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Syntheses, Structural Characterizations, and Heterocumulene Metathesis Studies of New Monomeric Bis(triorganosilylamido)tin(II) Derivatives

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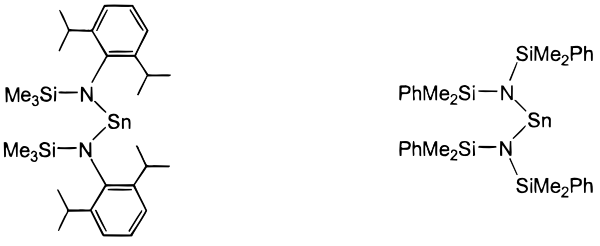
The syntheses and solid-state structures of two new monomeric bis(triorganosilyl)amido stannylenes, bis[*N*-trimethylsilyl-*N*-2,6-diisopropylphenylamido]tin(II) (**1**) and bis[*N*,*N*-bis(dimethylphenylsilyl)amido]tin(II) (**2**), are reported. Heterocumulene metathesis studies reveal that while **1** is inert toward carbon dioxide and isocyanates, **2** undergoes controlled metathesis with these reagents, including a range of *para*-substituted arylisocyanates, $X{-}C_6H_4NCO$ ($X = OCH_3$, CH_3, F, Cl, and CF_3), that allow for a Hammett investigation of the electronic factors that influence this process. This latter study shows that the rate of tin(II)-mediated heterocumulene metathesis is enhanced by an increased nucleophilicity of the heterocumulene.

Introduction

Recently, we have been developing heterocumulene metathesis, a process involving metathetical exchange between a metal triorganosilylamide, $M[NR(SiR'_3)]_2$ ($M = Ge$, Sn, Pb, Zn, and Cd, R = alkyl, aryl, or SiR'_3) and a heterocumulene, $X{=}C{=}E$ ($X = O$ or NR'', $E = O$, S, and Se), as a tool for the high-yield synthesis of metal triorganosilylchalcogenolates, $M(ESiR'_3)_2$, and of symmetric and unsymmetric carbodiimides, $RN{=}C{=}NR''$, under mild conditions.[1] During the course of these studies, it was necessary to extend the current database of structurally characterized bis(triorganosilylamido)tin(II) derivatives, $Sn[NR(SiR'_3)]_2$ (R = alkyl, aryl, or SiR'_3),[2] to elucidate some of the structure/property relationships that govern the tin(II)-mediated heterocumulene metathesis process. Herein, we report the syntheses and solid-state structures of two new monomeric stannylenes, bis[*N*-trimethylsilyl-*N*-2,6-diisopropylphenylamido]tin(II) (**1**) and bis[*N*,*N*-bis(dimethylphenylsilyl)amido]tin(II) (**2**) (Chart 1). Heterocumulene metathesis studies reveal that while **1** is inert toward carbon dioxide and isocyanates, **2** undergoes controlled metathesis with these reagents, including a range of *para*-substituted arylisocyanates, $X{-}C_6H_4NCO$ ($X = OCH_3$, CH_3, F, Cl, and CF_3), that allow for a Hammett investigation of the electronic factors that influence this process. This latter study shows that the rate of tin(II)-mediated heterocumulene metathesis is enhanced by an increased nucleophilicity of the heterocumulene.

Chart 1



1 **2**

Results and Discussion

Compound **1** was obtained as an orange crystalline solid in a 93% yield by reaction of lithium *N*-trimethylsilyl-*N*-2,6-diisopropylamide with tin(II) dichloride in diethyl ether.[3] Analytically pure material and single crystals were produced through recrystallization from toluene at −35 °C. ^1H NMR (400 MHz) spectra of **1** taken at 298 and 343 K indicated that substantial steric barriers to bond rotations exist in this compound due to two sharp resonances being observed in a 1:1 ratio

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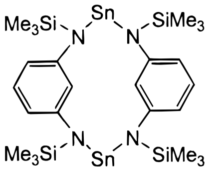
(1) (a) Sita, L. R.; Babcock, J. R.; Xi, R. *J. Am. Chem. Soc.* **1996**, *118*, 10912−10913. (b) Sita, L. R.; Xi, R.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 756−760. (c) Babcock, J. R.; Zehner, R. W.; Sita, L. R. *Chem. Mater.* **1998**, *10*, 147−149. (d) Babcock, J. R.; Sita, L. R. *J. Am. Chem. Soc.* **1998**, *120*, 5585−5586. (e) Xi, R.; Sita, L. R. *Inorg. Chim. Acta* **1998**, *270*, 118−122. (f) Weinert, C. S.; Guzei, I. A.; Rheingold, A. L.; Sita, L. R. *Organometallics* **1998**, *17*, 498−500. (f) Babcock, J. R.; Incarvito, C.; Rheingold, A. L.; Sita, L. R. *Organometallics*, in press.

(2) (a) Veith, M. *Z. Naturforsch.* **1978**, *33B*, 7−12. (b) Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639−641 (c) Braunschweig, H.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922−1928. (d) Westerhausen, M.; Greul, J.; Hausen, H.-D.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1295−1305. (e) Braunschweig, H.; Drost, C.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 261−263.

(3) For prior use of the *N*-trimethylsilyl-*N*-2,6-diisopropylphenylamido ligand, see: (a) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298−5301. (b) Voigt, A.; Murugavel, R.; Roesky, H. W. *Organometallics* **1996**, *15*, 5097−5101. (c) Waezsada, S. D.; Liu, F.-Q.; Murphy, E. F.; Roesky, H. W.; Teichert, M.; Uson, I.; Schmidt, H.-G.; Albers, T.; Parisini, E.; Noltemeyer, M. *Organometallics* **1997**, *16*, 1260−1264.

10.1021/om990526w CCC: $18.00

Chart 2



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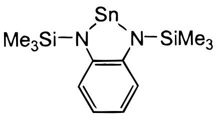

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Table 1. Crystal Structure and Refinement Data for Compounds 1 and 2

	1	2
formula	$C_{30}H_{52}N_2Si_2Sn$	$C_{32}H_{44}N_2Si_4Sn$
M_w	615.61	687.74
temp (K)	241(2)	244(2)
wavelength (Å)	0.71073	0.71073
space group	monoclinic, $P2(1)/n$	triclinic, $P\bar{1}$
a (Å)	14.960(1)	9.530(2)
b (Å)	9.795(2)	9.609(2)
c (Å)	24.208(2)	19.315(3)
α (deg)	90	100.505(13)
β (deg)	104.29(1)	93.77(2)
γ (deg)	90	92.85(2)
V (Å^3)	3437.7(5)	1731.8(5)
Z	4	2
D_{calcd} (mg/m^3)	1.190	1.319
abs coeff (mm^{-1})	0.832	0.899
F(000)	1296	712
crystal size, mm^3	0.30 × 0.30 × 0.30	0.50 × 0.30 × 0.20
θ range (deg)	2.25−22.50.	2.15−30.00
no. of reflns collected	5806	11799
no. of ind reflns	4486 ($R_{int} = 0.0341$)	10110 ($R_{int} = 0.0286$)
goodness of fit on F^2	1.219	1.056
final R indices [$I > 2\sigma(I)$]	R1 = 0.0361, wR2 = 0.0872	R1 = 0.0344, wR2 = 0.0789

Table 2. Selected Structural Parameters for Compounds 1 and 2

compound **1**		compound **2**	
Bond Lengths (Å)			
Sn−N(1)	2.095(3)	Sn−N(1)	2.133(2)
Sn−N(2)	2.093(3)	Sn−N(2)	2.124(2)
N(1)−C(6)	1.457(5)	N(1)−Si(1)	1.729(2)
N(2)−C(21)	1.449(5)	N(1)−Si(2)	1.724(2)
N(1)−Si(2)	1.737(3)	N(2)−Si(3)	1.729(2)
N(2)−Si(1)	1.737(3)	N(3)−Si(4)	1.726(2)
Bond Angles (deg)			
N(1)−Sn−N(2)	111.04(11)	N(1)−Sn−N(2)	101.51(7)
C(6)−N(1)−Sn	103.5(2)	Si(1)−N(1)−Sn	111.90(9)
C(6)−N(1)−Si(2)	116.5(2)	Si(2)−N(1)−Sn	122.51(9)
Si(2)−N(1)−Sn	139.0(2)	Si(1)−N(1)−Si(2)	124.70(10)
C(21)−N(2)−Sn	106.3(2)	Si(3)−N(2)−Sn	111.91(9)
C(21)−N(2)−Si(1)	119.1(2)	Si(4)−N(2)−Sn	124.84(9)
Si(1)−N(2)−Sn	134.2(2)	Si(3)−N(1)−Si(4)	121.58(10)

for magnetically nonequivalent methyls of the isopropyl fragments of the aryl groups at both temperatures. Evidence that **1** is monomeric in solution was obtained by a ^{119}Sn NMR (186 MHz, 298 K) spectrum that displayed a single resonance at 440 ppm. Interestingly, while this chemical shift is sandwiched between those of the known monomeric $Sn[N(SiMe_3)Ar]_2$ (Ar = aryl) related structures, the cyclic bis(stannylene) **3** (δ 505 ppm)[2e] and the more ring-constrained cyclic monostannylene **4** (δ 269 ppm) (Chart 2),[2c] it is found a few hundred ppm upfield from the more closely related derivative where Ar = 2,6-dimethylphenyl (δ 655 ppm).[4] Support for the monomeric nature of **1** in the solid state was provided by a crystallographic analysis.[5] Table 1 provides crystal structure and refinement data for this compound, while Table 2 lists selected bond lengths and bond angles. As can be seen in Figure 1, the tin atom in **1** resides at the bottom of a pocket formed by the two 2,6-diisopropylphenyl groups, which are both being projected in the same direction. Importantly, in the solid state, **1** adopts a chiral conformation that is dictated by a twist in the Si(1)−N(2)−Sn−N(1)−Si(2) backbone [cf. the torsional angles: Si(1)−N(2)−Sn−N(1), 31.8°, and Si(2)−N(1)−Sn−N(2), 32.3°]. Further, in this conformation, the two aryl groups are virturally identical due to the pseudo-C_2 axis that is present. Accordingly, it is likely that strong steric repulsions between the two trimethylsilyl groups, coupled with a barrier to rotation about the nitrogen−carbon bonds, also enforce this chiral conformation in solution, which gives rise to magnetically inequivalent isopropyl groups within the same aryl substituent. The two tin−nitrogen bond lengths, while somewhat elongated, are not particularly informative with respect to the nature of these steric interactions, as they both fall within the range observed for other sterically stabilized monomeric bis(triorganosilylamido)tin(II) derivatives.[2] That these strong nonbonded interactions are present in **1**, however, is most apparent in the unusually large N(1)−Sn−N(2) angle of 111.04(11)°, which is similar in magnitude to the largest value for this parameter yet found, which is 111.3(1)°.[2d] Further evidence for a strong steric repulsion between the two trimethylsilyl groups is provided by the large Si−N−Sn bond angles of 139.0(2)° and 134.2(2)°. Curiously, though, despite this steric congestion, the nitrogen atoms remain trigonal planar [cf., sum of the bond angles about each nitrogen atom, $\sum\theta_{N(1)} = 359.6°$ and $\sum\theta_{N(2)} = 359.0°$, respectively].

Compound **2** was prepared in a manner similar to **1** in a 75% yield starting with commercially available 1,3-diphenyl-1,1,3,3-tetramethyldisilazane. Once more, a ^{119}Sn NMR spectrum revealed that **2** was monomeric in solution by exhibiting a single resonance at 501 ppm. However, in contrast to **1**, a ^{1}H NMR spectrum did not reveal any diagnostic pattern of resonances that might reveal the nature of the conformation that **2** adopts in solution. Crystallographic analysis, on the other hand, showed that, as with **1**, the tin atom of **2** resides within a pocket formed by the cooperative arrangement of the phenyl groups and that the molecule assumes a chiral conformation in the solid state, as can be seen in Figure 2 (see Tables 1 and 2 for crystal structure and refinement data and selected structural parameters, respectively).[5] Given the expected strong steric interactions between the substituents, it is likely that this conformation is retained in solution as well. In contrast to the structure of **1**, however, where nonbonded interactions were revealed in abnormal bond angles, compound **2** appears to favor bond length distortions as a way to accommodate steric strain. More specifically, inspection of Table 2 shows that the tin−nitrogen bond lengths found for **2**, Sn−N(1), 2.133(2) Å, and Sn−N(2), 2.124(2) Å, are substantially longer than those found in other sterically stabilized bis(triorganosilylamido)tin(II) derivatives.[2] The bond angles in this compound, however, all fall within normal ranges. For instance, the N(1)−

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(4) Babcock, J. R. Ph.D. Dissertation, University of Chicago, 1998.
(5) Detailed information is provided in the Supporting Information.

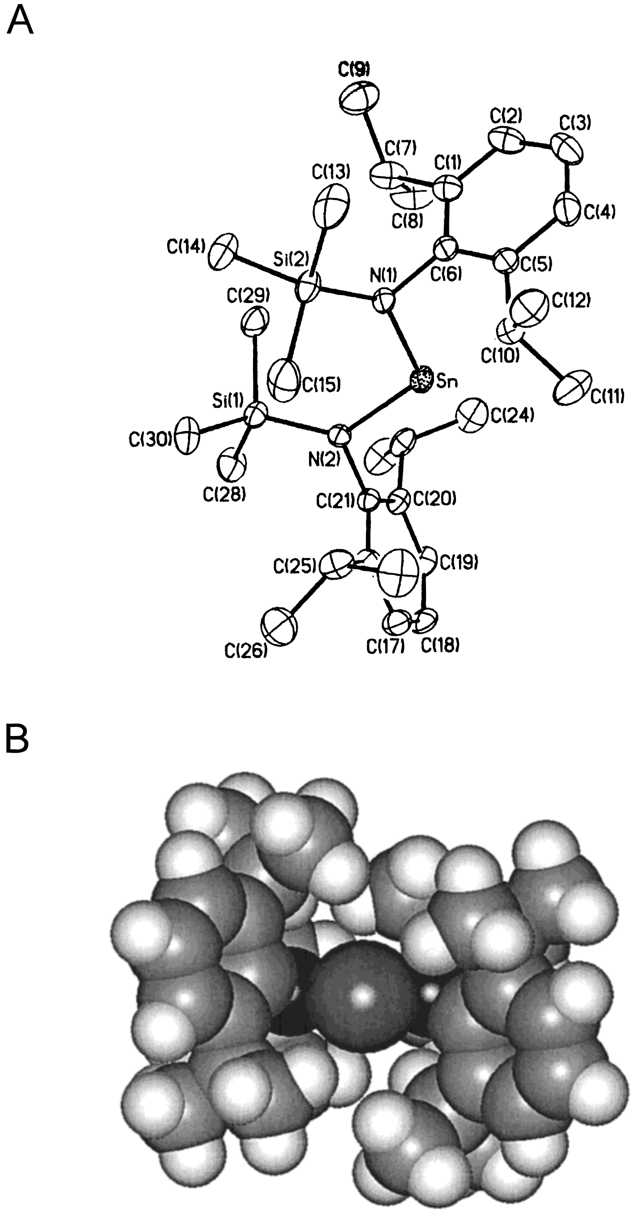


Figure 1. (a) ORTEP (30% thermal ellipsoids) representation of the molecular structure of **1**. Hydrogen atoms have been omitted for the sake of clarity. (b) Space-filling (van der Waals surface) representation of the molecular structure of **1**.

Sn−N(2) bond angle of **2** is only 101.51°, and the nitrogen atoms are both trigonal planar with no unusual bond angle contribution being made to the sum of the angles [cf., sum of the bond angles about each nitrogen atom, $\sum\theta_{N(1)} = 359.1°$ and $\sum\theta_{N(2)} = 358.3°$, respectively. The preference for **2** to undergo bond length elongation rather than bond angle distortion as the means by which to accommodate steric strain may be the result of weaker tin−nitrogen bonding in this compound relative to **1**. If so, it is possible that this difference also manifests itself in differences in chemical reactivity between the two compounds.

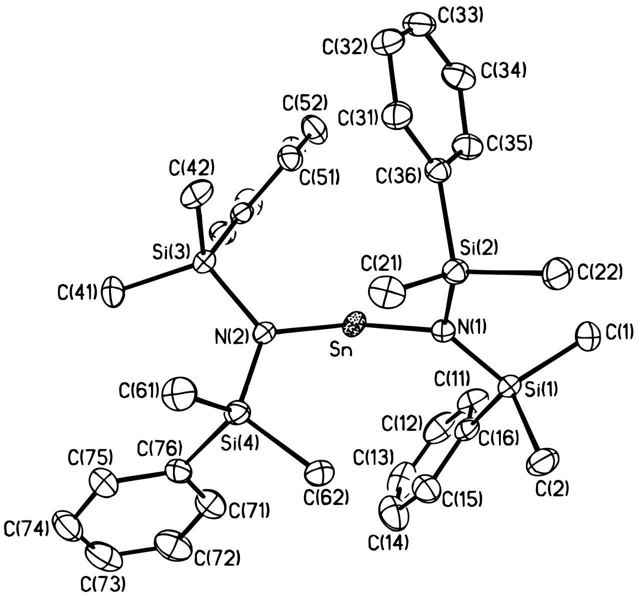
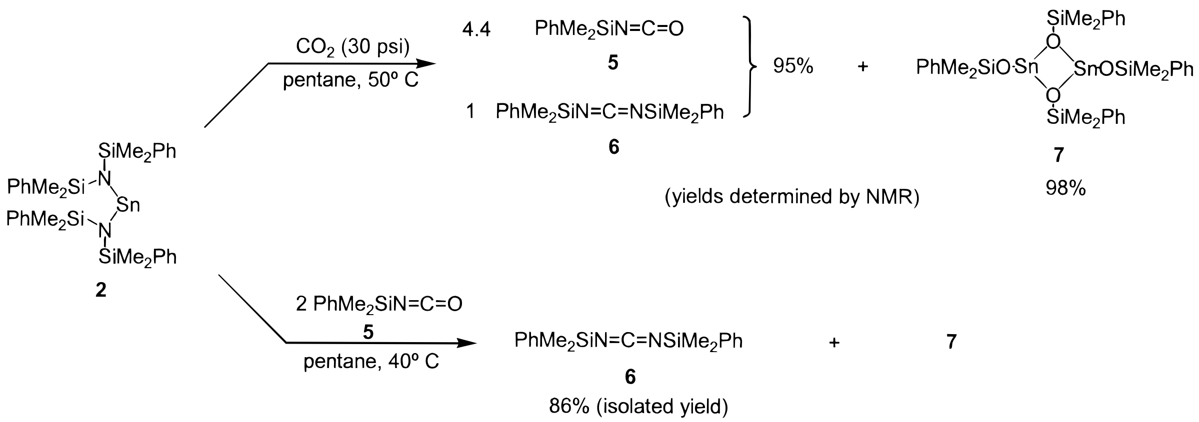


Figure 2. ORTEP (30% thermal ellipsoids) representation of the molecular structure of **2**. Hydrogen atoms have been omitted for the sake of clarity.

Regarding heterocumulene metathesis, in solution, compound **1** was found to be inert toward both carbon dioxide and *tert*-butylisocyanate, ^tBuNCO, even at elevated temperatures up to 80 °C. A solution of **2** in pentane, on the other hand, reacted readily at 50 °C with CO_2 (30 psi) to produce a mixture of dimethylphenylsilylisocyanate, $PhMe_2SiNCO$ (**5**), and 1,3-bis(dimethylphenylsilyl)carbodiimide, $PhMe_2SiN{=}C{=}NSiMe_2Ph$ (**6**), in a 4.4:1 ratio, according to Scheme 1. The identity of **5** was established through its synthesis by a known route,[6] while **6**, which has also been previously reported, was isolated in pure form (86% yield) through a preparative-scale reaction of **5** with 0.51 equiv of **2,** as shown in Scheme 1. Finally, the tin(II) coproduct of these heterocumulene metathesis reactions was determined to be the expected dimer, bis[bis(dimethylphenylsilanolato)tin(II)] (**7**), on the basis of the similarity between the observed ^{119}Sn NMR (186 MHz, benzene-d_6) data of this compound [δ −232, $^2J(^{119}Sn-^{117}Sn) =$ 128 Hz] and the known dimer, bis[bis(trimethylsilanolato)tin(II), [cf., δ −220].[1a] Attempts to obtain analytically pure **7** failed, however, due to its poor crystallinity and thermal instability.

The retarding effects of steric interactions on the reactivity of **2** with isocyanates were found to be pronounced, and to our advantage, in exploring the electronic factors that govern this process. Thus, while bis-[*N*,*N*-bis(trimethylsilyl)amido)]tin(II), $Sn[N(SiMe_3)_3]_2$,[2b] was previously found to rapidly react in solution with ^tBuNCO even at −78 °C,[1c] no reaction between **2** and this heterocumulene occurred at this temperature. Upon warming a well-mixed solution of these reagents to −10 °C, however, clean metathesis occurred to produce the corresponding carbodiimide at such a rate that the progress of the reaction could be conveniently monitored by ^1H NMR spectroscopy at this temperature. Qualitatively, comparing the rate of this reaction with that between **2** and trimethylsilylisocyanate, TMSNCO, revealed the latter reaction to be significantly slower. A similar decrease in reactivity on going from ^tBuNCO to TMSNCO had been noted previously in our heterocumulene studies of $Sn[N(SiMe_3)_3]_2$,[2b] and it had been assumed, at that time, that this difference was related to the enhanced nucleophilicity of the former reagent relative to the latter. This argument now appears to be

Scheme 1



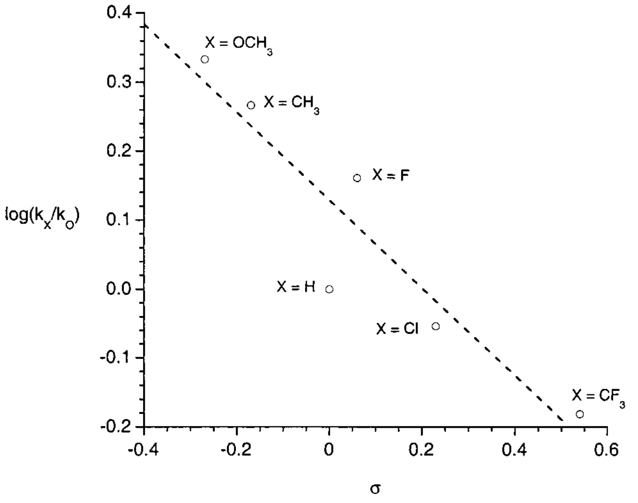
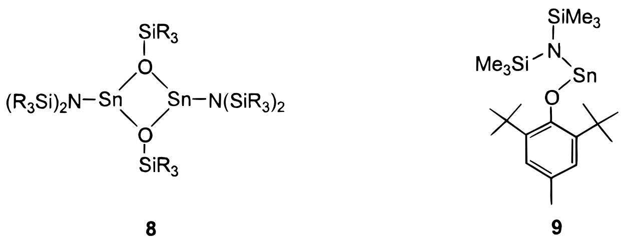


Figure 3. Hammett plot for the reaction of **2** with the *para*-substituted arylisocyanates, X−C_6H_5NCO (X = OCH_3, CH_3, H, F, Cl, and CF_3). The dashed line is the linear regression curve fit of the data [slope (ρ) = −0.64].

justified on the basis of the results of a Hammett study[7] of **2** with a range of *para*-substituted arylisocyanates, X−C_6H_4NCO (X = OCH_3, CH_3, F, Cl, CF_3), which possess both electron-donating and electron-withdrawing groups. As can be seen in Figure 3, a plot of log(k_X/k_0) vs σ, where k_X and k_0 are the rates for the substituted and unsubstituted (i.e., X = H) isocyanates, respectively, and σ is the Hammett constant for group X, provides a linear correlation with a negative slope of $\rho = -0.64$. This negative value for ρ is indicative of a reaction that is facilitated by electron-donating substituents, which we infer is related to the nucleophilicity of the isocyanate. On the basis of this result, it is likely that the rate-determining step in tin(II)-mediated heterocumulene metathesis is initial coordination of the isocyanate (or CO_2) to the electron-deficient divalent tin center. However, this simple assumption is complicated by the results of our previous mechanistic study, which revealed that the rate-determining step might involve the breakup of intermediate monometathesis dimers, such as **8** (Chart 3), that possess tricoordinate tin(II) centers.[1e] In an attempt to differentiate between these two processes, we are now pursuing a kinetic study of the monomeric monoamide stannylene **9** that has been reported by Lappert and co-workers.[8] The results of this investigation will be reported in due course.

Chart 3



Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk and/or glovebox techniques. All solvents were dried and distilled under nitrogen prior to use. Silica gel (400 mesh) was prepared for use in the glovebox by heating at 200 °C under vacuum (10^{-4} Torr) for 3 days. ^1H NMR and ^{119}Sn NMR spectra were recorded at 400 and 186 MHz, respectively, using benzene-d_6 as the solvent and tetramethyltin (0 ppm) for the external reference in the latter. Chemical analyses were performed by Oneida Research Services, Inc.

Synthesis of Bis(*N*-trimethylsilyl-*N*-2,6-diisopropylphenylamido)tin(II) (1). To a solution of 1 g (4.0 mmol) of *N*-trimethylsilyl-2,6-diisopropylaniline in 10 mL of diethyl ether (Et_2O) was added 1.25 mL of *n*-butyllithium (3.21 M in hexanes), and the resulting mixture was stirred for 2 h. This solution was then added dropwise by pipet to a stirred suspension of 380 mg (2 mmol) of tin(II) dichloride in 10 mL of Et_2O. After stirring for 12 h, the reaction mixture was filtered through a small pad of Celite on a glass frit. The volatiles were then removed from the orange-red filtrate in vacuo to provide the desired compound **1** as a deep orange crystalline material that was recrystallized from pentane at −35 °C to provide 1.14 g of pure product (93% yield). For **1**: ^1H NMR δ (ppm) 0.33 (s, 18H), 1.11 (d, 12H, $J = 6.9$ Hz), 1.27 (d, 12H, $J = 6.9$ Hz), 3.69 (sept. 4H, $J = 6.9$ Hz), 7.02 (m, 2H), 7.10 (m, 4H); ^{119}Sn NMR (298 K) δ (ppm) 440. Anal. Calcd for $C_{30}H_{52}N_2Si_2Sn$: C, 58.53; H, 8.51; N, 4.55. Found: C, 57.98; H, 8.56; N, 4.35.

Synthesis of Bis[*N*,*N*-bis(dimethylphenylsilyl)amido)tin(II) (2). To a solution of 4.04 g (14.1 mmol) of *N*,*N*′-bis(dimethylphenylsilyl)amine in 100 mL of Et_2O, cooled to 0°, was added 5.66 mL of *n*-butyllithium (2.5 M in hexanes), and the reaction mixture was warmed to room temperature and stirred for 2 h. The resulting solution was then added to a stirred suspension of 1.48 g (7.8 mmol) of tin(II) dichloride in

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(6) Schott, G.; Kelling, H.; Ahrens, R. *Z. Chem.* **1974**, *14*, 487−488.

(7) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992.

(8) Braunschweig, H.; Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1992**, 1311−1313.

75 mL of Et_2O, cooled to 0 °C. After warming to room temperature and stirring for 2 h, the volatiles were removed in vacuo and the crude product taken up in pentane and filtered through a 1 × 5 pad of Celite on a glass frit. After concentrating the filtrate in vacuo, 3.65 g (75% yield) of pure **2** were obtained as orange cubes through crystallization at −35 °C. For **2**: ^1H NMR δ (ppm) 0.44 (s, 24H), 7.17 (m, 12H), 7.50 (m, 8H); ^{119}Sn NMR (298 K) δ (ppm) 501. Anal. Calcd for $C_{32}H_{44}N_2Si_4Sn$: C, 55.88; H, 6.45; N, 4.07. Found: C, 55.31; H, 6.47; N, 4.11.

Synthesis of 1,3-Bis(dimethylphenylsilyl)carbodiimide (6). A solution of 789 mg (1.15 mmol) of **2** and 400 mg (2.25 mmol) of **5** in 50 mL of pentane was refluxed for 2 h, and then the volatiles were removed in vacuo after filtering the reaction mixture through a short pad of silica gel in the glovebox. Pure **6** (600 mg, 86% yield) was obtained as a colorless oil through bulb-to-bulb distillation of the crude product at 60 °C/0.01 Torr. For **6**: ^1H NMR δ 0.30 (s, 12H), 7.18 (m, 8H), 7.54 (m, 2H).

General Procedure for NMR Kinetic Study of 2 with Isocyanates. A NMR tube containing a solution of 21 mg (0.030 mmol) of **2** and 18 mg (0.095 mmol) of 1,4-di-*tert*-butylbenzene in 0.3 mL of toluene-d_8 was first cooled to 205 K, 0.2 mL of a stock solution (154 mg mL^{-1}) of ^tBuNCO in toluene-d_8 was added, and the mixture was well-shaken at this temperatue. The NMR tube was then placed into a precooled (243 K) NMR probe, which was brought to 263 K, at which time, NMR spectra (1 scan acquisition) were taken at measured time intervals.

Supporting Information Available: Details regarding the crystallographic analyses of **1** and **2**, including complete listings of atomic positions, isotropic and anisotropic temperature factors, and bond distances and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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