could, in principle, originate in **1** incorporated in the Etard complex. When the matrix conditions are simulated by dissolving the two reactants in a Freon mixture at $-80\,^\circ C$ and quenching the resulting solution at 77 K to form a glass, the amount of acetaldehyde among the oxidation products increases to 35% after subsequent photolysis at 77 K and usual work-up; this is then comparable to the yield in the matrix experiment.[21] Therefore, **1** should also occur intermediately in the thermal reaction of ethylene with CrO_2Cl_2. Since other olefins are quantitatively oxidized to carbonyl compounds by CrO_2Cl_2 in thermal reactions,[3] intermediates analogous to **1** could play a more important role in these cases, although, of course, other mechanisms for the formation of carbonyl compounds are imaginable.[5]

The isolation of an intermediate in an olefin oxidation by CrO_2Cl_2 was achieved for the first time. The presence of this intermediate could explain the occurrence of carbonyl compounds in the product spectrum of such reactions.

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Si$_6$, Si$_{14}$, and Si$_{22}$ Rings in Iodide Silicides of Rare Earth Metals[**]

Hansjürgen Mattausch and Arndt Simon[*]

Numerous metal-rich halides MX_nA ($n \leq 2$) of rare earth metals M with interstitial atoms $A = H,C,N,O$ have been prepared.[1–3] Recently we reported on boride and boride carbide halides.[4–6] Owing to the electropositive character of the rare earth metals, the interstitial atoms are present as anions, and in the case of carbon C_2^{6-} and C_2^{4-} units are found besides discrete C^{4-} ions.[1] In $M_4X_5B_4$ the boron atoms form rhomboids which are linked into chains.[6] Several factors influence the nature of the interstitial species: the number of

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electrons which can be donated by the MX_n framework[7] (thus determining the A–A bonding), the electronic balance between M–M, M–A, and A–A bonding, and the dimensions and distribution of voids in the metal atom arrangement.

So far, the only known compounds with silicon as interstitial atom are Gd_4I_5Si and Gd_3I_3Si.[8] Isolated Si atoms center Gd_6 octahedra, similar to carbon in the corresponding carbide halides. For binary rare earth silicides, however, structures involving Si–Si bonding exist, such as MSi,[9] which contains zig-zag chains, and MSi_2, which contains a three-dimensional network of Si atoms.[10] Compared to these binary and ternary[11] silicides, the variation of the halogen content in halide silicides offers an additional means for fine-tuning the valence-electron concentration and hence the nature of the Si Zintl anions. Since electron transfer to the interstitial Si species is decreased in the halide silicides, larger Si_n entities may be formed given appropriate geometrical conditions.

We prepared MISi (M = La, Ce, Pr), $La_4I_3Si_4$, and $La_5I_3Si_5$ by annealing stoichiometric mixtures of MI_3, M, and Si for several days.[12] The compounds were obtained as needles or laths with a metallic luster. Conductivity measurements[14] on pressed or sintered pellets revealed metallic behavior between 5 K and room temperature. The compounds are extremely sensitive towards moisture and ignite explosively upon contact with water.

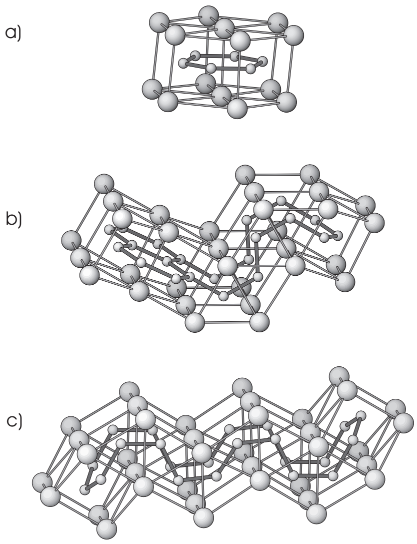

Figure 1. Building blocks in rare earth metal iodide silicides. Si and M atoms are represented by spheres of increasing size.[29] Silicon is coordinated by M in a trigonal-prismatic fashion. a) Si_6 rings with a Ce environment in CeISi, b) condensed Si_6 and Si_{14} rings with a La environment in $La_4I_3Si_4$, and c) Si_{22} rings with a La environment in $La_5I_3Si_5$.

Figure 1 depicts the characteristic M–Si building blocks in the structures of CeISi, $La_4I_3Si_4$, and $La_5I_3Si_5$.[15] All three structures contain Si_n rings (emphasized by bold lines): Si_6 rings which deviate from planarity by less than 7° are found in CeISi, planar Si_6 rings are condensed with strongly bent Si_{14} rings in $La_4I_3Si_4$, and Si_{22} rings are linked into corrugated layers in $La_5I_3Si_5$. All Si atoms are coordinated by M atoms in a trigonal-prismatic fashion, but the interconnection of the prisms differs in the three structures. There are two ways of fusing the prisms to attain optimal space filling[17] and these differ with respect to the relative directions of the quasi-threefold axes, which can be parallel (p) or orthogonal (o) to each other.[18] In the structure of CeISi prisms with (p) orientation form layers (see Figure 1a), and the occupation of the prism centers through Si results in Si_6 rings. The structural principle is closely related to that of β-$ThSi_2$.[19] Indeed, the structure of CeISi represents a two-dimensional section of the latter. As shown in the projection in Figure 2, the Ce-(SiSi)-Ce layers are surrounded on both sides by I atoms above the trigonal prism faces. The I-Ce-(SiSi)-Ce-I slabs with the sequence $C\alpha(bc)\alpha B$ are stacked parallel to (001) to provide close packing between layers of I atoms which are held together by van der Waals forces. The structure is in contrast with that of the composition-related compound $Gd_2Br_2C_2$, in which ethene-like C_2^{4-} anions occupy the octahedral voids of close-packed double layers of metal atoms.[20]

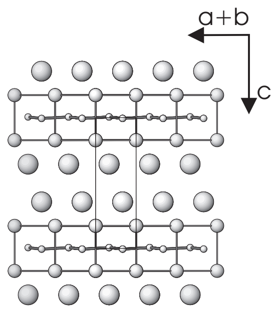

Figure 2. Projection of the structure of CeISi along [110]. The building blocks from Figure 1a are condensed to form layers parallel to the "threefold" axis of the trigonal prisms; between the layers are double layers of I atoms. Si, Ce, and I atoms are represented by spheres of increasing size.

Figure 3 shows the projection of the $La_4I_3Si_4$ structure along [010]. In contrast to CeISe the trigonal M prisms are fused in both (p) and (o) modes. Double strings of La_6 (o) prisms, shown as projections on the rectangular prism faces in Figure 3, are alternatingly condensed with (p) prisms to form corrugated layers parallel to (001). The (p)-linked prisms correspond to a section of the β-$ThSi_2$ structure (see insert of Figure 3) containing a ribbon of *trans*-condensed Si_6 rings formed from Si(1) and Si(2).

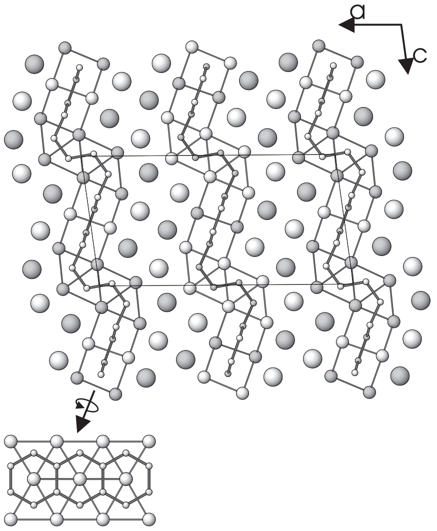

Figure 3. Projection of the structure of $La_4I_3Si_4$ along [010]. The building blocks from Figure 1a are condensed to form layers that are held together by the I atoms. The β-$ThSi_2$-analogous part of the structure is highlighted. Si, La, and I atoms are represented by spheres of increasing size.

The occupation of the (o) prisms by Si atoms and connection of these atoms with Si_6 rings (see Figures 1b and 3) leads to hitherto unknown Si_{14} rings composed of the atoms Si(1) – Si(4). In contrast to the nearly planar Si_6 rings (deviation from planarity less than 5°), the Si_{14} rings are strongly bent at Si(3) ($\sphericalangle$Si(4)-Si(3)-Si(3) = 115°).[21]

The Si_6 rings exhibit distances $d_{\text{Si–Si}} = 239$ and 244 pm and angles $\sphericalangle$Si(1)-Si(1)-Si(2) = 119 and $\sphericalangle$Si(1)-Si(2)-Si(2) = 121°. In spite of the different bonding modes of the atoms in the Si_{14} rings, the range of Si – Si distances is narrow (239 – 243 pm). Only the distance (2b)Si(3) – (2b)Si(3) in the bending position of the ring is significantly larger (247 pm). Using $d_n = 235 - 0.6 \lg n$[22] one calcultates Pauling bond orders of $n = 0.85$, 0.72, and 0.64 for the different Si – Si distances instead of the expected $n = 1.0$. Bond lengthening up to 10 pm was observed for singly charged (2b)X^- atoms (X = As, P) in phosphides and arsenides,[23] and in the case of $Li_{14}Si_6$ and related Li/Mg silicides single bond Si – Si distances of $d_0 = 251 - 258$ pm were assumed.[24, 25] However, a value within this range is too large for the halide silicides. Apparently, the distances depend strongly on the cations, the other anions, and the nature of the Zintl anion.

The slightly puckered La-Si-Si-La layers in $La_4I_3Si_4$ are arranged parallel to (001) and linked through I atoms. Part of the I atoms belong to only one slab (I(1), I(2)), and others connect adjacent slabs (I(3)).

A similar arrangement of corrugated layers is found in $La_5I_3Si_5$, whose structure is shown as projection along [010] in Figure 4. Here the slabs are again connected by van der Waals contacts (I(3)) and La-I-La bridges (I(1), I(2)). In the shown projection, an (o) prism is followed by eight (p) prisms. Fusion of (o) prisms through common rectangular faces leads to chains, and condensation of the eight prisms in (p) orientation through common triangular faces leads to ribbons parallel to (010). Chains and ribbons together form layers. Alternatively the structure of $La_5I_3Si_5$ can be described in terms of a combination of sections of the α- and β-$ThSi_2$ structural types. In the central part of Figure 4, the α-$ThSi_2$ part is hatched and the β-$ThSi_2$ part is dotted. A block of the α-type in which an (o) prism surrounded by (p) prisms on both sides is followed by a section of the β-type with (p) prisms in *cis*, *trans* arrangement but with only (2b)Si atoms, as in silicides of the CrB type.[26] This formal decomposition of the structure indicates that besides $La_5I_3Si_5$ further compounds with a general composition $(M_2Si_2I)_a\,(M_3Si_3I_2)_b$ may exist, where the coefficients *a* and *b* denote the number of condensed blocks of the α- and β-$ThSi_2$ structural type, respectively. The variation of *a* and *b* would allow different Si_n ring sizes to be synthesized. In the present case $a = b = 1$, the ring size corresponds to Si_{22}, and the rings are condensed parallel to (010) into layers. The Si – Si distances in the rings vary between 237 and 249 pm, independent of the functionality of the Si atoms, similar to $La_4I_3Si_4$ and CeISi. The bond angles deviate only slightly from 120° (114 – 120°); hence, the Si atoms are sp^2 hybridized. The lone pair on (3b)Si^- has p character, and those on (2b)Si^{2-} have sp^2 and p character.[11]

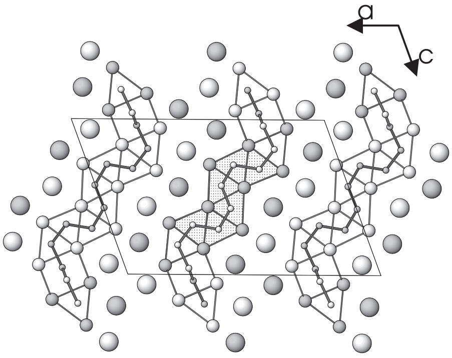

Figure 4. Projection of the structure of $La_5I_3Si_5$ along [010]. The lightly corrugated layers, made up of the units shown in Figure 1a, contain trigonal prisms around the Si atoms in the (p) and (o) orientation. The middle portion of the figure shows the partial structures that are analogous to α-$ThSi_2$ (hatched) and β-$ThSi_2$ (dotted). The I atoms connect the layers. Si, La, and I atoms are represented by spheres of increasing size.

The description of $La_4I_3Si_4$, CeISi and La_5I_3Si within the Zintl – Klemm formalism corresponds to $(La^{3+})_4(I^-)_3Si_4^{6-} \cdot 3\,e^-$, $Ce^{3+}I^-Si^- \cdot e^-$, and $(La^{3+})_5(I^-)_3[(3b)Si^-]_1[(2b)Si^{2-}]_4 \cdot 3\,e^-$, respectively. One or three electrons per formula unit occupy bands with M – M bonding character. In agreement with the observed metallic conductivity and the results of band structure calculations,[27] these electrons are delocalized. Halide silicides of the rare earth metals are a new class of compounds with structures based on layers of the Zintl polyanions $Si_{6/6}^{1-}$ (Si_6), $Si_{6/3}^{2-}Si_{8/2}^{8-}$ (Si_{14}), and $Si_{6/3}^{2-}Si_{16/2}^{16-}$ (Si_{22}).

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0.0057(3); (twin: $\bar{1}00$, $0\bar{1}0$, 001). $R_1 = 0.029$, $wR_2 = 0.071$ (all 325 independent reflections). Isotypic LaISi: $a = 421.9(2)$, $c = 1179.4(1)$ pm, PrISi: $a = 416.4(1)$, $c = 1161.9(1)$ pm. $La_5I_3Si_5$: $C2/m$; $a = 2401.9(1)$, $b = 425.34(2)$, $c = 1571.61(7)$ pm, $\beta = 119.38(1)°$. La(1): 0.0856(1), 0, 0.5629(1); La(2): 0.3390(1), 0, 0.9422(1); La(3): 0.2622(1), 0, 0.6693(1); La(4): 0.1638(1), 0, 0.8339(1); La(5): 0.4826(1), 1/2, 0.7100(1); I(1): 0.3274(1), 1/2, 0.5627(1); I(2): 0.4091(1), 0, 0.7956(1); I(3): 0.0597(1), 1/2, 0.9334(1); Si(1): 0.0759(1), 1/2, 0.7076(1); Si(2): 0.2499(1), 1/2, 0.9599(1); Si(3): 0.9912(1), 1/2, 0.5731(1); Si(4): 0.2601(1), 1/2, 0.8098(1); Si(5): 0.1719(1), 1/2, 0.6806(1); $R_1 = 0.024$, $wR_2 = 0.051$ (all 3000 independent reflections). b) Image plate (IPDS, Stoe); $Mo_{K\alpha}$ radiation. $La_4I_3Si_4$: $C2/m$; $a = 2436.0(5)$, $b = 424.0(1)$, $c = 1257.0(3)$ pm, $\beta = 97.59(3)°$. La(1): 0.5036(1), 0, 0.1653(1); La(2): 0.5747(1), 1/2, 0.4456(1); La(3): 0.3613(1), 0, 0.2918(1); La(4): 0.3548(1), 0, 0.9760(1); I(1): 0.6328(1), 0, 0.2889(1); I(2): 0.2014(1), 0, 0.5729(1); I(3): 0.2435(1), 0, 0.1311(1); Si(1): 0.5230(3), 0, 0.5902(2); Si(2): 0.5428(3), 1/2, 0.6828(2); Si(3): 0.5510(3), 1/2, 0.0168(2); S(4): 0.5967(3), 1/2, 0.8600(2); $R_1 = 0.044$, $wR_2 = 0.081$ (all 1952 independent reflections). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-407246 (CeISi), CSD-407247 ($La_4I_3Si_4$), and CSD-407248 ($La_5I_3Si_5$).

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Tris(tetramethylethylenediamine-sodium)-9,9-bianthryl—The Salt of a π Hydrocarbon Radical Trianion with Three Na^+–C_π Contacts to One Molecular Half

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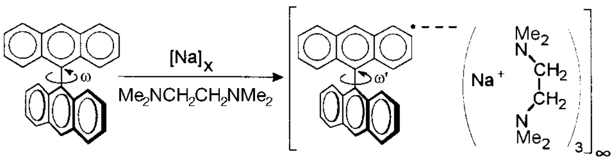
Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

Reductions of π hydrocarbons by sodium metal in aprotic solutions[1] of efficient cation-solvating ethers[2] facilitate the growth of single crystals (and thus the determination of the structures) of a wide variety of solvent-separated or solvent-shared contact-ion multiples containing radical ions, dianions, or even tetraanions.[1–3] Representative examples are the bare naphthalene radical anion that can be isolated from diglyme solution as a salt with an advantageously solvated sodium cation,[3a] the tetraphenylbutadiene dianion that crystallizes in stoichiometrically 1:1 solvent-separated and solvent-shared ion triples,[3b] or the rubrene tetraanion that has been structurally characterized as contact-ion quintuple with four THF-coordinated Na^+ countercations.[3c]

Still missing is a salt of a radical trianion. By reduction of 9,9′-bianthryl with sodium in a solution containing a mixture of tetramethylethylenediamine and benzene [Eq. (1)], the sodium salt of a π hydrocarbon radical trianion has been isolated as black blocks.[4a]



(1)

The structure determination of the radical trianion salt[4b] (Figure 1) reveals a surprise: In the solvent-shared contact ion quadruple, all three TMEDA-solvated sodium ions are η^6-coordinated to the same anthryl moiety of the 9,9′-bianthryl radical trianion (Figure 1B), whereas the perpendicular hydrocarbon residue forms only two η^1 and η^2 contacts to the centers Na1 and Na3 of an adjacent contact-ion aggregate in the *y* direction of the polymer string (Figure 1A, B). The shortest Na^+–C η^6 contacts are found for Na2 (average 269 pm); the ones for Na3 and Na1 of 285 and 289 pm are longer because of the additional relatively short contacts of

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