suggested a fast, reactive path leading to the isomerized state (J) and a slower, nonreactive path leading back to the educt. This model cannot be ruled out by the IR transients reported here, which rise within 0.5 ps or less; however, it is not supported by our own optical experiments (26).

The more likely model is model B, which could be realized by vibrational relaxation (for example, vibrational cooling) processes in S_0 that accompany the full recovery to the vibrational ground state of bR_{570} within 1.0 to 1.7 ps and the transformation from J to K in 3 ps. The J-K transition might take longer than the bR_{570} recovery because substantial conformational changes, including parts of the protein, are involved in the former. Vibrational cooling would be indicated by the decay of small shoulders on the low-energy side of the vibrational bands as the vibrational ground state recovers, an effect which is easily obscured by the 13-cis product bands. However, this view is also supported by time-resolved IR experiments on the isomerization reaction of protonated SB retinal in solution (29) and the observation of anti-Stokes RR bands of the chromophore in bR (20, 30).

A small negative shoulder at about 1660 cm^{-1} (Fig. 2, A to C) appears within 1 ps or less (the apparent rise time is again limited by the dephasing time). Because no chromophore vibrational band is expected in this spectral region, it is possibly a contribution of the protein amide I band or a result of the bending vibration of a protein-bound water molecule. The molecular structure of bR is determined from x-ray diffraction (31) indicates a water molecule close to the SB as part of the hydrogen bond network in the chromophore binding pocket. Photoexcitation, that is, an electric field jump, or isomerization of the chromophore, might affect the absorption cross section, orientation, or even location of this water molecule or of a protein constituent and may lead to the observed bleach signal. In this case, the observed signal would indicate a fast response not of the chromophore but of the environment, that is, the cofactor binding pocket.

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Crystallographic Evidence for a Free Silylium Ion

Kee-Chan Kim,[1] Christopher A. Reed,[1*] Douglas W. Elliott,[1] Leonard J. Mueller,[1] Fook Tham,[1] Lijun Lin,[2] Joseph B. Lambert[2*]

Evidence for a three-coordinate silyl cation is provided by the crystal structure of $[(Mes)_3Si][H-CB_{11}Me_5Br_6]\cdot C_6H_6$ (where Mes is 2,4,6-trimethylphenyl). Free $(Mes)_3Si^+$ cations are well separated from the carborane anions and benzene solvate molecules. *Ortho*-methyl groups of the mesityl substituents shield the silicon atom from the close approach of nucleophiles, while remaining innocent as significant ligands themselves. The silicon center is three-coordinate and planar. The downfield ^{29}Si nuclear magnetic resonance chemical shift in the solid state (226.7 parts per million) is almost identical to that in benzene solution and in "gas phase" calculations, indicating that three-coordination can be preserved in all phases.

The silylium ion problem has exercised the minds of many (1–5). The essential debate concerns the existence of three-coordinate silicon cations, R_3Si^+ (where R is an alkyl or aryl group), unfettered by interactions with solvent, counterion, or neighboring groups. The fundamental question concerns how far the analogy to carbocations, R_3C^+, known now for more than 100 years (6), extends down group 14 of the periodic table.

Despite ready mass spectrometric detection in the gas phase, there has been no convincing evidence for the existence of free R_3Si^+ ions in condensed phases when R is an alkyl group. The closest approach is found in "ion-like" species, $R_3Si^{\delta+}Y^{\delta-}$, where R is *iso*-propyl and Y is a very weakly coordinating anion, such as the perfluorinated tetraphenylborate ion or a carborane (7). These species behave like silylium ions toward arenes (8) and in the production of superacidity (9), but they are not free silylium ions.

However, when R is a bulky aryl group, there is growing spectroscopic evidence and theoretical support for truly free, three-coordinate silyl cations. Species formulated as $[Ar_3Si][Y]$ have been reported for Ar = mesityl or duryl and $Y = B(C_6F_5)_4^-$ (10, 11). Silyl cation character is indicated by downfield shifted resonances in the ^{29}Si nuclear magnetic resonance (NMR) spectrum near 220 parts per million (ppm). The NMR shifts have been reproduced computationally in the calculated structures of these triarylsilylium ions (12, 13). An arylated silatropilium ion (14) and a *cyclo*-tetrasilenylium ion with bulky substituents (15) provide convincing evidence for three-coordination in other sili-

[1]Department of Chemistry, University of California, Riverside, CA 92521–0403, USA. [2]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208–3113, USA.

*To whom correspondence should be addressed. E-mail: chris.reed@ucr.edu (C.A.R.); jlambert@northwestern.edu (J.B.L.)

Die Zusammenfassung

Strukturbeschreibung „ohne Zahlen"

Zusatzinfo: NMR-Spektroskopie und Theorie, die weitere Strukturinfos liefern…

…anstelle eines Satzes zur Synthese

Achtung: in der Zusammenfassung wird in der Regel nicht zitiert!

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„WAS wurde WIE gemacht"

Einführung

Warum ist das Thema von Interesse

…einfach, wenn das Paper „abwendungsorientiert" ist…

Vorsicht: „halten die Ergebnisse, was die Einleitung verspricht"? *Understatement ist besser als Boasting*
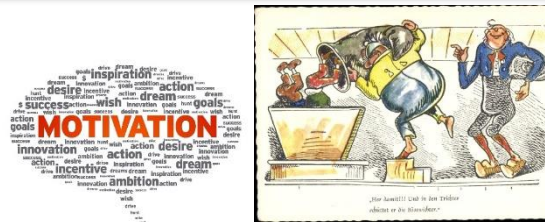
Was ist der „Kenntnisstand" Wo sind „die Lücken" und Probleme

Erfordert gründliche Literatur-Recherche

Achtung: der Gutachter ist Experte und kennt die Literatur…!

Was ist Ihr Beitrag, diese „Lücken" zu füllen/ Probleme zu lösen

…als Überleitung zum Hauptteil („Methods & Experimental" und „Results & Discussion")

„WARUM wurde etwas gemacht"

Achtung: hüten Sie sich vor „Allgemeinplätzen"…

„Catalysis is an interesting subject"

„Cancer is a horrible disease"

…und vor „niederen Motiven"

„Upon browsing all structural databases, we could not find any compound with…, and therefore…"

Zur „Beruhigung": Das Rad wird „nur selten" neu erfunden!

…deshalb: „In the following we report on our contributions to…" ist völlig legitim!

Einführung

Dieses Paper ist nicht anwendungsorientiert – warum ist es dennoch „interessant"?

The silylium ion problem has exercised the minds of many.[1-5] The essential debate concerns the existence of three-coordinate silicon cations, R_3Si^+ (where R is an alkyl or aryl group), unfettered by interactions with solvent, counterion, or neighboring groups. The fundamental question concerns how far the analogy to carbocations, R_3C^+, known now for more than 100 years[6], extends down group 14 of the periodic table.

„WARUM wurde etwas gemacht"

Einführung

1. Was ist bisher bekannt

selbsterklärend....

Das ist der schwierigste Teil eines Papers:

- Der „Kenntnisstand" muss vollständig sein,
- die „Notwendigkeit des Papers" muss klar herausgearbeitet werden,
- die bisherigen Ergebnisse müssen analysiert
- und kurz und prägnant zusammengefasst werden!

„<u>WARUM</u> wurde etwas gemacht"

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[1]Department of Chemistry, University of California, Riverside, CA 92521–0403, USA. [2]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208–3113, USA.

*To whom correspondence should be addressed. E-mail: chris.reed@ucr.edu (C.A.R.); jlambert@northwestern.edu (J.B.L.)

2. Was sind die Probleme und wie wurden sie gelöst

The definitive structural characterization of a triarylsilylium ion by X-ray crystallography <u>has been hampered</u> by the tendency of B$(C_6F_5)_4$ salts to form oils or liquid clathrates rather than crystallize. [...] These <u>problems are overcome</u> by carborane anions, [...].

„jetzt kann's losgehen"!

„<u>WARUM</u> wurde etwas gemacht"

The scanned article:

con cations. N...
characterized b...
The definiti...
of a triarylsily...
phy has been hampered by the tendency of B$(C_6F_5)_4$ salts to form oils or liquid clathrates rather than crystallize. Fluorocarbon and hydrocarbon entities are not particularly compatible. In addition, the B–C_6F_5 bond in the anion is prone to electrophilic cleavage. These problems are overcome by carborane anions, whose properties can be optimized for applications with reactive cations (16). In particular, the icosahedral carborane anion, H-CB$_{11}$Me$_5$Br$_6^-$, has 7,8,9,10,11,12-hexahalo substituents for inertness and 2,3,4,5,6-pentamethyl substituents for good solubility of its salts (17).

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Mes$_3$Si(CH$_2$–CH=CH$_2$)
+ Et$_3$Si(H-CB$_{11}$Me$_5$Br$_6$)
→ [Mes$_3$Si][H-CB$_{11}$Me$_5$Br$_6$]
+ (CH$_2$=CH–CH$_2$)SiEt$_3$ (1)

Yellow crystals of the benzene solvate [Mes$_3$Si][H-CB$_{11}$Me$_5$Br$_6$]·C_6H_6 suitable for x-ray crystallography were grown in 1 day at 5°C by vapor diffusion with hexanes. Higher temperatures led to cleavage of Si-Ar bonds from which crystals of protonated arenes (18) can be isolated.

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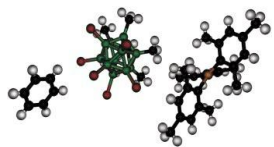
packing can be described as alternating columns of cations and anions, with benzene filling space primarily in the anion columns.

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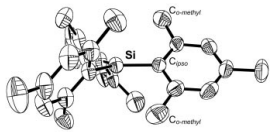
average value (49.2°) is very close to those computed for an isolated Mes$_3$Si$^+$ ion, 47.3° to 49° depending on the calculation (12, 13). This result suggests that the conformation is intrinsic, a balance struck between minimizing nonbonded repulsions of the o-Me groups at high twist angles and maximizing conjugative 2p(C) → 3p(Si) π stabilization at low twist angles.

Further comparisons with theory are made in Fig. 3. The calculated bond angles agree extremely well with experiment. The calculated bond lengths involving the π system are mostly longer than experiment, suggesting that theory slightly underestimates conjugative stabilization. However, the differences are less than 1.2%. Theory has performed well in part because the large cation with its buried charge is probably insensitive to the surrounding environment.

The ^{29}Si NMR chemical shift of the Mes$_3$Si$^+$ ion provides an excellent means to assess structural consistency between phases. In benzene solution with B$(C_6F_5)_4^-$ as counterion, the value is 225.5 ppm (10). It is unperturbed by the addition of more basic bulky arenes such as toluene or xylene (20). The calculated ("gas phase") value lies in the range 226 to 230 ppm, depending on the method used (12, 13). The solid state value obtained via magic angle spinning methods for the present species is 226.7 ppm. Such close congruence provides a powerful argument that the structure of the Mes$_3$Si$^+$ ion is

Fig. 1. Perspective view of the asymmetric unit in the crystal structure of [Mes$_3$Si][H-CB$_{11}$Me$_5$Br$_6$]·C_6H_6 (green, B; red, Br; black, C; gray, H; brown, Si).

Fig. 2. Perspective drawing of the Mes$_3$Si$^+$ cation. Thermal ellipsoids are shown at the 50% probability level.
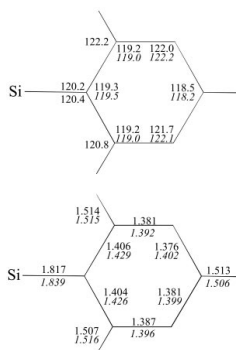
Fig. 3. Comparison of experimental and calculated (italics) average bond angles (in degrees, top) and bond lengths (in angstroms, bottom) in the Mes$_3$Si$^+$ cation.

Ergebnisse und Diskussion

Wir gehen ins Detail: <u>Was</u> wurde <u>wie</u> gemacht?

<u>Achtung:</u> Abbildungen müssen im Text erwähnt werden….

„….as shown in Fig.1"

„….(Fig.1)"

….und brauchen eine (sinnvolle) „Legende"

Details zu den Experimenten/Methoden → „Supplementary Information"

Synthesevorschriften

Strukturdaten

Rechnungen

…

1. Beschreibung von Synthese und Kristallzucht kein „Experimentalteil"!

- <u>Welche</u> Verbindungen wurden eingesetzt
- evtl. Ansatz<u>größe</u> / Ausbeute
- <u>Welche Eigenschaften</u> hat das Produkt
- <u>Wie</u> wurden die Kristalle gezüchtet

2. Beschreibung der Kristallstruktur

- <u>Detaillierte</u> Beschreibung (→ Titel) mit Abbildungen

3. Vergleich mit der berechneten Struktur (Gas)

4. Vergleich mit der Struktur in Lösung (NMR)

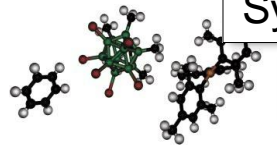Fig. 1. Perspective view of the asymmetric unit in the crystal structure of [Mes₃Si][H-CB₁₁Me₅Br₆]·C₆H₆ (green, B; red, Br; black, C; gray, H; brown, Si).
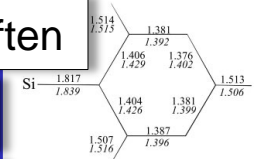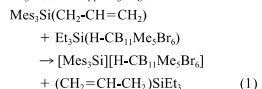
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Ergebnisse und Diskussion

Wir gehen ins Detail: Was wurde wie gemacht?

- Folgen Sie Ihrer „Gliederung", und springen Sie nicht zwischen den einzelnen Topics hin und her!

- „Bleiben Sie sachlich", und gehen Sie sparsam mit „glorifizierenden" Adjektiven um (novel, amazing, first….)!

- Verwenden Sie die richtige Terminologie (Fachsprache)!

- Achten Sie auf Konsistenz:
  einmal °C, immer °C   (K)
  einmal Å, immer Å   (pm)
  einmal „Dezimalpunkt", immer „Dezimalpunkt"
  ….

1. Beschreibung von Synthese und Kristallzucht

2. Beschreibung der Kristallstruktur

3. Vergleich mit der berechneten Struktur (Gas)

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con cations. None with a Si-C bond has been characterized by x-ray crystallography.

The definitive structural characterization of a triarylsilylium ion by x-ray crystallography has been hampered by the tendency of $B(C_6F_5)_4^-$ salts to form oils or liquid clathrates rather than crystallize. Fluorocarbon and hydrocarbon entities are not particularly compatible. In addition, the $B–C_6F_5$ bond in the anion is prone to electrophilic cleavage. These problems are overcome by carborane anions, whose properties can be optimized for applications with reactive cations (16). In particular, the icosahedral carborane anion, $H–CB_{11}Me_5Br_6^-$, has 7,8,9,10,11,12-hexahalo substituents for inertness and 2,3,4,5,6-pentamethyl substituents for good solubility of its salts (17).

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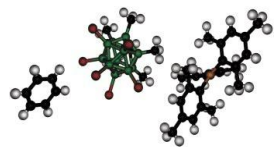
cluster is highly delocalized. The crystal packing can be described as alternating columns of cations and anions, with benzene filling space primarily in the anion columns.

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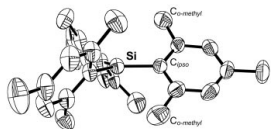
41.9° relative to the coordinate plane. The average value (49.2°) is very close to those computed for an isolated Mes_3Si^+ ion, 47.3° to 49° depending on the calculation (12, 13). This result suggests that the conformation is intrinsic, a balance struck between minimizing nonbonded repulsions of the o-Me groups at high twist angles and maximizing conjugative 2p(C) → 3p(Si) π stabilization at low twist angles.

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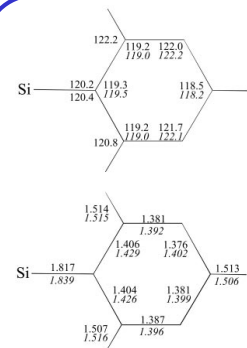

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Fazit

„In summary…."

Hier wird es richtig gemacht, indem ein Aspekt diskutiert wird, der im gesamten Paper bisher nicht erwähnt wurde….

These results bring the differences between carbon and silicon into sharp focus[3]. Because of its small size and intermediate value of electronegativity, carbon readily sustains coordinative unsaturation [...]

…und auf eine „Zusammenfassung" wurde komplett verzichtet!

„…wohl dem, der solche Aspekte hat!"

---

as solvent, anion, or the nearby Me groups closely approached the Si center, less downfield-shifted values would be expected. Similar shifts have been observed in related tin chemistry where the downfield ^{119}Sn chemical shift of the Bu_3Sn^+ cation is attenuated by axial interactions from Me groups of the counterion (21).

Additionally, the full ^{29}Si chemical shielding tensor can be determined in the solid state. The best fit to the slow magic-angle spinning spectrum (Fig. 4) gives 226.7 ppm for the isotropic shift, 185.5 ppm for the anisotropy (δ), and 0 for the asymmetry parameter (η). An axially symmetric tensor ($\eta = 0$) is required in the presence of a threefold rotational axis. On the basis of molecular symmetry, the equivalent δ_{xx} and δ_{yy} tensor components (319.5 ppm) lie within the coordination plane, whereas the δ_{zz} component (41.2 ppm) is aligned with the local C_3 axis. This distinctively large anisotropy under axial symmetry provides complementary structural characterization for the planar sp^2-hybridized silylium center. Related large anisotropies are seen in disilenes (22).

These results bring the differences between carbon and silicon into sharp focus (3). Because of its small size and intermediate value of electronegativity, carbon readily sustains coordinative unsaturation. Positive charge is readily stabilized by π conjugative (and hyperconjugative) effects. Silicon and the remainder of the group 14 elements are significantly larger in size and considerably more electropositive, so unsaturation is less easily stabilized by conjugative effects. Charge is less easily delocalized, and longer bonds to substituents invite access by nucleo-
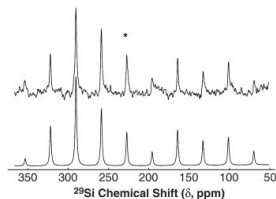
Fig. 4. The ^{1}H-decoupled ^{29}Si CPMAS (condensed phase magic angle spinning) NMR spectrum of $[Mes_3Si][H\text{-}CB_{11}Me_5Br_6]\cdot C_6H_6$ at a spinning rate of 2.5 kHz (top). The nonlinear least-squares fit of the sideband manifold (bottom) using the method of (24) gives a fit within an axially symmetric chemical shift tensor [$\sigma_{iso} = 226.7$ ppm (*); $\delta = 185.5$ ppm; $\eta = 0$].

ylium ion problem" that now appears to be solved. The situation with germylium and stannylium ions is less resolved (20, 21, 23).

References and Notes
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19. X-ray data for $C_{39}H_{55}B_{11}Br_6Si$ at 223(2) K with Mo 0.71073 Å. Monoclinic P2(1)/c, $a = 12.771(1)$, $b = 29.227(1)$, $c = 13.601(1)$ Å, $\beta = 102.152(2)°$, $Z = 4$, $\theta = 1.39°$ to 23.26°; 7132 independent reflections [R(int) = 0.0556]; 528 parameters; goodness of fit, 1.012; R ($I > 2\sigma$) 0.0397; wR2, 0.0826; largest diff. peak and hole, 0.598; and -0.486 e.Å³. Full data have been deposited in the Cambridge Crystallographic Database.
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25. Supported by the National Science Foundation CHE 0095206 (to C.A.R.), CHE 0091162 (to J.B.L.), CHE-9982362 and ACS PRF Grant 35320-G6 (to L.J.M.), and Department of Education Graduate Fellowship (GAANN) P200A000208 (to D.W.E.).

Laminar Growth of Ultrathin Metal Films on Metal Oxides: Co on Hydroxylated α-Al$_2$O$_3$(0001)

S. A. Chambers,[1]* T. Droubay,[1] D. R. Jennison,[2] T. R. Mattsson[2]

Metals deposited in vacuum on metal oxides such as alumina normally grow as three-dimensional clusters because of weak adatom-substrate interactions. This tendency hinders our ability to form interfaces of ultrathin, laminar metal films on oxides for use in microelectronics and other technologies where nanostructural control is desired. We present experimental and theoretical results showing that room temperature Co deposition on fully hydroxylated clean sapphire (α-Al$_2$O$_3$) produces a surface chemical reaction that leads to laminar growth, despite a large mismatch in lattice constants. This process should be applicable to a wide range of metals and metal oxides.

Durable interfaces between disparate materials, such as metals and metal oxides (1), are critical for nanotechnology [e.g., for the manufacture of microelectronics (2), seals, and sensors]. We lack the ability to form multi-layer structures of metals and oxides in which the interface is strong and ultrathin layers grow in a laminar fashion. In contrast, non-laminar island growth is often seen, because adatom-adatom interactions are stronger than adatom-substrate interactions. In this case, the surface–free energy change for film growth [($\Delta\gamma$) = (γ_{film} + γ_{int} – γ_{sub})] is greater than zero because the surface free energy of the film (γ_{film}) may be larger than

that of the substrate (γ_{sub}), and the interface free energy (γ_{int}) is small because of weak adsorbate-substrate interactions. In addition, metal/metal-oxide interfaces are of critical importance for understanding heterogeneous catalysis (3), corrosion, and adhesion.

Co on alumina is especially important because of a proposed use in magnetoresistive random access memory (2). A thin (~1 nm) alumina layer is sandwiched between two magnetic layers to form a tunnel junction. High-quality alumina films can be produced by plasma oxidation of Al films (2). However, it is problematic to grow a thin magnetic Co layer on top of the alumina film in a

Literatur

… manchmal auch „References and Notes"

19. X-ray data for $C_{39}H_{55}B_{11}Br_6Si$ at 223(2) K with Mo 0.71073 Å. Monoclinic P2(1)/c, $a = 12.771(1)$, $b = 29.227(1)$, $c = 13.601(1)$ Å, $\beta = 102.152(2)°$, $Z = 4$, $\theta = 1.39°$ to 23.26°; 7132 independent reflections [R(int) = 0.0556]; 528 parameters; goodness of fit, 1.012; R ($I>2\sigma$) 0.0397; wR2, 0.0826; largest diff. peak and hole, 0.598; and -0.486 e.Å³. Full data have been deposited in the Cambridge Crystallographic Database.

beide Vorgehensweisen „fallen einem beim Peer Review auf die Füße"

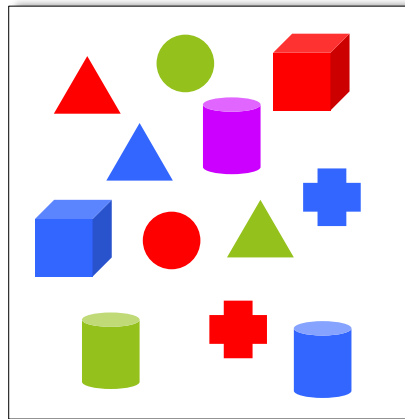Achtung: ein Autor, der nur „sich selbst zitiert" ist von vornherein suspekt…

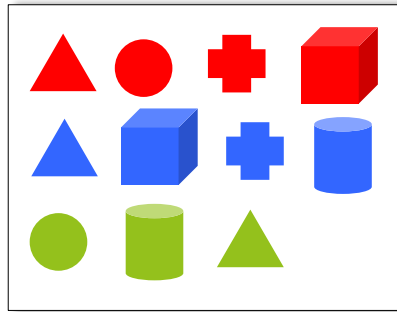…und einer, der nur „Reviews" zitiert, ist „ein fauler Hund".
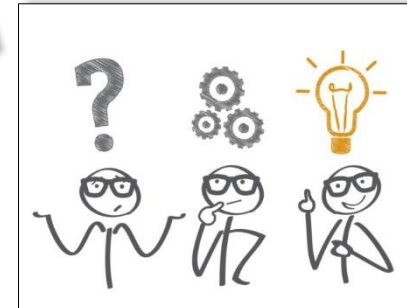
Workflow

A. „Stoff sammeln"

Was wurde gemacht?
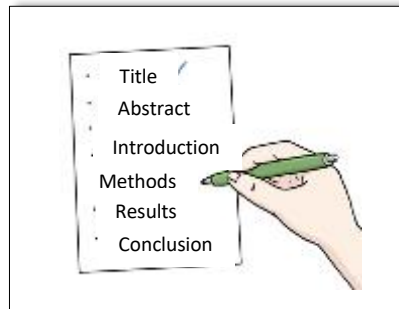
B. „Stoff ordnen"

Nicht alles, was gemacht wurde, passt zusammen…
→ Treffen Sie eine Auswahl!

C. „Gedanken ordnen"

Was ist das Leitmotiv des Papers?
→ „Gehe zurück auf B." – Stimmt die Stoffauswahl noch?

D. „Konzept erstellen"

- Title
- Abstract
- Introduction
- Methods
- Results
- Conclusion

Welche Inhalte sollen präsentiert werden?
→ „Gehe zurück auf B." – Stimmt die Stoffauswahl noch, und liegen alle notwendigen Informationen vor?

Angewandte Chemie
2017–129/51
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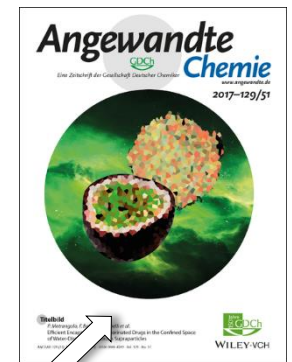
| 1. Methoden/Experimentelles | 2. Ergebnisse & Diskussion | 3. Einführung | 4. Fazit & Zusammenfassung | 5. Titel |

„Erster Entwurf"

Aaa bbb ccc dddddd ee cihcah
Abcöao öowzc öo woz öuz
wc
Ncehc ö

Acx whc uwzc luwec iw c
we
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iwuc io x iwu cäow cwiu iuw
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Wi c ggg c öwai iw cwo c iw
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Woiqc siju
Ic powicpouqwipuoiue vewou

„Ist die Message angekommen"?

„Erster überarbeiteter Entwurf"
→ Einpassen in „Templat"

„Final Version"

Crystallographic Evidence for a Free Silylium Ion

EO
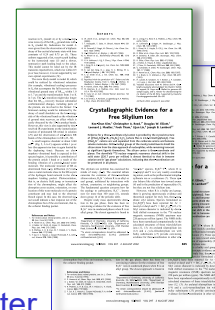
Peer Review

Peer Review

„Peer Review" im Rahmen von ITSC-IC

- **Innovationsgehalt**
- Titel
- Zusammenfassung
- Ein**führung** [Kenntnisstand]
- Methoden/Experimentelles
- Ergebnisse & Diskussion
- Fazit
- **Literatur** [Vollständigkeit]
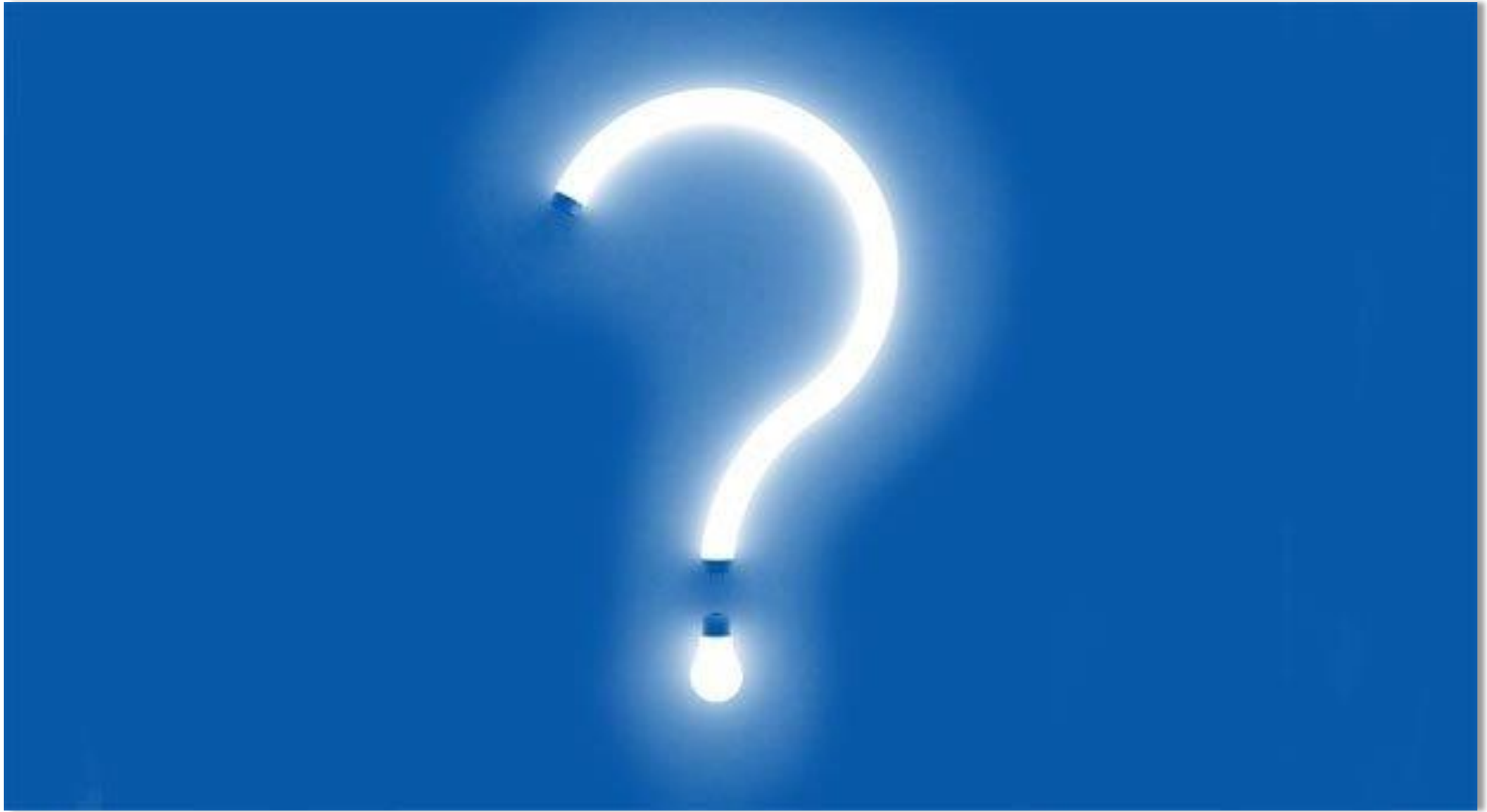
Seminar 2 im Sommersemester

„Peer Review" bei wiss. Zeitschriften, „Geldgebern" etc.
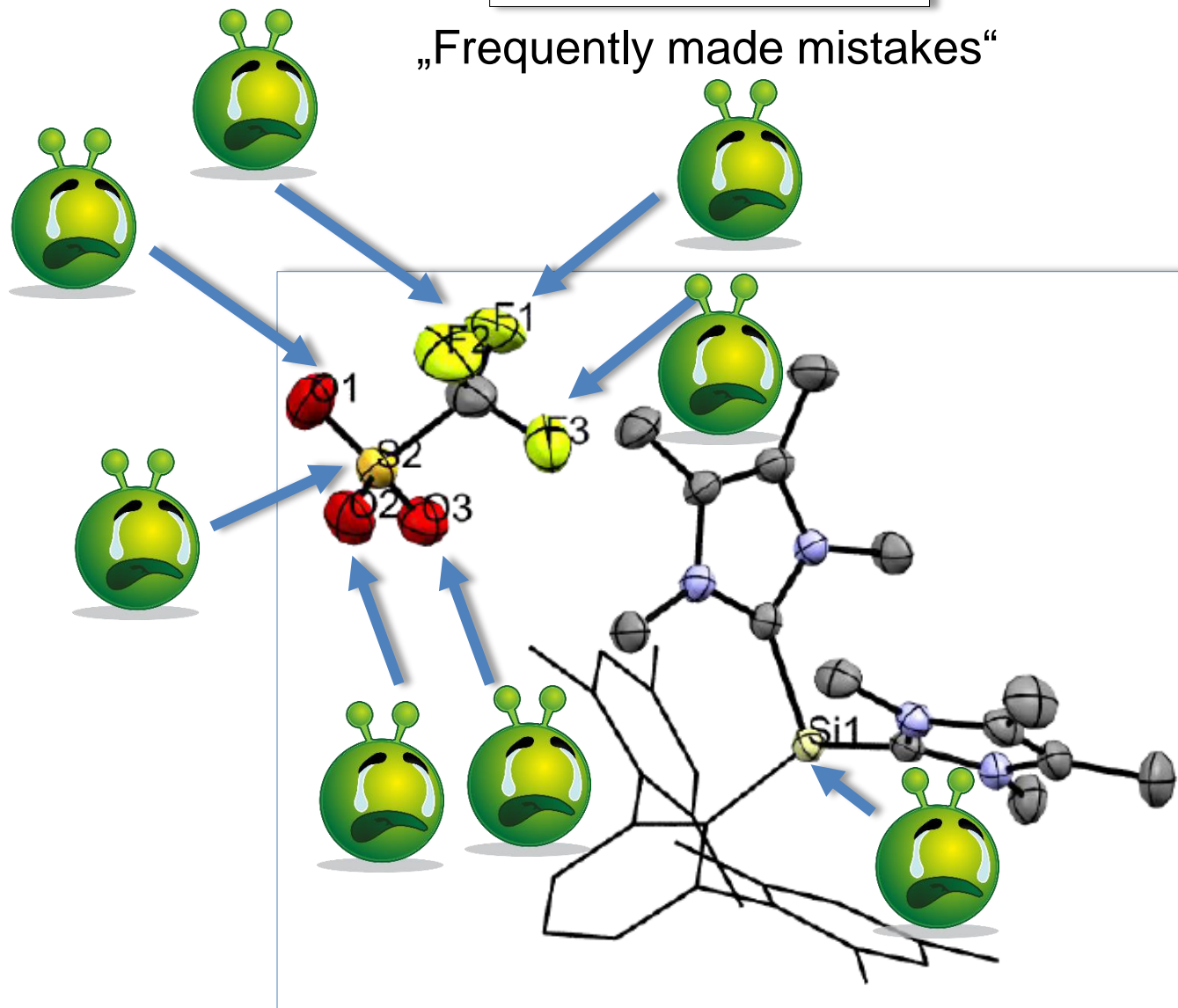
- **Innovationsgehalt**

Conditio-sine-qua-non:

- Title
- Abstract
- Introduction
- Methods/Experimental
- Results and Discussion
- Conclusions
- References

Glossary

„Frequently made mistakes"

…so viel Zeit muss sein!!

Glossary

„Frequently made mistakes"

Falsch	Richtig
thermal ellipsoids	displacement ellipsoids
bond distances	bond lengths, interatomic distances, Si-C distances

... within experimental error (0.2°) of 360°. As expected, the Si-C bonds [1.808(5), 1.820(5), and 1.823(5) Å, where values in parentheses represent the estimated SD; average, 1.817 Å] are significantly shorter than those observed in the neutral sp^3 trimesitylallylsilane precursor (avg., 1.91 Å) (11).
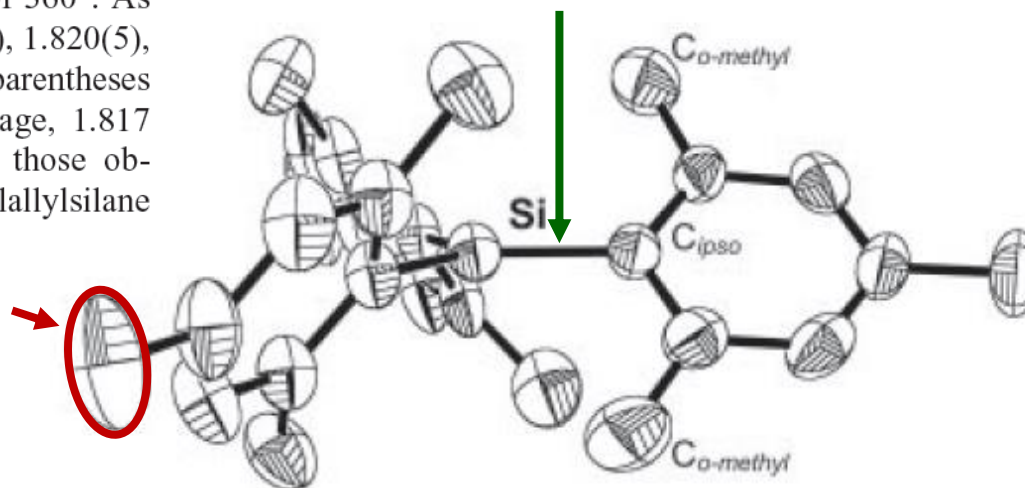

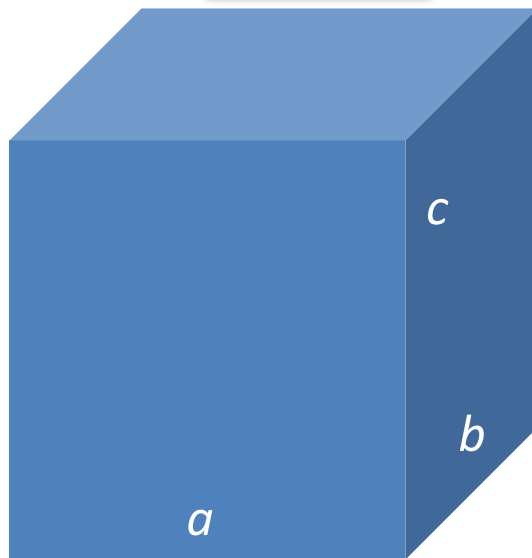**Fig. 2.** Perspective drawing of the Mes_3Si^+ cation. Thermal ellipsoids are shown at the 50% probability level.

Oups!

Glossary

„Frequently made mistakes"

Falsch	Richtig
cell constants	cell parameters

unit cell

$P2_1/c$

19. X-ray data for $C_{39}H_{55}B_{11}Br_6Si$ at 223(2) K with Mo 0.71073 Å. Monoclinic P2(1)/c, $a = 12.771(1)$, $b = 29.227(1)$, $c = 13.601(1)$ Å, $\beta = 102.152(2)°$, $Z = 4$, $\theta = 1.39°$ to $23.26°$; 7132 independent reflections [R(int) = 0.0556]; 528 parameters; goodness of fit, 1.012; R ($I>2\sigma$) 0.0397; wR2, 0.0826; largest diff. peak and hole, 0.598; and -0.486 e.Å³. Full data have been deposited in the Cambridge Crystallographic Database. **?**

(CCDC XXXXXXXX)
depository number

e·Å^{-3} oder e Å^{-3}

Glossary

„Frequently made mistakes"

Falsch	Richtig
…the NMR shows… …the NMR of…	…the NMR spectrum shows… …the NMR spectrum of…
…peaks	…resonances, signals, chemical shifts
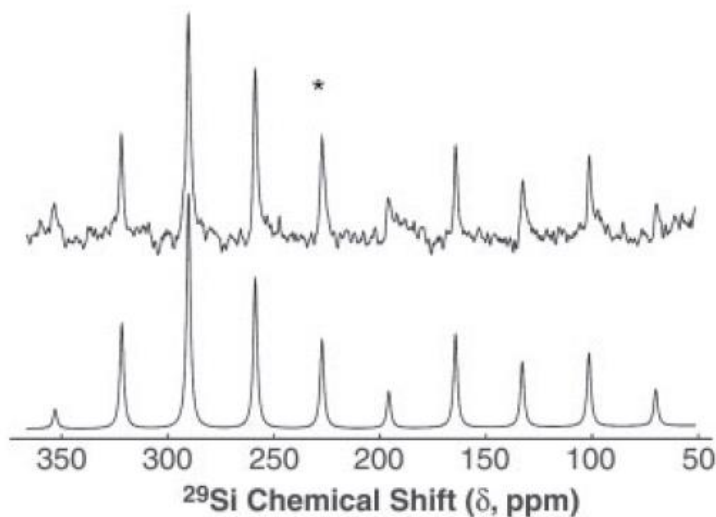
^{29}Si Chemical Shift (δ, ppm)

Fig. 4. The ^{1}H-decoupled ^{29}Si CPMAS (condensed phase magic angle spinning) <u>NMR spectrum of</u> [Mes$_3$Si][H-CB$_{11}$Me$_5$Br$_6$]·C$_6$H$_6$ at a spinning rate of 2.5 kHz (top). The nonlinear least-squares fit of the sideband manifold (bottom) using the method of (24) gives an axially symmetric chemical shift tensor [σ_{iso} = 226.7 ppm (*); δ = 185.5 ppm; η = 0].

The ^{29}Si NMR chemical shift of the Mes$_3$Si$^+$ ion provides an excellent means to assess structural consistency between phases.

Glossary

„Frequently made mistakes"

Falsch	Richtig
…the IR/Raman shows…	…the IR/Raman spectrum shows…
…peaks	…(absorption) bands
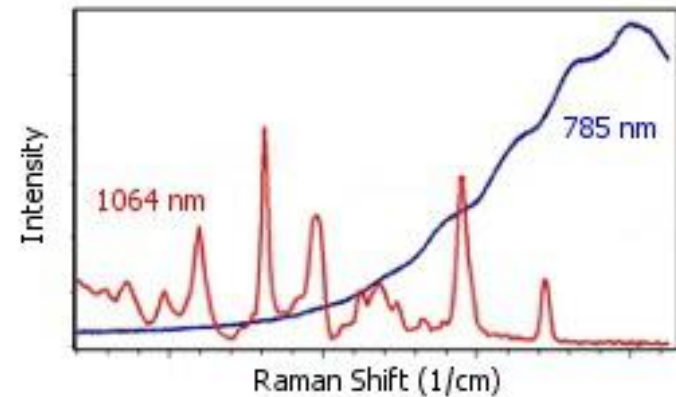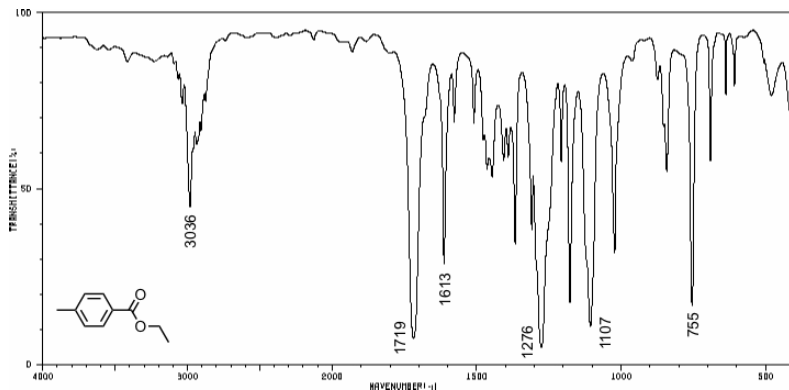
Beispiel: gefärbtes Plexiglas (PMMA)
Bei Anregung durch den 785 nm-Laser zeigt der gefärbte Kunststoff eine starke Fluoreszenz, wodurch die charakteristischen Peaks überdeckt werden. Mit dem Spektrum des 1064 nm-Lasers kann das Material aber zweifelsfrei identifiziert werden.
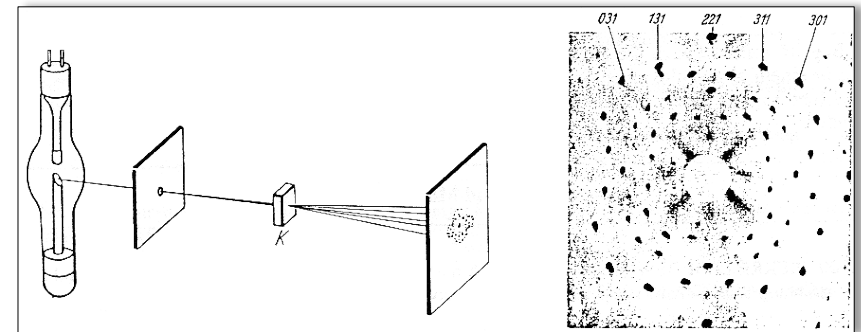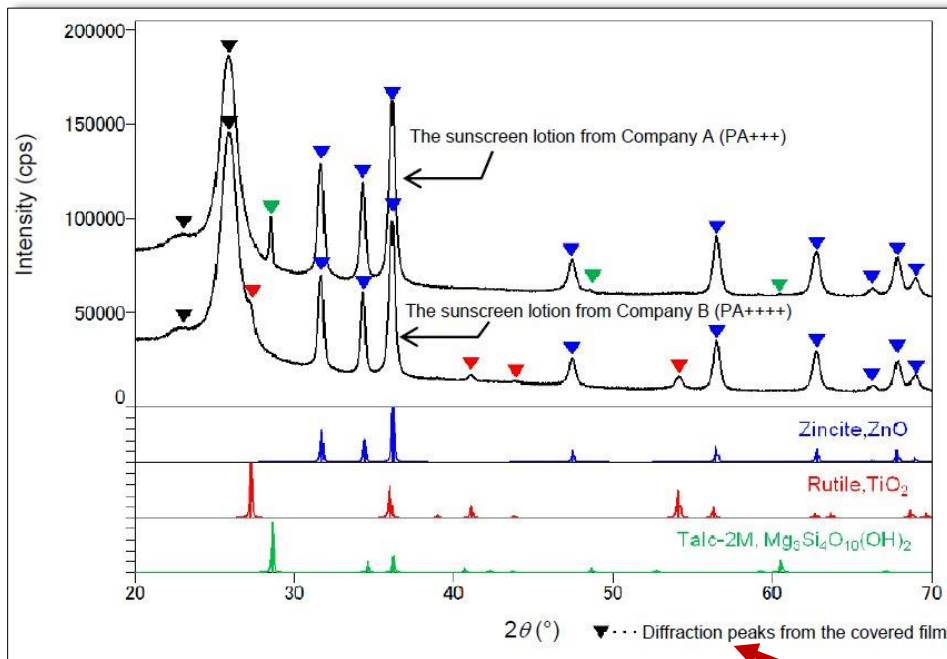**Lumoscope-R mit Dual-Laser ist klar im Vorteil.**

Oups!

Glossary

„Frequently made mistakes"

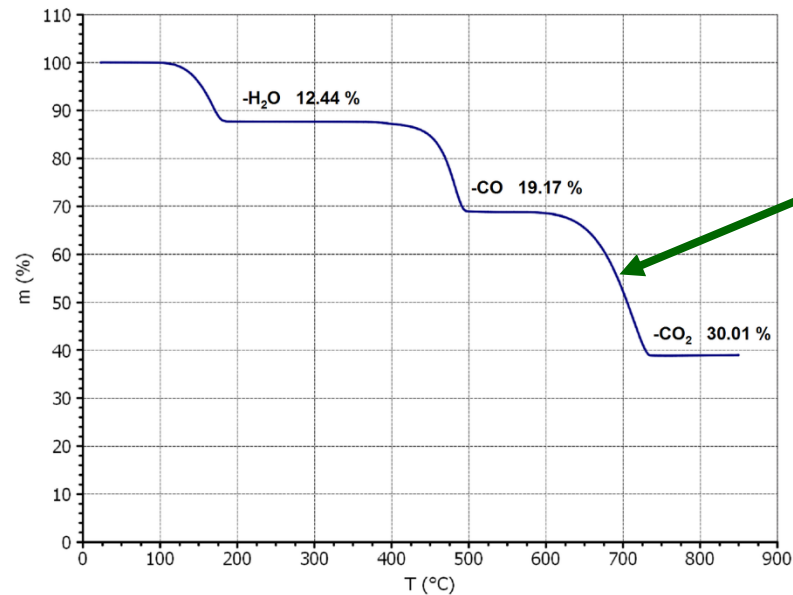| Falsch	Richtig
X-ray powder diffraction (XPD)	powder X-ray diffraction (PXD) single crystal X-ray diffraction
spectrum	diffractogram
peaks, signals…	reflections

Naja!

Glossary

„Frequently made mistakes"

Falsch	Richtig
	thermal gravimetric analysis thermogravimetric analysis
Spektrum	themogravimetric measurement, ...analysis

mass loss