tin—carbon bond, formation of Sn(OMe),, R2H, and the ylide 10 in almost quantitative yield.[10] The reaction with 2,3-dimethylbutadiene (DMB) occurs by [1 + 4]cycloaddition to give 11; a [2 + 4]cycloaddition does not occur (cf. 19). Compound 8 does not react with aldehydes even at elevated temperatures. Our assumption that there is a tin–carbon multiple bond in the planar molecular framework of 8 (P1, C1, C2, Sn1, C12) is largely based on the significant shortening of the Sn1–C1 bond. A shortening of about 0.1 Å for a Sn–N bond in the stannane [(Me3Si)2N]Sn=NC(6-Pr2C6H4)2 (12) was recently reported by Meller et al., the tin atom having a trigonal-planar coordination.[11] Together with the observations on 3 and 12, this would seem to indicate that planar multiple bonding systems between the main group metal elements of the higher periods and the nonmetal elements of the second period may be accessible. In addition, an interesting ligand coupling reaction on a low-coordinate tin atom was observed, which extends still further the synthetic potential of organotin compounds.

Experimental Procedure

8 (5.225 g, 3.3 mmol) and 6 (1 g, 3.3 mmol) were placed in an apparatus consisting of two 100 mL round-bottomed flasks fitted with taps, and connected to each other by a glass iris (GIII). The apparatus was treated with hot HNiSiMe3 prior to use. Subsequently, toluene (20 mL) was condensed into the apparatus and the solution stirred for about 24 h at 25°C. All volatile components were then removed under vacuum, and n-hexane (20 mL) was condensed on to the oily yellow residue. A beige colored crystals. Yield 85–92%; m.p. 148–150°C.

For example: R5Sn(CH3)2Mes=Sn–C2 2.23 and 2.25 Å; R3Sn(SPh)2: Sn–C 2.23 and 2.22 Å; R5SnOOC(CF3)2: Sn–C 2.18 Å (H. Grützmacher, H. Pritzko, unpublished results).
dines can be considered to have a common mechanism in view of the fact that a range of these alkaloid derivatives are effective glucosidase inhibitors and are thus of increasing interest because of their Anti-HIV activity. In the following we report on a new intramolecular Lewis acid catalyzed imino-ene reaction for the diastereoselective construction of 7-alkenyl-8-yl)pyrrolidin-2-methylidene benzylamine which is extremely interesting because of their Anti-HIV activity. In the following we report on a new intramolecular Lewis acid catalyzed imino-ene reaction for the diastereoselective construction of 7-alkenyl-8-yl)pyrrolidin-2-methylidene benzylamine (1) with FeCl₃ affords three stereoisomeric indolizidines in a ratio of 90.3:7.0:2.7 (Scheme 1, Table 1). After chromatographic purification the main product was isolated with an enantiomeric excess of >98%.

If, however, TiCl₃ is used as Lewis acid, the isomeric ratio was altered completely (Table 1), and an additional indolizidine was also formed. As a result of the X-ray structure analysis the formation product was carried out on the imine (9) [the resulting product was then acetylated with acetic anhydride. The vicinal coupling constants for H-8 obtained from the 1H NMR spectrum of 4 (Table 2) clearly show the all-cis arrangement of H-8a, H-8, and H-7. This arrangement was confirmed by a NOESY experiment

Table 1. Reaction of 1 with Lewis acids [a,b].

<table>
<thead>
<tr>
<th>Lewis acid</th>
<th>t[h]</th>
<th>Product ratio [c]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃</td>
<td>48</td>
<td>90:3:1</td>
<td>62 (2)</td>
</tr>
<tr>
<td>TiCl₃</td>
<td>21.5</td>
<td>1.2:3:1</td>
<td>94.7 (4)</td>
</tr>
</tbody>
</table>

[a] The reactions were carried out with 2.5 equiv Lewis acid in CH₂Cl₂ at room temperature. [b] Enantiomeric purity of the isolated products 2 and 4 >98% ee. For the determination of the ee values see ref. [9]. [c] Isomeric ratios were determined from the crude products by capillary GC.

The formation of the products 2 was assigned with an enantiomeric excess of >98%.

If, however, TiCl₃ is used as Lewis acid, the isomeric ratio was altered completely (Table 1), and an additional indolizidine was also formed. As a result of the X-ray structure analysis, product 2 can be assigned unambiguously to the all-trans configuration shown in Scheme 1. NMR spectroscopic investigations showed that one benzylideneamino group is bound to the indolizidine framework of 4 at position 8 and one isopropyl group at position 7; however, the unequivocal stereochemical assignment of 4 was only achieved after its transformation into the N-acetyl derivative 6 (Scheme 2). For this, first a hydrogenolysis in the presence of PdCl₂ was carried out on the imine 4 [12] the resulting product was then acetylated with acetic anhydride. The vicinal coupling constants for H-8 obtained from the 1H NMR spectrum of 4 (Table 2) clearly show the all-cis arrangement of H-8a, H-8, and H-7. This arrangement was confirmed by a NOESY experiment in which a nuclear Overhauser effect (NOE) was observed between H-8a and H-8 and also between H-8 and H-7. The application of the same hydrogenation/hydrogenolysis/acetylation sequence on 2 yielded the diastereomeric N-acetyl product 7, whose vicinal coupling constants of H-8 confirm the all-trans configuration of 4. Although, the stereochemical configuration of the two by-products 3 and 5 could not be elucidated unambiguously, the assignment made according to Scheme 1 is supported by the mass spectra of 3 and 5. The mass spectrum of 3 shows an almost identical fragmentation pattern and comparable intensities to that of 2; accordingly, the spectrum of 5 is extremely similar to that of 4. The formation of the products 2 and 3 can

Scheme 2. Synthesis of N-acetylindolizidines 4 and 7. Reaction conditions: a) 1 equiv PdCl₂, MeOH, 1 atm H₂, 20° C, 4 h; b) 1.1 equiv Ac₂O, 3 equiv NEt₃, CH₂Cl₂, reflux, 12 h.

\[4 \rightarrow 5\]
be explained by an intramolecular type 1 hetero-ene reaction (Scheme 3). An alternative multistep mechanism is also conceivable, in which at first the alkene attacks the initially formed iminium ion 9 leading to the formation of the carbenium ions 10.14,15 Starting from 10 either a reprotonation via 11, leading to the benzylamines 2 and 3, or a hydride shift takes place to give the benzyl cation 12, from which the imines 4 and 5 are formed after the elimination of the Lewis acid. The stereochemistry of the cyclization products 2–5 indicates that the competing pathways of reprotonation or hydride shift depend on the relative configuration at C-7/C-8 of the carbenium ion 10, that is, a hydride shift is only favored when the benzyl and the isopropyl group (C-7/C-8-cis) lie in close proximity to each other. However, so far we have not found a reasonable explanation for why the two Lewis acids FeCl₃ and TiCl₄ react so differently with regard to the stereochemistry of the ring closure. The different coordination geometry of the two Lewis acids cannot be the reason, since other Lewis acids, for example SnCl₄, show isomeric ratios comparable to the FeCl₃ case. A similar dependence of the diastereoselectivity on the Lewis acid used is also observed for the analogous reaction of racemic piperidine carbaldimine 13 to give the quinolizidines 14–16 (Scheme 4). Other products were not observed, and the diastereoselectivities are significantly lower than those for the corresponding indolizidines (Table 3).

Regardless of the mechanisms discussed above, the hetero-ene reactions of 1 and 13 described here provide a simple and diastereoselective access to α-amino-functionalized indolizidines and quinolizidines, respectively, which opens new perspectives in natural product chemistry.

Experimental Procedure
To an ice-cooled solution of imine 1 or 13 (1.00 mmol) in dry CH₂Cl₂ (28 mL), Lewis acid (2.5 mmol; FeCl₃; 1.0 mL solution in Et₂O; TiCl₄; 1.0 mL solution in CH₂Cl₂) was added dropwise over 30 min. and the resulting mixture was stirred at room temperature. Following complete conversion (GC control) the mixture was hydrolyzed by addition of 2 mL NaOH and extracted three times with CH₂Cl₂ (100 mL). After the organic phase had been dried over MgSO₄ and concentrated, the crude product was purified by flash chromatography (silica gel, hexane/ethyl acetate/triethylamine 79:16:5).

Table 3. Reaction of 13 with Lewis acids [a].

<table>
<thead>
<tr>
<th>Lewis-acid</th>
<th>t [h]</th>
<th>Product ratio [b]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃</td>
<td>48</td>
<td>14:16</td>
<td>68 (14)</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>48</td>
<td>15:15</td>
<td>50 (16)</td>
</tr>
</tbody>
</table>

[a] Reaction conditions see Table 1, footnote [a]. [b] Compare Table 1, footnote [c].

Scheme 3. Possible reaction mechanisms for the formation of the products 2–5.

14-16

Scheme 4. Cyclization of rac-13. For clarity only one enantiomer of 14–16 is shown in each case. Reaction conditions: 2.5 equiv Lewis acid, CH₂Cl₂, room temperature.

[6] To date very little has been reported on the synthesis of indolizidines by in...


The enantiomeric purity of the products 2 and 4 (each > 98% ee) was determined by using one mirror equivalent of (−)-(R)-4-(9-anthryl)2,2,2-trifluoro-ethanol in the 200 MHz 1H NMR spectrum see: W. Pirkle, D. L. Sikkenga, M. S. Pavlin, *J. Org. Chem.* **1977, 42, 384.

The isolated products 2 or 4 do not epimerize on renewed reaction with 2.5 equiv Lewis acid in CH₂Cl₂ at room temperature. After a reaction time of more than 4 h, however, increasing decomposition leading to the formation of benzylamine is observed in the gas chromatogram. The same effect occurs on much longer reaction times for the benzylamine I.

The complex anions *MoF₅⁻*, *WF₅⁻*, and *ReOF₆⁻* **

Steffi Giese and Konrad Seppelt*

It was recently shown that main group molecules or molecular anions like IF₅, TeF₅⁻, ROTTF₆⁻ (RO)₂TeF₅⁻, and IOF₆⁻ always form as pentagonal bipyramids. This is remarkable considering that the interligand repulsions that result from this special geometry are greater, albeit only slightly, than those arising from the competing capped octahedral and capped trigonal-prismatic geometries. It thus appears that as long as lattice forces or special electronic effects do not influence the structure in some other way, molecules of this type having the coordination numbers (CN) five, seven, and eight will always form the highest symmetry coordination polyhedra of the possible structural alternatives (trigonal bipyramidal vs. square pyramidal; pentagonal bipyramidal vs. capped octahedral; square antiprism vs. trigonal dodecahedron). The highest symmetry may be defined as that which requires the smallest number of parameters for its complete description. In the case of CN = 7 this principle of the highest possible symmetry clearly dominates, and the greater ligand–ligand repulsions of this coordination polyhedron are alleviated through small systematic deviations from the ideal *D₇h* structure ("ring puckering"). As yet, there has been no attempt to transpose this principle of highest possible symmetry into a unified bonding model.

Is this structure principle also valid for subgroup compounds? Ideally, an accurate structural investigation of a homoleptic neutral compound should be used to approach this problem; the only molecule that comes into consideration here is ReF₅. However, just as with IF₅, the structure of ReF₅ is very difficult to determine experimentally. Electron diffraction investigations suggest a distorted *D₃h* structure. Since the thermal fluctuations of the ligands in molecules with CN = 7 are expected to cause large-amplitude vibrations, no definitive structural information is possible with electron diffraction alone. Because of the existence of several solid phases, including one that is plastic, the crystal structure of ReF₅ has not yet been determined with certainty.

To clarify this problem we have investigated the structures of the anions MoF₅⁻ and WF₅⁻. The influence of the lattice energy on the structures of these anions should be precluded by variation of the counterions. MoF₅ and WF₅ are known to form complexes with fluorides which, according to their elemental analyses, have the compositions MF₅ and MFi⁻ (M = Mo, W). Reliable structure information on these, however, does not exist.

The complexes Cs⁺MoF₅⁻ and Cs⁺WF₅⁻ are formed from the reaction of CsF with an excess of MoF₅ and WF₅, respectively. The colorless salts recrystallize well from acetone. Crystal structure analyses showed that both salts have isotypic structures which in the anions take the form of capped octahedra (Fig. 1). Each anion lies on a threefold axis of the cubic crystal system which coincides with the symmetry axis of the anion. Thus, the structure of the anion could be dictated by the crystal system itself.

To clarify this we synthesized NO₂⁻MoF₅⁻ from the reaction between NO₂F and MoF₅, obtained single crystals, and examined the salt by X-ray crystallography. The compound crystallizes as NO₂⁻MoF₅⁻CH₂CN. The MoF₅⁻ ion has

** Structural Principles in Seven-Coordinate Subgroup Compounds: The Complex Anions MoF₅⁻, WF₅⁻, and ReOF₆⁻ **


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**[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

![Fig. 1. The structure of the MoF₅⁻ ion in Cs⁺MoF₅⁻. Left: view along the threefold axis; right: view perpendicular to the Cg axis (ORTEP representation with thermal ellipsoids at the 50% probability level)]. The structure of the anions in Cs⁺WF₅⁻ and in the other hexafluoromolybdates (iv) is qualitatively the same.