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Double Heterocumulene Metathesis of Cyclic Bis(trimethylsilylamido)stannylenes and Tethered Bimetallic Bisamidinates from the Resulting α,ω-Biscarbodiimides[†]

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Summary: Reaction of 2 equiv of tert-butylisocyanate with the cyclic bisamidostannylenes, ***3a*** *and* ***3b****, provides the α,ω-biscarbodiimides,* $^tBuN{=}C{=}N(CH_2)_nN{=}C{=}N^t$*-Bu (****2a*** *and* ***2b****;* $n = 3$ *and 4, respectively) in high yield. Reaction of* ***2b*** *with 2 equiv of* $(\eta^5\text{-}C_5H_5)TiMe_3$ *results in clean formation of the tethered bimetallic bisamidinate represented by meso/rac -****1****. The crystal structures of* ***3b*** *and rac-****1*** *are reported.*

In recent years, considerable interest has focused on the development of the amidinate ligand, $[N(R^1)C(R^2)N(R^3)]^{-1}$, as a surrogate for the ubiquitous cyclopentadienyl (Cp) ligand in the design of new transition and main group metal complexes.[1−3] In theory, the amidinate group is an ideal candidate for this role, as its steric and electronic effects are amenable to manipulation through programmed variation of the substituents, R^1, R^2, and R^3. Unfortunately, despite this promise, the amidinate ligand still lags far behind the Cp group with respect to the degree of design sophistication that has, to date, been implemented.[4] Herein, we extend the range of amidinate chemistry through the synthesis of the tethered bimetallic bisamidinate, *meso/rac*-$\{CpTi(Me)_2[N(^tBu)C(Me)N(CH_2CH_2)-]\}_2$ (**1**), the structure of which complements known group 4 linked bimetallic bis-Cp complexes that have been the subject of investigation for possible cooperative behavior in Ziegler Natta α-olefin polymerization.[5,6] Importantly, access to compound **1** is via a facile insertion process involving the α,ω-biscarbodiimides **2** that are produced in one step through a novel double heterocumuluene metathesis of the cyclic bis(trimethylsilylamido)stannylenes, **3a** and **3b**, according to Scheme 1. As a range of isocyanates can be employed in tin(II)-mediated heterocumulene metathesis,[7] and as other types of metal−carbon bonds can engage in the carbodiimide insertion reaction,[2s,3d,8] the chemistry presented here should prove widely

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[†] Taken in part from the Ph.D. Dissertation of J. R. Babcock, University of Chicago, 1998.

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(4) Notable exceptions are the chiral bisamidinate ligand of Arnold and co-workers[2m] and the tridentate amidinate ligand of Teuben and co-workers.[2k]

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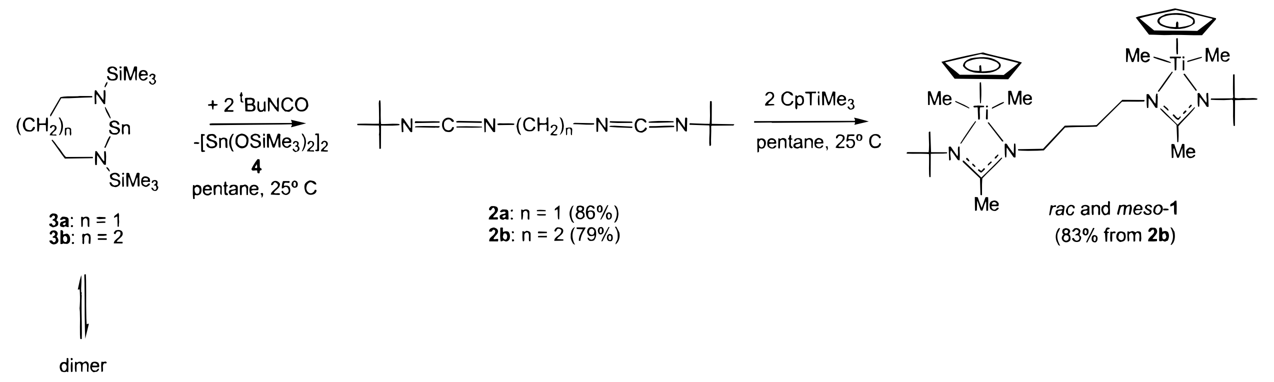
Scheme 1



general in scope for the synthesis of both linked bimetallic complexes and *ansa*-bridged mononuclear metal bisamidinates. Further, full characterizations of **3a** and **3b**, including a crystallographic analysis of the latter, are presented since their existence, as first reported by Zuckerman and co-workers[9] over 25 years ago, has been called into question.[10] Finally, although existing as a rapidly equilibrating mixture of *meso* and *d,l* stereoisomers in solution at room temperature, single crystals of *rac*-**1** could be isolated and its structure determined by crystallographic analysis. These data reveal that, in the solid state, no close intramolecular interactions exist between the two titanium metal centers in this stereoisomeric form of **1**.

Compounds **3a** and **3b**, prepared according to the previously reported procedure using diethyl ether as the solvent,[9] were each obtained as pale yellow needles through recrystallization from pentane at −78 °C (65% and 82% yield, respectively). ^{1}H NMR spectra[11] of these compounds recorded at room temperature are consistent with the original formulation proposed by Zuckerman and co-workers. However, at this temperature, the rather broad ^{119}Sn NMR resonance for **3a**,[11] and the lack of a corresponding ^{119}Sn NMR resonance for **3b**, suggested that both might be engaged in rapid monomer−dimer equilibria. Indeed, upon cooling to −20 °C, a ^{119}Sn NMR (186 MHz, toluene-d_8) spectrum of **3b** now displayed a broad resonance centered at 165 ppm, which sharpened and moved upfield to 148 ppm upon further cooling to −40 °C. The direction of this chemical shift change is consistent with a higher population of the dimer at lower temperature since ^{119}Sn chemical shifts are known to move upfield with an increase in the coordination number of the tin nucleus. In the solid state, **3b** exists solely as the dimer which forms a four-membered ring complex with a significantly puckered conformation [angle between the planes defined by N(2)−Sn(1)−N(2A) and N(2)−Sn(1A)−Sn(2A); 19.7°].[12,13] The unique *cis*-geometry of this structure guarantees that trimethylsilyl groups on the two types of nitrogen atoms (i.e., bridging and nonbridging) are furthest removed from one another, thereby minimizing steric interactions. This molecular framework also possesses a feature common to the only other known structure of a dimeric bisamido stannylene[14a] in having three different types of tin−nitrogen bonds [cf. Sn(1)−N(1), 2.083(6) Å; Sn(1)−N(2), 2.256(6) Å; and Sn(1)−N(2A), 2.397(6) Å]. For each tin atom, the shortest of these is associated with the bond made to a nonbridging nitrogen atom, while the intermediate one is made within a monomeric subunit to the other, bridging nitrogen atom. The longest tin−nitrogen bond is then formed between two subunits to generate the dimeric structure. Other structural features of the dimer of **3b** fall within expected ranges.[14]

We have previously shown that mono- and bis(trimethylsilylamido)tin(II) derivatives can undergo heterocumulene metathesis with isocyanates to produce symmetric and unsymmetric carbodiimides in high yield.[7] With dimeric tin(II) complexes possessing a tricoordinate tin atom, we have further proposed that this metathesis process requires prior generation of a monomeric tin(II) species.[7c] In the present study, reaction of 2 equiv/Sn atom of *tert*-butyl isocyanate, ^{t}BuNCO, with the equilibrated monomer−dimer mixture of **3b** resulted in rapid and clean formation of dimeric bis(trimethylsilanolato)tin(II), $[Sn(OSiMe_3)_2]_2$ (**4**), as the expected tin product of metathesis[7a,b] and the new α,ω-biscarbodiimide **2b** that could be isolated in a 79% yield after distillation.[15] When 1 equiv/Sn atom of ^{t}BuNCO

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[9] Schaeffer, C. D., Jr.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 7160−7162.

[10] Braunschweig, H.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922−1928.

[11] For **3a**: ^{1}H NMR (500 MHz, benzene-d_6, 25 °C) δ 0.28 (s, 18 H), 1.65 (m, 2 H), 3.39 (m, 4 H); ^{119}Sn NMR (186 MHz, benzene-d_6, 25 °C) δ 118 ppm. For **3b**: ^{1}H NMR (500 MHz, benzene-d_6, 25 °C) δ 0.24 (s, 18 H), 1.56 (m, 4 H), 3.71 (m, 4 H); ^{119}Sn NMR (186 MHz, toluene-d_8, −40 °C) δ 148 ppm.

[12] Crystallographic details: compound **3b** is, at 255(2) K, monoclinic, space group *C*2/*c*, $a = 16.379(3)$ Å, $b = 15.690(2)$ Å, $c = 12.7328(14)$ Å, $\beta = 91.235(11)°$, $V = 3271.4(6)$ Å^3, $Z = 4$ ($D_{calcd} = 1.418$ mg m^{-3}, μ(Mo Kα) = 16.87 cm^{-1}), final *R* indices [$I > 2\sigma(I)$], R1 = 0.0520, wR2 = 0.1252; *R* indices (all data), R1 = 0.928, wR2 = 0.1533; GOF on F^2 = 0.88.[13]

[13] Details are provided in the Supporting Information.

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[15] General procedure (conducted in a glovebox): To a solution of 0.88 g (2.5 mmol) of **3b** in 40 mL of pentane was added dropwise a solution of 0.53 g (5.3 mmol) of ^{t}BuNCO in 10 mL of pentane and the reaction mixture stirred at room temperature for 12 h. After filtering the reaction mixture through a short pad (3 cm) of silica gel (400 mesh, dried 3 days at 150 °C/10^{-4} Torr) to remove **4**, the volatiles were removed in vacuo and the crude product was bulb-to-bulb distilled (85 °C/0.01 Torr) to provide 0.5 g of pure **2b** (79% yield). Compound **2a** (bp 88 °C/0.2 Torr) was prepared in a similar fashion using 1.37 g of **3a** and 0.83 g of ^{t}BuNCO. For **2a**: ^{1}H NMR (500 MHz, benzene-d_6) δ 1.16 (s, 18 H), 1.56 (quint, 2H, J = 6.4 Hz), 3.12 (t, 4H, J = 6.6 Hz). For **2b**: ^{1}H NMR (500 MHz, benzene-d_6) δ 1.17 (s, 18 H), 1.44 (m, 4H), 2.95 (m, 4H).

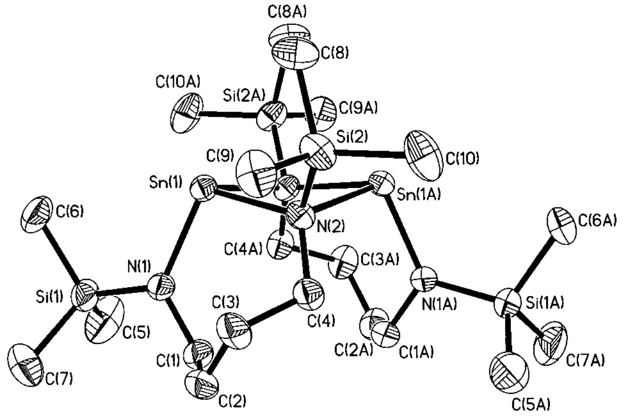
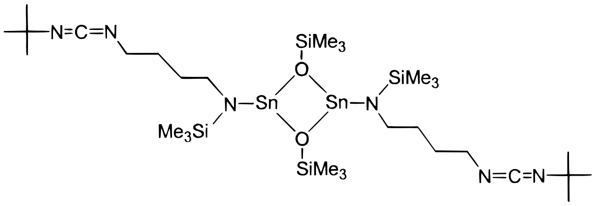


Figure 1. ORTEP representation of the molecular structure of dimeric **3b** (30% thermal ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and bond angles (deg): Sn(1)−N(1) 2.083(6), Sn(1)−N(2A) 2.397(6), Sn(1)−N(2) 2.256(6), Si(1)−N(1) 1.721(6), Si(2)−N(2) 1.775(6), N(1)−C(1) 1.476(9), N(2)−C(4) 1.506(9), N(1)−Sn(1)−N(2) 101.2(2), N(2)−Sn(1)−N(2A) 83.1(2), N(1)−Sn(1)−N(2A) 99.6(2), C(1)−N(1)−Sn(1) 124.3(5), C(1)−N(1)−Si(1) 113.5(5), Si(1)−N(1)−Sn(1) 121.7(3), C(4)−N(2)−Sn(1) 117.9(4), C(4)−N(2)−Si(2) 108.9(5), Si(2)−N(2)−Sn(1) 113.9(3), Sn(1)−N(2)−Sn(1A) 95.0(2).

Scheme 2



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is used, a single new compound was produced, which we tentatively assign as being the intermediate dimeric monometathesis product **5** (Scheme 2) on the basis of the chemical shift (δ −44.4 ppm) and quadrupolar-^{14}N broadening of the new ^{119}Sn NMR resonance that is observed for this species. Further, reaction of **5** with 1 equiv/Sn atom of ^{t}BuNCO once more cleanly produced **4** and **2b**. The ability to observe **5** as a stable intermediate in double heterocumulene metathesis suggests the possibility of extending this methodology for the production of *unsymmetric* α,ω-biscarbodiimides by using two different isocyanates in a similar process. Finally, as shown in Scheme 1, the α,ω-biscarbodiimide **2a** was prepared in a similar fashion from **3a** and 2 equiv of ^{t}BuNCO in 86% yield after distillation.

Since carbodiimides are known to insert into a metal−carbon bond of transition and main group organometallic complexes,[2s,3d,8] α,ω-biscarbodiimides are attractive starting materials for the formation of either tethered bimetallic bisamidinate complexes or *ansa*-bridged mononuclear bisamidinates. Accordingly, as an extension of our own work with dimethyl, monocyclopentadienyltitanium(IV) acetamidinates,[2s,t] it was gratifying to find that the bimetallic bisamidinate **1** could be accessed through the simple reaction of **2b** with 2 equiv of CpTiMe$_3$ in pentane at room temperature as shown in Scheme 1.[16] The ability to obtain **1** in such a high yield is due to deactivation of the remaining Ti−C$_{\mathrm{Me}}$ bonds toward carbodiimide insertion after the initial monoamidinate complex (with respect to each titanium center) has been formed. It is also important to point out here that attempts to prepare either bimetallic bisamidinates such as **1**, or *ansa*-bridged mononuclear bisamidinates, through reaction of a metal halide with the in situ generated dilithio bisamidinate **6** (from 2 equiv of methyllithium and **2b**) have so far all met with failure, as with our attempts to verify actual formation of **6**. Hence, carbodiimide insertion appears to be the best method to prepare both tethered bimetallic and *ansa*-bridged amidinates at least at the present time. As a final note, variable-temperature ^{1}H NMR (400 MHz, toluene-d_8) spectra of **1** indicated that this compound exists as an equilibrating mixture of the *rac* and *meso* forms in solution, a result that is not surprising given our previous studies on the low configurational stability of similar types of complexes.[2s,t]

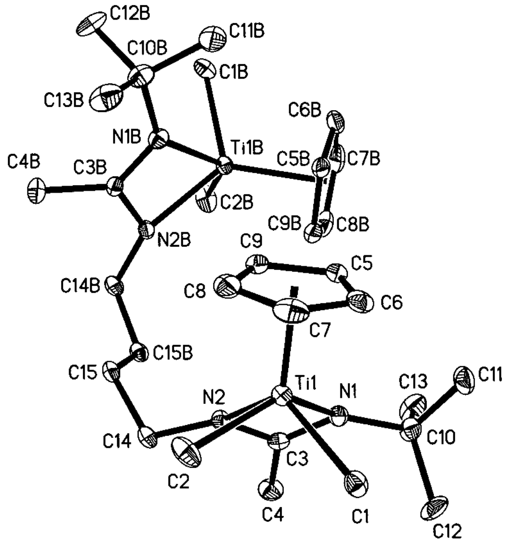

Figure 2. ORTEP representation of the molecular structure of *rac*-**1** (30% thermal ellipsoids). Hydrogen atoms have been removed for clarity and only the (*R*,*R*)-stereoisomer of **1** is shown. Atoms labeled with a B are symmetry equivalent to those without. Selected bond lengths (Å) and bond angles (deg): Ti1−N1 2.183(7), Ti1−N2 2.072(2), Ti1−C1 2.171(7), Ti1−C2 2.152(3), N1−C3 1.310(6), N2−C3 1.338(3), C1−Ti1−C2 85.03(17), N1−Ti1−N2 61.76(15), N1−C3−N2 111.3(3), Ti1−N1−C3 89.3(3), Ti1−N1−C10 140.1(4), C3−N1−C10 126.0(5), Ti1−N2−C3 93.36(15), Ti1−N2−C14 138.53(17), C3−N3−C14 124.8(2).

Despite the rapid equilibration of *rac* and *meso* forms of **1** in solution, single crystals of *rac*-**1** could be isolated through crystallization from pentane at −35 °C.[13,17] As

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[16] To a solution of 600 mg (3.8 mmol) of CpTiMe$_3$ in 10 mL of pentane was added a solution of 540 mg (1.9 mmol) of **2b** in 10 mL of pentane and the reaction stirred overnight. After removal of the solvent in vacuo, the dark red solid material was taken up in a minimum volume of pentane and crystallized at −30 °C to provide 0.95 g of *rac*/*meso*-**1** as a dark orange-red crystalline material. For *rac*/*meso*-**1**: ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) δ 0.88 (s, 12H), 1.032 (m, 4H), 1.22 (s; 18H), 1.82 (s, 6H), 3.0 (m, 4H), 6.33 (s, 10H). Anal. Calcd for $C_{30}H_{54}N_4Ti_2$: C, 63.78; H, 9.63; N, 9.92. Found: C, 63.55; H, 9.64; N, 9.95.

[17] Crystallographic details: compound *rac*-**1** is, at 153(2) K, monoclinic, space group $C2/c$ $a = 16.814(2)$ Å, $b = 8.7464(11)$ Å, $c = 21.573(3)$ Å, $\beta = 101.456(2)°$, $V = 3109.4(7)$ Å^3, Z = 4 ($D_{\mathrm{calcd}} = 1.210$ Mg m^3, μ(Mo Kα) = 0.537 mm^{-1}, final R indices [$I > 2\sigma(I)$], R1 = 0.0433, wR2 = 0.1085, R indices (all data), R1 = 0.0677, wR2 = 0.1186, GOF on F^2 = 0.939.[13]

shown in Figure 2, crystallographic analysis reveals that, in the solid state, *rac*-**1** adopts a conformation that does not possess any close intramolecular contacts between the two titanium metal centers.[13,17] Bond lengths and bond angles for this complex are in keeping with the corresponding parameters obtained for other monocyclopentadienyl titanium amidinates.[2t]

Supporting Information Available: Detailed crystallographic data for **3b** and *rac*-**1**, including complete listings of data collection parameters, methods, atom 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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