

Although these scrunch states exist on the continuum model studied by Rey and Skolnick, they have not been previously reported as the ground state.¹ The apparent failure of the BD simulations to locate the scrunch state may be due to the relative inefficiency of dynamics methods for searching conformational space.⁷ Alternatively, it may be that the entropy of the scrunch states is so low that they are very improbable at the finite temperatures used in the BD simulations.¹ These configurations are also absent from the more efficient Monte Carlo lattice simulations reported in that same study. This may be due to the truncation of configuration space by the lattice or from differences in the discrete and continuous potentials. Our results suggest that the physical characteristics of the lattice and off-lattice models may not be the same, contradicting the results of that study. However, they are not conclusive, and further investigation is required to determine whether a significant difference exists.

As can be seen in Figure 1, the scrunch configuration has the N-terminal bead twisted from its torsionally favored gauche (-) state into the trans state (nomenclature from ref 1), allowing it to form an additional hydrophobic contact with the interior of the protein at the expense of increased torsional energy. Although the structural difference appears minor, the energy difference is significant (2 K, units from ref 1). The degree to which the scrunch conformation is favored relative to the α -hairpin depends on the relative strengths of the trans and gauche (-) minima, which favor helix formation, and the depth of the phobic-phobic well, which favors formation of a hexagonal close-packed structure. For example, the scrunch state depicted in Figure 1 is 2 K below the accompanying α -helical state. This results in an energy increase of roughly 6 K in torsion, 3 K in the repulsive philic-philic/philic-phobic term, and 2 K in bond angle energy. The bond length energy and helical cooperative energies are virtually unchanged, while the phobic-phobic energy decreases by 13 K.

One of the great advantages to using simulated annealing for this type of optimization problem is that it is based on statistical mechanics and therefore can be used to extract a great deal of chemically relevant information about a system in addition to its ground-state configuration. We have chosen a conservative cooling schedule, so that during the later portion of each sweep, the system is in thermal equilibrium, allowing one to measure equilibrium thermodynamic features of the system. By combining the data for all of the temperature sweeps using the Ferrenberg-Swendsen multiple histogram method,⁵ $\Omega(E)$ and $C_v(T)$ have been determined and are shown in Figure 2.

The peak in C_v vs T near $T = 6$ suggests that the system undergoes a phase transition there. This was further corroborated by examining the conformations during annealing (i.e., the populations of the dihedrals) and the corresponding density of states. Above $T \approx 6$ K little secondary structure is observed. However, when T is below 6 K, large helical fragments and some phobic contacts form and persist over many structural perturbations. Examination of the dihedral angle variance as a function of temperature shows that it undergoes a decrease of 1-2 orders of magnitude over about a 1 K range in the region of the peak in C_v . This phase transition is consistent with the results of Honeycutt and Thirumalai.^{2,3} Further analysis of the statistics and reaction coordinates is required to confirm the nature of this phase transition.

Further application of our methodology to study protein models should greatly aid in understanding the behavior of these simplified representations and their physical significance. It is also important to note that our approach should be applicable to a wide variety of problems and systems in computational chemistry, biology, and physics. The determination of the density of states allows the complete characterization of all thermodynamic properties of molecular systems, providing a new route to calculate important quantities such as free energy and entropy.

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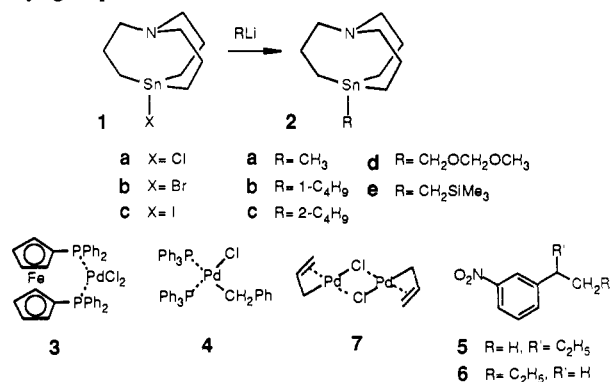
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Internal Coordination at Tin Promotes Selective Alkyl Transfer in the Stille Coupling Reaction

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The $\text{CH}_3\text{-Sn}$ bond in 1-aza-5-stannabicyclo[3.3.3]undecane **2a** is ca. 0.1 Å longer than the $\text{CH}_2\text{-Sn}$ bonds.¹ The contrasting $^{13}\text{C-}^{119}\text{Sn}$ coupling constants (methyl $^1J_{\text{C-Sn}} = 171$ Hz; methylene $^1J_{\text{C-Sn}} = 405$ Hz)¹ also suggest unusual $\text{CH}_3\text{-Sn}$ hybridization and the possibility of increased reactivity.² However, **2** and the precursor halides **1** have been difficult to prepare, and very little is known about this intriguing ring system. We now report that **1a** can be obtained by the hydrosilylation of triallylamine, followed by in situ metal exchange with SnCl_4 (one-pot method; 50% isolated).³ The air-stable alkyl derivatives **2^{3b}** (from **1** + RLi) are unusually reactive in Stille coupling with aryl and alkenyl halides. Metal-alkyl exchange occurs at the exocyclic Sn-C bond and solves the problem of selective transfer of a single primary alkyl group from tin.⁴



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(3) (a) A 250-mL flask was purged (N_2) and charged with Cp_2ZrHCl (6.45 g), dry THF (160 mL), and *N,N,N*-triallylamine (1.10 g). After 3 h of stirring at 23 °C, the solution was cooled to -78 °C, treated with freshly distilled SnCl_4 (2.19 g), and allowed to warm to 23 °C over 4 h. After 14 h, the mixture was added to water (400 mL), extracted ($\text{C}_2\text{H}_5\text{O}_2\text{CCH}_3$; 200 mL; 100 mL), dried (Na_2SO_4), filtered, and evaporated (aspirator) to give a pale yellow solid (1.44 g). Recrystallization (CH_3OH) gave **1a** (1.18 g, 50%), mp 222-224 °C (lit.¹ mp 240-242 °C). The NMR spectrum matches that reported.¹ (b) New compounds gave satisfactory exact mass and NMR data: $\delta^{13}\text{C}$ ($^1J_{\text{C-Sn}}$) [$\delta^1\text{H}$]; endocyclic CH_2Sn , **2b**, 6.9 ppm (376 Hz) [0.60 ppm], **2c**, 5.7 ppm (255 Hz) [0.61 ppm], **2d**, 6.29 ppm (398 Hz) [0.74 ppm]; exocyclic RCH_2Sn , **2b**, 16.3 (214 Hz) [0.38 ppm], **2c**, 27.0 ppm (355 Hz) [0.87 ppm], **2d**, 64.2 ppm (213 Hz) [3.36 ppm].

Table I. Coupling of Aryl Bromides (YC₆H₄Br) with **2** in Toluene

entry	reactant	Y	R	catalyst	conditions (°C, h)	yield (%)
1	2a	<i>p</i> -CH ₃ O	CH ₃	(Ph ₃ P) ₄ Pd	75, 7	67
2	2a	<i>p</i> -CH ₃ O	CH ₃	3	75, 2	94
3	2a	<i>p</i> -(CH ₃) ₂ N	CH ₃	3	105, 30	56
4	2a	<i>m</i> -NO ₂	CH ₃	3	105, 2	93
5	2b	<i>p</i> -CH ₃ O	<i>n</i> -C ₄ H ₉	3	105, 48	64
6	2b	<i>m</i> -NO ₂	<i>n</i> -C ₄ H ₉	3	105, 12	86
7	2d	<i>p</i> -CH ₃ O	CH ₂ OMOM	(Ph ₃ P) ₄ Pd	105, 3	61 ^a
8	2d	<i>p</i> -(CH ₃) ₂ N	CH ₂ OMOM	(Ph ₃ P) ₄ Pd	105, 3	63 ^b
9	2d	<i>m</i> -NO ₂	CH ₂ OMOM	(Ph ₃ P) ₄ Pd	105, 3	80 ^c
10	2e	<i>m</i> -NO ₂	CH ₂ SiMe ₃	(Ph ₃ P) ₄ Pd	105, 20	85

^a Byproduct: 4,4'-dimethoxybiphenyl, 25%. ^b Byproduct: 4,4'-bis(dimethylamino)biphenyl, 21%. ^c Byproduct: 3,3'-dinitrobiphenyl, 5%.

Table II. Coupling of 1-Iodo-1-heptene with **2**

entry	reactant	geometry	R	catalyst	conditions	yield (%)
1	2a	<i>E</i>	CH ₃	7	CH ₃ CN/THF/rt, ^a 5 min	85
2	2a	<i>Z</i>	CH ₃	7	CH ₃ CN/THF/rt, 5 min	85
3	2d	<i>E</i>	CH ₂ OMOM	PdCl ₂ (CH ₃ CN) ₂	DMF/rt/3 h	81
4	2d	<i>Z</i>	CH ₂ OMOM	PdCl ₂ (CH ₃ CN) ₂	DMF/rt/3 h	81

^a Room temperature.

Aryl halide coupling reactions with **2a** were performed using the dppf-PdCl₂ catalyst **3**⁵ (75–110 °C, C₆H₅CH₃), but (Ph₃P)₄Pd was also effective (entry 1 vs 2, Table I). Coupling was most difficult with the electron-rich 4-bromo-*N,N*-dimethylaniline (entry 3), a substrate that is reported not to couple with the conventional reagent Bu₃SnCH=CH₂.^{4b} Qualitative comparisons show that derivatives of **2** are more reactive than are analogous reagents R₄Sn. Thus, **2a** afforded a 67% yield of 4-methoxytoluene from *p*-bromoanisole (7 h, 75 °C; (Ph₃P)₄Pd in C₆H₅CH₃) while less than 5% conversion occurred using Me₄Sn in place of **2a**. It is likely that **2a** accelerates the conversion from ArPdL₂X to ArPdL₂CH₃, the presumed intermediate for Ar-CH₃ coupling.

Selective alkyl transfer was likewise achieved with **2b**, **2d** (Table I, entries 5–9), and also **2e** (entry 10). The analogous Me₃SnCH₂SiMe₃ reagent is known to react by dominant methyl transfer with a related substrate.^{4c} Attempts to couple the *sec*-butyl derivative **2c** with 3-bromo-1-nitrobenzene produced the rearranged *n*-butyl product **6** (12%) in addition to **5** (36%; 40 h at 110 °C, C₆H₅CH₃, **3** as catalyst). The rearrangement involves β -hydride elimination and has also been reported using organozinc or organomagnesium reagents in palladium-catalyzed cross-coupling reactions.^{5–7} Anomalous behavior was also observed when **2c** was reacted with benzoyl chloride. There was no reaction at 20 °C, but heating to 75 °C with or without palladium catalysts gave benzaldehyde as the dominant product via β -hydride elimination. In contrast, **2a** or the unbranched **2b** reacted at 20 °C (**4**⁸ as catalyst) to give acetophenone or butyrophenone (75–80%).

The unbranched reagents **2a** or **2d** can also be used for stereospecific coupling with (*E*)- or (*Z*)-1-iodo-1-heptene (Table II;

7 or PdCl₂(CH₃CN)₂ catalysts, 20 °C). This reaction provides either the (*E*)- or the (*Z*)-alkene product with >98% retention of geometry (gas liquid phase chromatographic analysis). However, attempts to achieve alkenyl iodide coupling with the *n*-butyl reagent **2b** failed.

Other methods for the utilization of primary alkyl groups in palladium-catalyzed cross-coupling reactions employ Al, B, Zn, Mg, Zr, or Si reagents.^{5,6,9–11} Aryl or alkenyl transfer to palladium is inherently faster than alkyl transfer⁴ and can often be achieved using the above reagents, as well as organotin⁴ and organomercury⁹ reagents. Selective CH₂OR' transfer reactions are possible in the specific case of Bu₃SnCH₂OR' derivatives.¹² However, competing butyl transfer can take place unless the reagent is used in excess (4–5 equiv).^{12b} Furthermore, the desired products can be difficult to separate from the trialkyltin halide byproduct. In contrast, reactions using **2** afford the highly crystalline halides **1b** or **1c**, byproducts that are easily recovered and recycled because they crystallize from solution during coupling experiments.

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The increased reactivity of **2** in the metal-exchange step appears to be associated with internal tin-nitrogen coordination in the transition state.^{1,2} At least two pathways are conceivable, both of which would benefit from the unusual bonding that is available in **2**. A simple four-center exchange process between Sn-C and the Pd-X bond (X = Br or I) of L₂ArPdX would be facilitated because the exocyclic bond of **2** is unusually long¹ and, therefore, more reactive. Alternatively, metal exchange might involve electron transfer from tin bonds to L₂ArPdX. In this case, an electron-deficient tin center could be stabilized by nitrogen coordination, resulting in partially positive nitrogen and a tricyclic organotin transition structure. Tzschach et al. have presented evidence for bonding interactions of this type in **1**, and they have also suggested at least some Sn---N bonding in **2a** based on the X-ray structure.¹ Since the ring C-Sn bonds of **2** are constrained to occupy pseudoequatorial sites in trigonal bipyramidal derivatives, only the apical alkyl group is activated by internal coordination, and selective transfer is thereby assured. The mechanistic details cannot be specified with confidence, but there are other indications that **2a** is unusually reactive toward electrophiles.¹³ We are exploring related systems where geometric constraints may provide selective activation of carbon-heteroelement bonds.

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(13) **2a** is more reactive than is Me₄Sn toward iodolysis. Thus, a 1:1:1 mixture of **2a**:Me₄Sn:I₂ in CDCl₃ afforded **1c** (80%) with <5% of Me₃SnI or ring cleavage.

Structure Dependence of Ammonia Adsorption on Alkali Halide Clusters

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Molecular adsorption on solid surfaces is a process of great technological importance that has also been used as a means of studying surface structure.¹ From systematic exploration of initial adsorption rates on crystalline surfaces² combined with intensive theoretical investigation, important rules have been established about the role of specific structural and electronic features of the surface in controlling adsorption. A similar approach can also be used to characterize the nanocrystalline surfaces of larger clusters. This is in contrast to approaches that use either the number of adsorbed molecules³ or the initial reactivity⁴ to help determine the (unknown) structures of transition metal or silicon clusters. In this communication we describe a clear correlation between the adsorption reactivity of alkali halide clusters and the structures previously established by other experiments and theory,⁵⁻¹⁰ leading to the identification of a certain active site.

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Alkali halide clusters (AHCs) are ionic systems M_n⁺X_m⁻, the most stable of which have ions arranged in a rock salt structure of cuboidal morphology.⁵ They serve as good theoretical and experimental models for microscopic aspects of ionic crystals, their surfaces,⁶ and even defect states.⁷ Here we use pulsed flow reactor methods and time-of-flight mass spectrometry to investigate, for the first time,¹¹ the adsorption reactions of a number of alkali halide systems in ±-charge states. Neutral and charged clusters are formed and equilibrated in helium in a laser-ablation source using previously described methods.¹² A dilute NH₃/He mixture is introduced downstream from the cluster formation region. The flow of reactants and products expands into vacuum at the end of the reactor channel, and charged products are measured mass spectrometrically without further ionization.

The initial reaction of sodium fluoride clusters toward ammonia at ambient temperature is the elementary process:

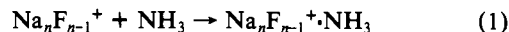


Figure 1 plots the relative reactivity¹³ of process 1 at ambient temperature, as extracted from a number of experiments at different NH₃/He concentrations (0.1-10%). The reactivity is strongly dependent on cluster size, with certain sizes (*n* = 14, 23, 32, 38, 53) showing no definite evidence of reactivity at even the highest concentration, whereas other sizes, *n* = 13 and 22, can be reacted completely by process 1 at moderate concentration. Smaller clusters in particular tend to show secondary adsorption at higher concentrations. The pattern shown in Figure 1 for ammonia adsorption is also found for other M_nX_{n-1}⁺ clusters, MX = KF and NaCl, with precisely the same values of *n* for reactivity maxima and minima. However, negatively charged clusters, Na_{n-1}F_n⁻, are found to be much less reactive.

The reactivity pattern can be associated very well with the structures established previously for AHCs.⁵⁻¹⁰ Relaxed structures¹⁰ calculated for the most important of these are shown in Figure 1. The clusters that are nonreactive toward ammonia adsorption at ambient temperature (*n* = 14, 23, 32, 38, and 53) are the cuboidal nanocrystals with lattice dimensions 3 × 3 × 3, 3 × 3 × 5, 3 × 3 × 7, 3 × 5 × 5, and 3 × 5 × 7. The least reactive smaller cluster (*n* = 5) is a single sheet (3 × 3). The lowest energy structures for other less-reactive clusters, *n* = 10 and 17, also have entirely convex surfaces, unlike those of more reactive clusters which have various lattice defects. The most reactive clusters, *n* = 13, 22 and 31, 57, 52 (not shown), have several closely related, low-lying isomers based on removal of a contiguous MX unit from the cuboid structure. However, the lowest in energy is the basketlike structure shown, and the others are weakly stable with respect to collapse to this structure.^{8,10} We therefore associate high reactivity with this defect.

The adsorption activity of alkali halide crystal surfaces toward ammonia is not known, but it is known for the related MgO ionic crystal surface.¹⁴ We find no adsorption of NH₃ on cuboidal nanocrystals, so that our results might indicate that (100) faces, edges, and corners, might be nonadsorbing at ambient temperature. In contrast, the AHCs with a basket defect are extremely reactive, suggesting that such defects are well suited to adsorption. Seeking a structural explanation, we have examined models and favor one in which the NH₃ molecule fills the basket with the nitrogen end

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