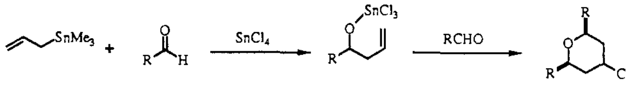
Table I. Control Experiments with **2a**, **2b**, and **2c**[a]

		temp, °C	
aldehyde	Lewis acid	−80	20
2a	$BF_3 \cdot OEt_2$	100% trimer[b]	free and complexed **2a**,[c] no trimer
2a	$SnCl_4$	100% complexed **2a**	100% complexed **2a**
2b	$BF_3 \cdot OEt_2$	10% trimer,[d] free **2b**	weakly complexed **2b**
2b	$SnCl_4$	100% complexed **2b**	100% complexed **2b**
2c	$BF_3 \cdot OEt_2$	complexed **2c**/**2c** (44:56)[e]	f
2c	$SnCl_4$	100% complexed **2c**	100% complexed **2c**

[a] All reactions were run at 0.5 M in $CDCl_3/CD_2Cl_2$ (1:1) with 1 equiv of Lewis acid. [b] Paraldehyde. [c] Trace contamination by crotonaldehyde. [d] Obtained by integration of the ^1H NMR signals for trimer ($\delta(CH_3)_3C$ 0.78 ppm) versus **2b** (υ $(CH_3)_3C$ 0.97 ppm). [e] Obtained by integration of the ^1H NMR signals for the complex (δ CHO 9.93 ppm) versus **2c** (δ CHO 9.55 ppm). [f] Signals broad due to rapid exchange.

Scheme II



3

The condensation reactions were performed by addition of **1** (neat) to a −80 °C solution of precomplexed **2a–c**. In all reactions equimolar amounts of **1** and **2** were used. The results are shown in Figure 1; spectra A–C are the $BF_3 \cdot OEt_2$-induced reactions. For **2a** the −80 °C spectrum was a clean superposition of **1** and $(\mathbf{2a})_3$. At −60 °C (spectrum A) the redistribution of **1** is clearly occurring in the presence of $(\mathbf{2a})_3$ without reaction. The product, 4-penten-2-ol,[16] was first evident at −20 °C (as $(\mathbf{2a})_3$ began to dissociate) and was the dominant species at 0 °C (spectrum B). It is noteworthy that the product was formed as diastereomeric boron ethers; Me_3Sn ethers were never detected. In contrast, reaction of **1** with **2b** showed immediate formation of products at −80 °C, together with $(\mathbf{2b})_3$ which persisted to 20 °C. Finally reaction of **1** with **2c** (spectrum C) was complete upon mixing at −80 °C! Thus, the extent of reaction depends upon the degree of trimerization at −80 °C (**2a** > **2b** > **2c**), which in turn affects the extent of $BF_3 \cdot OEt_2$-catalyzed redistribution of **1**.

The results of reaction of **1** with $SnCl_4$-complexed aldehydes fundamentally differed from those with $BF_3 \cdot OEt_2$. These reactions are highly sensitive to temperature and stoichiometry.[17] The first series of experiments employed a 1:1 stoichiometry of **2** and $SnCl_4$ which by ^1H, ^{13}C, and ^{119}Sn NMR analysis constituted an equimolar mixture of $(\mathbf{2})_2$ $SnCl_4$ and free $SnCl_4$.[18] For **2a**, **2b**, and **2c** the *metathesis of **1** to allylSnCl$_3$ was instantaneous and quantitative at −80 °C with little evidence of addition.* The reaction with **2b** (spectrum D) is illustrative. The presence of Me_3SnCl and the unreacted aldehyde was clearly seen in all cases. Only in the case of **2a** could signals due to the addition product be detected at −80 °C. As the samples were warmed signals for the addition product appeared and were replaced (−40 °C → 20 °C) by signals for the chloropyrans **3**, Scheme II.[12b] A second series of experiments using a 2:1 stoichiometry of **2** and $SnCl_4$ (no free $SnCl_4$) gave different results. With **2a**, complete addition was observed as low as −95 °C. Thus, while traces of metathesis products were also observed, their intermediacy in the addition cannot be established. For **2b** and **2c** *only metathesis of **1** without addition was observed as evidenced by the immediate formation of Me$_3$SnCl.* Now, however, the metathesis products were different ((allyl)$_4$Sn, (allyl)$_3$SnCl, (allyl)$_2$SnCl$_2$)).[19] Spectrum E (**2b**) clearly shows the conversion of **1** to Me_3SnCl within 3–4 min (traces i and ii (4×)). After 10 min (trace iii) the allylchlorostannanes and **2b** are still present. A final series of experiments with $(\mathbf{2b})_2 \cdot SnCl_4$ and $(\mathbf{2c})_2 \cdot SnCl_4$ and allyltributylstannane (allylBu$_3$Sn) was performed at −90 °C to confirm our observations. In both cases the allylBu$_3$Sn was instantaneously consumed, and only allyl$_2$SnCl$_2$ and Bu_3SnCl were detected (within 5 min) as products (see spectrum F for $(\mathbf{2b})_2 \cdot SnCl_4$).

In summary we have demonstrated that (1) with $BF_3 \cdot OEt_2$, a ligand redistribution of **1** may occur depending upon the amount of trimeric aldehyde present under the reactions conditions and (2) with $SnCl_4$, **1** is not involved in aldehyde additions when free $SnCl_4$ is present, and metathesis with fully complexed $SnCl_4$[20] is demonstrably faster than addition in most if not all cases. Studies on the behavior of allylic silanes and (*E*)- and (*Z*)-2-butenylmetals with $SnCl_4$ and other Lewis acids will be the subject of future reports.

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(16) Authentic samples of all homoallylic alcohol products as well as their Me_3Si, Me_3Sn, and Cl_3Sn ethers were prepared.

(17) (a) Similar observations have been made by Professor Gary E. Keck (University of Utah). (b) To assure full complexation of $SnCl_4$ a 5–10% excess of **2** was used. To assure temperature control the precooled solution (2 mL) of the complex $(\mathbf{2})_2 \cdot SnCl_4$, in a 10-mm NMR tube, was carefully layered with neat **1**, then reintroduced to the probe, the equilibrated at the desired temperature without spinning. Reaction was initiated by vortexing the solution at 70 rps. The results of these experiments did not differ from externally shaking the solution. We thank Professor Keck for suggesting this technique and for providing the experimental details.

(18) This is seen in the ^{119}Sn NMR spectrum which shows signals for both $SnCl_4$ (−156 ppm) and $(\mathbf{2a})_2 \cdot SnCl_4$ (−571 ppm), $(\mathbf{2b})_2 \cdot SnCl_4$ (−572 ppm), or $(\mathbf{2c})_2$ $SnCl_4$ (−585 ppm).

(19) The same mixture could be generated by mixing (allyl)$_4$Sn and $SnCl_4$ at room temperature in a 3:1 ratio. Only upon standing at room temperature for 3 days did (allyl)$_3$SnCl form completely. Mixing these reagents in a 1:1 ratio produced only (allyl)$_2$SnCl$_2$.

(20) For a thorough study of the mechanism of ligand exchange in L_2SnCl_4 complexes, see: Knight, C. T. G.; Merbach, A. E. *Inorg. Chem.* **1985**, *24*, 576.

$[Th^{III}\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_3]$, an Actinide Compound with a $6d^1$ Ground State

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The free ion of trivalent thorium [Th(III)] has a $5f^1$ ground state electronic configuration whose center of gravity is 9897 cm^{-1} below the center of gravity of the excited state $6d^1$ configuration. The $7s^1$ level is at 23 120 cm^{-1} while the $7p_{1/2,3/2}$ levels are found at energies greater than 60 000 cm^{-1} above the ground state.[1] Although the free ion spectrum of the isoelectronic ion Pa(IV) is not known, the difference between the centers of gravity of the ground state $5f^1$ configuration and the excited state $6d^1$ configuration for this ion is estimated to be ~50 000 cm^{-1} from the interpolation of the known free ion data for the isoelectronic series Ra(I), Ac(II), Th(III), and U(V).[2,3] Optical spectra of Pa(IV)/$ThBr_4$ and $[PaCl_6^{2-}]$ showed that the lowest $5f^1 \rightarrow 6d^1$ crystal field transition appeared at ~20 000 cm^{-1}.[4,5] Two factors con-

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Table I. Spin Hamiltonian Parameters for [Th{η^5-$C_5H_3(SiMe_3)_2$}$_3$] as a Function of Temperature

	$g_\parallel$	$g_\perp$	g_{av}	temp (K)
methylcyclohexane soln			1.910 ± 0.001	300
methylcyclohexane soln	1.9725 ± 0.001	1.879 ± 0.001	1.910[a]	10–110
powdered solid	1.972 ± 0.001	1.878 ± 0.001	1.909[a]	10–300

[a] Calculated from $^1/_3(g_\parallel + 2g_\perp)$.

tribute to the decrease of the energy of this transition as compared to the free ion. The first is the decrease of the $6d^1$ center of gravity relative to the center of gravity of the $5f^1$ configuration which is caused by the electrostatic interaction of the metal ion orbitals with the negatively charged ligands. The second is the much greater crystal field splitting of the 6d orbitals relative to the 5f orbitals. The first interaction is formulated as the spherically symmetric term in crystal field theory and is usually ignored when relative crystal field energies within a configuration are determined.[6] Assuming the total crystal field splitting for the $6d^1$ orbitals for [$PaCl_6^{2-}$] is ~20 000 cm^{-1}, we estimate the splitting between the centers of gravity of the $5f^1$ and $6d^1$ configuration for $PaCl_6^{2-}$ to be ~25 000 cm^{-1}. Thus in this compound, the Pa(IV) $5f^1 \rightarrow 6d^1$ (centers of gravity) splitting is lowered by 25 000 cm^{-1} from the free ion to the crystal. These arguments suggest that for Th(III) in a crystal field, the ground state could arise from the $6d^1$ configuration.

The Th(III) compound, [ThCp″$_3$] [Cp″ = η^5-C_5H_3-$(SiMe_2)_3$-1,3], has recently been synthesized and structurally characterized.[7] EPR (electron paramagnetic resonance) spectra of powdered samples and solutions in dry, degassed methylcyclohexane were obtained at 10–300 K.[8] The spectra obtained could be fit with the parameters of the spin- Hamiltonian[9]

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y)$$

Representative values of the g tensor components at various temperatures are given in Table I.

The coordination environment about the Th(III) ion in the Cp″ compound can be approximated as trigonal planar (considering only Th(Cen)$_3$, where Cen denotes the centroid of the Cp″ ligand),[7] and in the following discussion we assume D_{3h} symmetry about the Th(III) ion. In this symmetry the d orbitals split into an orbital singlet $^2A'$ and two orbital doublets $^2E'$ and $^2E''$. From simple crystal field arguments the $^2A_1'$ state should be lowest in energy. This assignment is consistent with the observed EPR spectrum. Spectra are observed at room temperature, and there is essentially no difference between the powder spectrum and that of the frozen glass. If an $^2E'$ or $^2E''$ state were lowest, the rapid spin-lattice relaxation time would result in a broadened or unobservable room temperature spectrum. If the $5f^1$ configuration were lowest, no room temperature spectrum would be observed, and the g values would be markedly different from $g = 2$. If the $7s^1$ configuration were lowest, only an isotropic EPR spectrum would be observed with $g = 2.00$.

If we assume the above simplified crystal field model and allow spin-orbit coupling to mix the higher lying $^2E''$ state with the ground A_1' state, we can calculate values for the g tensor. The Th(III) free ion value for ζ_{6d} is equal to 2117 cm^{-1}. Assuming the orbital reduction factor $(k\bar{l}_i)$ for both the spin-orbit coupling constant and the orbital angular momentum operator is ~0.4 and the $^2E''$ state is approximately 20 000 cm^{-1} above the ground $^2A_1'$ state, we calculate $g_\parallel = 1.994$ and $g_\perp = 1.896$ which are in satisfactory agreement with the experimental result. The parameters in the above calculation are certainly not unique but show that plausible values of the various parameters give a reasonable fit.

We conclude the EPR spectrum is only consistent with a $6d^1$ ground state for this Th(III) compound.[10]

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Registry No. ThCp″$_3$, 107040-62-0.

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(9) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Oxford University Press: Oxford, 1970.

(10) Gaseous ThCp″$_3$ also has an unusually low value of 4.87 eV for the first ionization potential (Brennan, J.; Edelman, M. A.; Green, J. C.; Lappert, M. F., unpublished work).