Alkylation

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Synthesis and Characterization of Tricarbastannatranes and Their Reactivity in $B(C_6F_5)_3$-Promoted Conjugate Additions**

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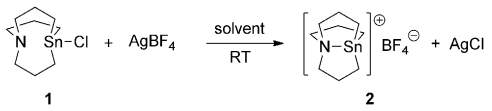
Abstract: *The synthesis and characterization of a series of tricarbastannatranes, in the solid state and in solution, are described. The structures of the complexes $[N(CH_2CH_2CH_2)_3Sn](BF_4)$, $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$, $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$, and $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$ were determined by X-ray crystallography. Furthermore, the $B(C_6F_5)_3$-promoted conjugate addition of alkyl-tricarbastannatranes to benzylidene derivatives of Meldrum's acid was investigated, and detailed mechanistic studies are presented.*

Alkyl-tricarbastannatranes are compounds with three fused five-membered rings, in which the transannular N–Sn interaction makes the apical Sn–C bond longer, and consequently more reactive.[1,2] These reagents are air- and moisture-stable, and readily prepared from chloro-tricarbastannatrane (**1**) and the corresponding Grignard,[3] organolithium,[4,5] and dialkylzinc reagents.[6d] It has been shown that alkyl-tricarbastannatranes efficiently and selectively transfer the apical alkyl group to a palladium(II) center.[3,4,6] The transfer generates a Lewis acidic tricarbastannatrane which is stabilized by delocalization of the positive charge to the nitrogen atom through formation of a transannular N–Sn bond.

Utilizing alkyl-tricarbastannatranes as nucleophilic alkylating agents in C–C bond-forming reactions is of great synthetic interest. To the best of our knowledge, the direct transfer of the apical alkyl group of alkyl-tricarbastannatranes to an electrophilic carbon center has not yet been reported. Herein, we present the $B(C_6F_5)_3$-promoted conjugate addition of alkyl-tricarbastannatranes to benzylidene derivatives of Meldrum's acid. Furthermore, the structure and Lewis acidity of tricarbastannatranes were established using NMR spectroscopy, mass spectrometry (MS), and X-ray crystallography.

The formation of the tricarbastannatrane $[N(CH_2CH_2CH_2)_3Sn](BF_4)$ (**2**) in THF was reported by Tzschach and Jurkschat, and it has a characteristic ^{119}Sn NMR shift at $\delta = 103$ ppm (deshielded; see Scheme 1).[7] It was suspected that the chemical shift might not be indicative of free $[N(CH_2CH_2CH_2)_3Sn]^+$ (**3**) in solution, as **3** could potentially interact with THF.

The formation of **2** was reinvestigated in the absence of a Lewis-basic solvent by the addition of $AgBF_4$ to a solution of **1** in 1,2-dichloroethane (Scheme 1). A ^{119}Sn NMR chemical



1 2

Scheme 1. Preparation of the tricarbastannatrane **2**.

shift of $\delta = 145.8$ ppm, corresponding to $[N(CH_2CH_2CH_2)_3Sn]^+$ (**3**) in complex **2** was observed (Table 1, entry 2). NMR experiments also revealed that **2** was stable at room temperature for more than one week and remained unchanged for more than 2 hours at 70 °C. Crystallization of **2** from a *n*-pentane/1,2-dichloroethane mixture yielded crystals that were analyzed by X-ray crystallography. As depicted in Figure 1, the salient feature of the structure is its exceptionally short Sn–N bond (2.22 Å).[8,9] In addition, the counterion $[BF_4]^-$ interacts with the positively charged **3** (Sn–F 2.37 Å),[10] and HRMS (ESI) supported the formation of **2** with an ion peak at *m*/*z* 260.04512, which corresponds to **3**.

Additional information about the structure of tricarbastannatranes was obtained by preparing $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$ (**4a**) through the reaction of $AgSbF_6$ with **1** (Figure 2a). The formation of **4a** in solution was supported by a deshielded ^{119}Sn NMR signal at $\delta = 197.8$ ppm (Table 1,

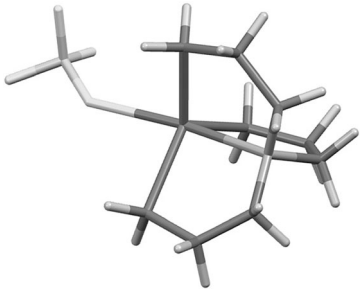


Figure 1. X-ray Structure of $[N(CH_2CH_2CH_2)_3Sn](BF_4)$ (**2**).

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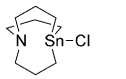
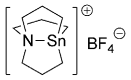
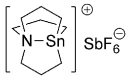
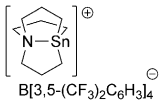
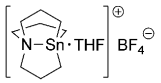
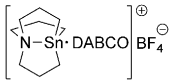
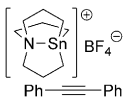
Table 1: NMR studies on tricarbastannatranes.

Entry	Tricarbastannatranes	NMR chemical shifts [ppm] ^{1}H	^{13}C	^{119}Sn	^{11}B
1		1.13 (t) 1.78 (m) 2.42 (t)	13.0 22.9 54.3	17.6	n.a.
2		1.47 (t) 1.96 (m) 2.57 (t)	12.6 23.6 55.0	145.8	−2.1
3		1.61 (t) 2.04 (m) 2.64 (t)	14.2 24.4 55.4	197.8	n.a.
4		1.64 (t) 2.04 (m) 2.63 (t)	16.5 24.7 55.5	198.1	−7.2
5		1.37 (brs) 1.94 (m) 2.56 (t)[a]	11.5 23.3 54.7[b]	131.8	−1.6
6		broad	13.0 22.8 54.3[c]	61.4	−1.7
7		1.45 (t) 1.95 (m) 2.57 (t)[d]	12.5 23.6 54.9[d]	142.5	−1.6
8		1.46 (t) 1.95 (m) 2.56 (t)[e]	12.5 23.6 54.9[f]	144.2	−1.6

[a] One broad signal observed for THF at $\delta = 1.82$ ppm and the other THF signal overlaps with the 1,2-dichloroethane signal. [b] Two signals at $\delta = 25.01$ and 68.12 ppm belong to THF. The carbon chemical shifts of free THF in 1,2-dichloethane are $\delta = 25.2$ and 66.9 ppm. [c] Two signals at $\delta = 44.6$ and 46.9 ppm belong to DABCO. Chemical shift of free DABCO in 1,2-dichloroethane is $\delta = 47.09$ ppm. [d] CH_3CN signals in ^{1}H and ^{13}C NMR spectra were $\delta = 2.16$ and 1.5 ppm, respectively. [e] Diphenylacetylene proton chemical shifts are $\delta = 7.35$ and 7.51 ppm. [f] ^{13}C NMR chemical shifts of diphenyl acetylene are $\delta = 88.5$, 122.3, 127.9, 127.9, and 131.0 ppm. n.a. = not applicable. DABCO = 1,4-diazabicyclo[2.2.2]octane.

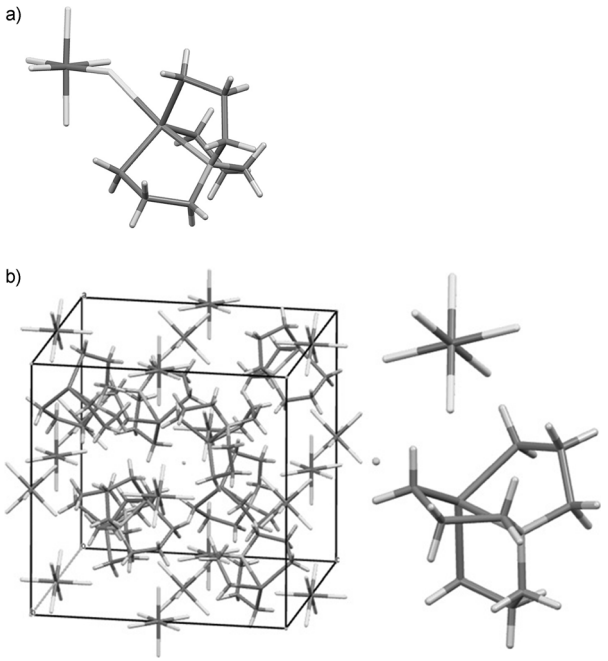


Figure 2. X-ray Structure of a) $[N(CH_2CH_2CH_2)_3Sn](SbF_6)$ (**4a**) and b) $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$ (**4b**).

entry 3). In this complex, a longer Sn–F interaction (Sn-F 2.48 Å and 2.52 Å) and a more deshielded Sn center depict a looser interaction between **3** and $[SbF_6]^-$ compared to its interaction with $[BF_4]^-$ in **2**. In addition, the Sn–N bond length is 2.21 Å, thus suggesting a stronger transannular Lewis-acid–base interaction than in **2**. Of note, the complex **4a** was stable for more than a week in 1,2-dichloroethane at room temperature. A solution of **4a** containing traces of chloride ion crystallized to yield $[N(CH_2CH_2CH_2)_3Sn]_4[(SbF_6)_3Cl]$ (**4b**). The crystal lattice of this complex is defined by the space group I23, in which one chlorine atom is surrounded by four tricarbastannatranes and the $[SbF_6]^-$ counter ions are shared along the edge of the unit cell (Figure 2b). The Sn–N bond length in **4b** is 2.22 Å and the distance between chlorine and tin atoms is 2.92 Å, which is significantly longer than the Sn–Cl bond of 2.61 Å in **1**.[8] According to the X-ray structure, there is no interaction between the chlorine and tin atoms in **4b**, thus establishing the formation and stability of **3**.

Then, complex $[N(CH_2CH_2CH_2)_3Sn][B[3,5\text{-}(CF_3)_2C_6H_3]_4]$ (**5**), containing the bulky and noncoordinating counter ion $[B[3,5\text{-}(CF_3)_2C_6H_3]_4]^-$[11] was synthesized from $Ag[B[3,5\text{-}(CF_3)_2C_6H_3]_4]$. A deshielded ^{119}Sn NMR signal was observed at $\delta = 198.1$ ppm (Table 1, entry 4). The coordination of various Lewis bases to **2** was then studied (Table 1, entries 5–8). While the addition of one equivalent of DABCO showed a significant change of the ^{119}Sn NMR chemical shift from $\delta = 145.8$ to 61.4 ppm (Δppm = 84.4), adding one equivalent of CH_3CN (Δppm = 3.3) or diphenylacetylene (Δppm = 1.6) showed negligible changes. A ^{119}Sn NMR chemical shift of $\delta = 131.8$ ppm was observed after one equivalent of THF was added to **3** (Δppm = 14.0), thus indicating its moderate coordinating ability toward **3**.[12] This data reflects the exceptional stability and moderate Lewis acidity of **3**, thus resulting in the transannular Lewis acid/Lewis base Sn–N interaction.

The ability of $N(CH_2CH_2CH_2)_3SnMe$ (**6**) to transfer its apical methyl group was then examined by using $B(C_6F_5)_3$ (**7**).[13] The complex $[N(CH_2CH_2CH_2)_3Sn][MeB(C_6F_5)_3]$ (**8**) was formed upon addition of **7** to a solution of **6** in 1,2-dichloroethane. The generation of **8** was monitored by ^{119}Sn NMR spectroscopy, and a remarkable change in the ^{119}Sn NMR chemical shift from $\delta = -16.3$ to 253.0 ppm (Δppm = 269.3 ppm) was observed (Table 2, entry 2). Furthermore, the presence of $[MeB(C_6F_5)_3]^-$ was detected by HRMS (ESI), thus showing an ion peak at m/z 527.00751. After the addition of one equivalent of DABCO to **8**, the ^{119}Sn NMR signal at $\delta = 61.9$ ppm suggested formation of a strong Lewis base/Lewis complex with **3** (Table 2, entry 3), as previously observed for **2** (Table 1, entry 6). In addition to NMR data, the formation of the DABCO·tricarbastannatrane was supported by HRMS (ESI) analysis, which showed an ion peak at m/z 372.14609.

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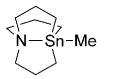
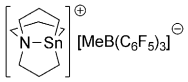
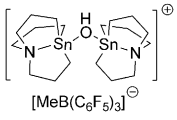
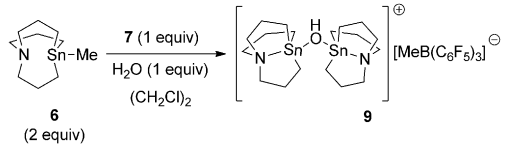
Table 2: NMR studies on **8** and **9**

Entry	Tricarbastannatranes	NMR chemical shifts (ppm) ^{1}H	^{13}C	^{119}Sn	^{11}B
1		−0.39 (s) 0.59 (t) 1.59 (m) 2.33 (t)	−5.3 7.5 22.9 54.2	−16.3	n.a.
2		0.43 (brs) 1.76 (m) 2.12 (m) 2.71 (t)	17.6 25.3 55.9[b]	253.0	−15.5[a]
3		0.42 (brs) 1.20 (t) 1.87 (m) 2.48 (t)[c]	7.5 22.5 53.9[d]	61.9	−15.5
4		0.50 (brs) 1.05 (m) 1.84 (m) 2.46 (t)	11.3 23.2 54.7	43.1	−14.9[e]

[a] The ^{11}B NMR chemical shift of $B(C_6F_5)_3$ in 1,2-dichloroethane is $\delta = 57.3$ ppm. [b] No signal for a methyl group bonded to boron is observed because of the quadrupolar relaxation of the boron. [c] Two signals at $\delta = 2.61$ and 2.84 ppm belong to DABCO. [d] Two signals at $\delta = 45.1$ and 45.9 ppm belong to DABCO. [d] NMR studies on **9** were carried out in $CDCl_3$.

Although **8** was stable at room temperature for more than 24 hours, decomposition to unidentified products was observed upon warming the solution to 35 °C in a sealed NMR tube. The complex **8**, an oil, could not be characterized by X-ray crystallography. However, when one equivalent of water was reacted with two equivalents of **6** and one equivalent of **7** in 1,2-dichloroethane, the complex $[(N(CH_2CH_2CH_2)_3Sn)_2OH][MeB(C_6F_5)_3]$ (**9**) was obtained as colorless crystals (Scheme 2, Figure 3). In solution, NMR (Table 2, entry 4) and HRMS (ESI) data supported the formation of **9**, and the ion peak at m/z 527.09664 was attributed to $[(N(CH_2CH_2CH_2)_3{}^{115}Sn)_2OH]^+$.



Scheme 2. Synthesis of compound **9**.

The reactivity of **8** in the conjugate addition reaction to the Meldrum's acid **10a**, was then investigated.[14] Unexpectedly, in the presence of one equivalent of **6** and one equivalent of **7**, no reactivity was observed (Table 3, entry 1), while the reaction displayed full conversion into the product **11a** with two equivalents of **6** and one equivalent of **7** (Table 3, entry 4). By using 0.2 equivalents of **7** less than 20% conversion into product **11a** resulted (Table 3, entry 5).

With an optimized procedure in hand, we investigated the scope of the electrophile. The reaction was found to be

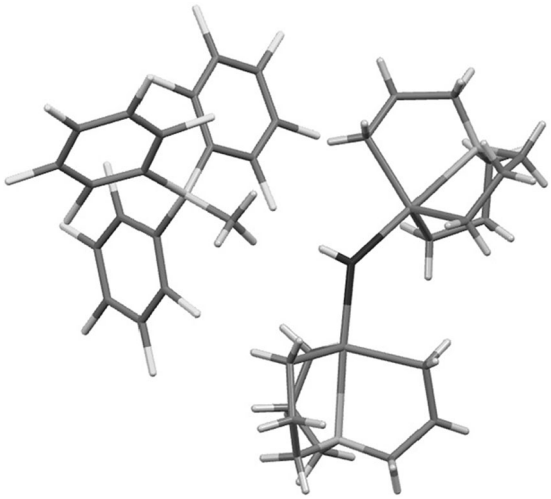
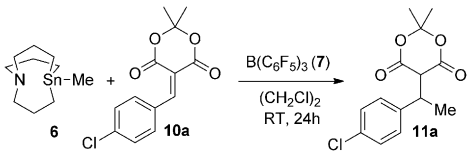


Figure 3. X-ray structure of the compound **9**.

Table 3: $B(C_6F_5)_3$-Promoted reaction of **6** with **10a**.



Entry	Equiv of **6**	Equiv of **7**	Equiv of **10a**	Conv. [%][a]	Yield [%][b]
1	1	1	1	0	n.d.
2	1.2	1	1	< 20	n.d.
3	2	0	1	0	n.d.
4	2	1	1	> 95	92
5	2	0.2	1	< 20	n.d.

[a] Determined by analysis of the ^{1}H NMR spectra of the crude reaction mixtures. [b] Yield of isolated product. n.d. = not determined.

compatible with a series of functional groups and afforded good to excellent yields (78–92%) of methylated products **11a–l** (Table 4).

We then sought to gain more insight into the mechanism by which the methyl group is delivered from **6** to **10a**, as complex $[N(CH_2CH_2CH_2)_3Sn][MeB(C_6F_5)_3]$ (**8**) was shown to be inert (Table 3). As illustrated in Scheme 3, $[CD_3]$-**6** and **10a** were added to **8** to provide $[CD_3]$-**11**. This result indicates that **6** is the sole methyl donor in this transformation. Therefore explaining the need for two equivalents of **6**, and that $[MeB(C_6F_5)_3]^-$ only serves as a bystander (Scheme 3). The tricarbastannatrane **3** likely acts as a Lewis acid and binds to **10a**.

According to the above observations, we propose that the first step in the $B(C_6F_5)_3$-promoted conjugate reaction is the formation of **8** (Scheme 4). Then, **10a** is activated through coordination of one of its carbonyl groups to **3** to form the complex **12**. The latter was detected by a ^{119}Sn NMR spectra showing a signal at $\delta = 129.6$ ppm (Δppm = 123.4). Subsequently, methyl delivery from the second equivalent of **6** yields the tin enolate **13**, in addition to **8**. The tricarbastannatrane **8** is then scavenged by the Lewis basic **13**, thus yielding **14**, and rationalizing the lack of turnover and the need for two

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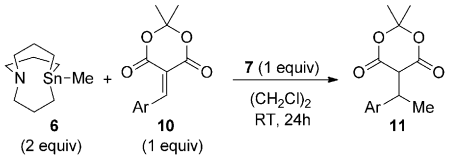
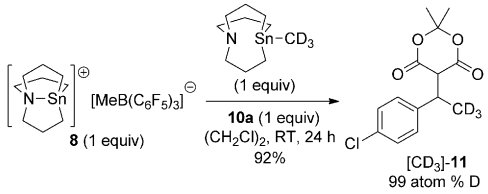
Table 4: $B(C_6F_5)_3$-Promoted reaction of **6** with benzylidene derivatives of Meldrum's acid (**10a–l**).

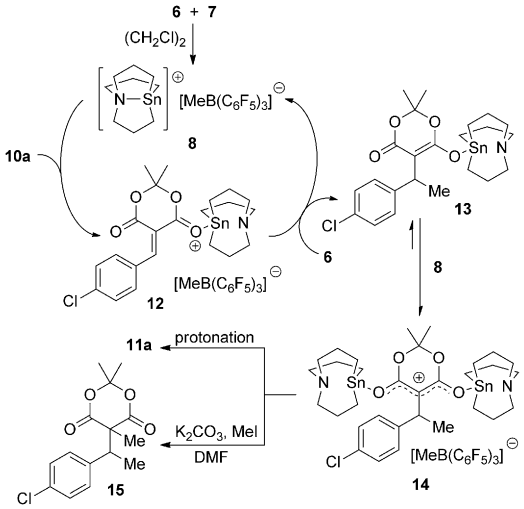


Entry	Ar	Product	Yield [%][a]
1	4-ClC_6H_4 (**10a**)	**11a**	92
2	3-$(MeO)C_6H_4$ (**10b**)	**11b**	90
3	2-Naphthyl (**10c**)	**11c**	78
4	4-$(CN)C_6H_4$ (**10d**)	**11d**	83
5	4-BrC_6H_4 (**10e**)	**11e**	88
6	3-$[B(O_2C_6H_{12})]C_6H_4$ (**10f**)	**11f**	91
7	4-$[B(O_2C_6H_{12})]C_6H_4$ (**10g**)	**11g**	81
8	3-FC_6H_4 (**10h**)	**11h**	92
9	3-BrC_6H_4 (**10i**)	**11i**	90
10	4-$(CO_2CH_3)C_6H_4$ (**10j**)	**11j**	82
11	4-FC_6H_4 (**10k**)	**11k**	85
12	4-$(NO_2)C_6H_4$ (**10l**)	**11l**	79

[a] Yield of isolated product.



Scheme 3. Reaction of $[CD_3]$-**6** and **8** with **10a**.

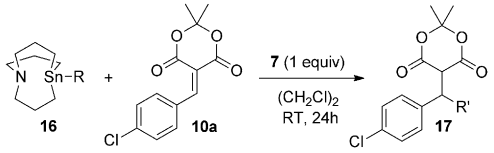


Scheme 4. Proposed mechanism. DMF = *N*,*N*-dimethylformamide.

equivalents of **6** for the reaction to proceed. Monitoring the reaction by NMR spectroscopy showed a single ^{119}Sn NMR signal at $\delta = 47.7$ ppm, which is consistent with symmetrical **14**. In addition, the formation of **14** was further confirmed by HRMS (ESI), which displays an ion peak at m/z 801.15004 with an isotope distribution pattern attributed to the ion $[C_{32}H_{50}O_4N_2ClSn_2]^+$. The intermediate **14** was stable for about one week at room temperature and it was trapped in situ with iodomethane to form product **15**.

As shown in Table 5, the substrate scope was explored by adding the alkyl-tricarbastannatranes **16a**, **16c**, and **16f** to

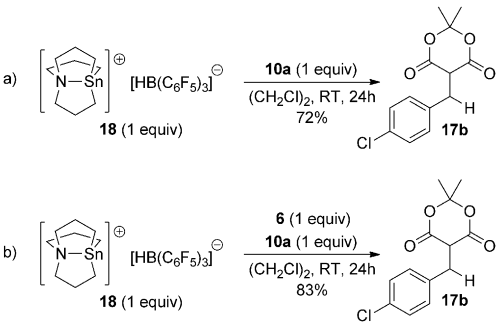
Table 5: $B(C_6F_5)_3$-promoted reaction of **16** with **10a**.



Entry	R	R′	Product	Yield [%][a]
1	*n*Bu (**16a**)	*n*Bu	**17a**	89
2	*i*Pr (**16b**)	H	**17b**	74[b]
3	allyl (**16c**)	allyl	**17c**	96
4	benzyl (**16d**)	benzyl	**17d**	49
5	vinyl (**16e**)	vinyl	**17e**	34
6	$H_2C{=}CMe$ (**16f**)	$H_2C{=}C{=}CMe$	**17f**	86

[a] Yield of isolated product. [b] See the Supporting Information for NMR studies on the reactivity of **16b**.

10a, thus yielding products **17a**, **17c**, and **17f**, respectively, in high yields. Moderate yields were obtained with derivatives **16d** and **16e** (Table 5, entries 4 and 5). Interestingly, addition of *i*Pr-tricarbastannatrane (**16b**) to **10a** led to **17b**, the reduced alkene product (Table 5, entry 2). When the reaction was monitored by ^1H NMR spectroscopy, the presence of propene gas[15] and the complex $[N(CH_2CH_2CH_2)_3Sn][HB(C_6F_5)_3]$ (**18**) was detected. In addition, $[HB(C_6F_5)_3]^-$ was identified by HRMS, thereby showing an ion peak at m/z 512.99267.[16] The product **17b** was obtained in 72% yield by the reaction of only one equivalent of **10a** with one equivalent of **7** and **16b** (Scheme 5a). Therefore, $[HB(C_6F_5)_3]^-$ is likely



Scheme 5. Reactions of **18** with **10a**.

the hydride source in this transformation. In addition, **17b** was obtained in 83% yield as the only product in the reaction involving one equivalent of **18** and one equivalent of **6** with **10a** (Scheme 5b).

In conclusion, the structures of a series of tricarbastannatranes in solution and in the solid state have been determined. The formation of the stable tricarbastannatrane **3** and its moderate Lewis acidity was confirmed by ^{119}Sn NMR spectroscopy. In addition, the structures of the tricarbastanna-

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tranes **2**, **4a, 4b**, and **9** were determined by X-ray crystallography. Important features of these tricarbastannatranes are their stability, as well as their short transannular Sn–N bond. Moreover, the conjugate addition of alkyl-tricarbastannatranes to benzylidene derivatives of Meldrum's acid was carried out in the presence of $B(C_6F_5)_3$ under mild reaction conditions. The mechanism of the addition has been investigated, and NMR and HRMS techniques have been used to determine the structure of the symmetrical bis(tricarbastannatrane) intermediate **14**. Future work will focus on applying these reaction conditions to other electrophiles so as to expand the reaction scope.

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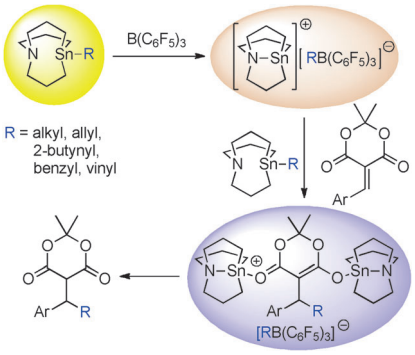
Communications

Alkylation

A. Kavoosi, E. Fillion* _____ ■■■■–■■■■

Synthesis and Characterization of Tricarbastannatranes and Their Reactivity in $B(C_6F_5)_3$-Promoted Conjugate Additions



Trane of thought: Spectroscopic investigation on the structure of tricarbastannatranes has been carried out. The B-$(C_6F_5)_3$-promoted conjugate addition of alkyl-tricarbastannatranes to benzylidene derivatives of Meldrum's acid and detailed mechanistic studies are presented.

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