NJC

Accepted Manuscript

Volume 40 | Number 1 | January 2016 | Pages 1–846

NJC

New Journal of Chemistry
www.rsc.org/njc

A journal for new directions in chemistry

ISSN 1144-0546

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PAPER
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The role of atropisomers on the photo-reactivity and fatigue of
diarylethene-based metal–organic frameworks

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PAPER

Triorganotin(IV) cation-promoted dimethyl carbonate synthesis from CO₂ and methanol: Solution and solid-state characterization of an unexpected diorganotin(IV)-oxo cluster

Petr Švec[a]*, Hélène Cattey[b], Zdeňka Růžičková[a], Josef Holub[c], Aleš Růžička[a] and Laurent Plasseraud[b]*

Two novel *C,N*-chelated organotin(IV) complexes bearing weakly coordinating carborane moieties were prepared by the reaction of the corresponding *C,N*-chelated organotin(IV) chloride (*i.e.* L^{CN}R₂SnCl, R = *n*-Bu (**1**) and Ph (**2**); L^{CN} = 2-(*N,N*-dimethylaminomethyl)phenyl)-) with monocarba-*closo*-dodecaborate silver salt (AgCB₁₁H₁₂; Ag·**3**). Both products of the metathesis, [L^{CN}(*n*-Bu)₂Sn]⁺[CB₁₁H₁₂]⁻ (**4**) and [L^{CN}Ph₂Sn]⁺ [CB₁₁H₁₂]⁻ (**5**), respectively, were characterized by both multinuclear NMR spectroscopy and elemental analysis. Instability of **4** and **5** towards water is discussed. The solid-state structure of L^{CN}(*n*-Bu)₂SnOH·B(C₆F₅)₃ (**4a**) as a model compound with a Sn−O(H)···B linkage is also reported. The evaluation of the catalytic activity of **4** and **5** was carried out within the direct synthesis of dimethyl carbonate (DMC) from methanol and CO₂. While **5** shown to be definitively inactive, presumably due to cleavage of the Sn-Ph bond, compound **4** exhibits a beneficial action, since leading to an amount of DMC higher than the stoichiometry (n$_{DMC}$/n$_{Sn(cat)}$ = 1.5). In addition, the solid state structures of [BnNMe₃]⁺[CB₁₁H₁₂]⁻ (**6**) and [(*n*-Bu)₂₀Sn₁₀O₂(OMe)₆(CO₃)₂]²⁺·2[CB₁₁H₁₂]⁻ (**7**), isolated as single-crystals and resulting of the recombination of **4** in the reaction conditions (methanol/CO₂), were established by sc-XRD analyses within the term of this work as well. **6** and **7** were also fully characterized by IR spectroscopy, multinuclear NMR in solution and elemental analysis.

1. Introduction

For more than two decades, organotin(IV) compounds are known to promote the chemical transformation of carbon dioxide into chemicals with higher value-added. Thus, since the preliminary work of Kizlink described during the nineties and focusing on the linear organic carbonates,[1] numerous studies have also reported the efficiently of tin complexes for the direct synthesis of 2-oxazolidones,[2] cyclic organic carbonates,[3] and carbamates.[4] In the past, our group has acquired significant structural and spectroscopic knowledge, particularly using high pressure NMR conditions,[5] on the organometallic tin(IV) species

involved in some of these CO₂-based reactions. It emerges from these previous studies that the nature of ligands bound to tin atoms greatly influences the robustness and reactivity of precursors. Recently, we also reported the synthesis and the activity evaluation of (*n*-Bu₂Sn)₂O(CO₃), an organotin carbonate, for the direct carbonation of various primary alcohols. This study showed the robustness and versatility of this type of species, and highlighted the relationship between (*n*-Bu₂Sn)₂O(CO₃) and the deca-tin complex, (*n*-Bu₂SnO)₆[(*n*-Bu₂SnOCH₃)₂(CO₃)]₂.[6]

In this quest we have already shown that the incorporation of the 2-(*N,N*-dimethylaminomethyl)phenyl- as a *C,N*-chelating ligand (L^{CN}) within the structure of various organotin(IV) species leads to the elongation of the Sn-X bond (X = any substituent) which is mutually *trans* to the N→Sn dative bond. This phenomenon, known as the *trans*-effect, enables the use of selected *C,N*-chelated triorganotin(IV) halides as very efficient halogenating agents *via* the S$_{N1}$ mechanism.[7] Structurally related organotin(IV) complexes were studied as promising transesterification catalysts[8] or as potential catalysts within the direct synthesis of DMC from methanol and CO₂ by us earlier as well.[9] It was found that increase of the ionic nature of the catalytically active species leads to significant improvement of the yield of DMC. Thus the non-ionic (L^{CN}(*n*-Bu)₂Sn)₂O provided the n$_{DMC}$/n$_{Sn(cat)}$ ratio of 0.75 while L^{CN}(*n*-Bu)₂SnOTf (for which

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‡ Electronic Supplementary Information (ESI) available: CCDC 1590298, 159029 and 1590300 numbers for compounds **6**, **7** and **4a** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. Supplementary data containing general NMR numbering of substituents, molecular structure of **6** as well as selected crystallographic data of **4a**, **6** and **7** may be found in the Electronic Supplementary Information file.

we propose at least partially ionic character) gave the $n_{DMC}/n_{Sn(cat)}$ ratio of 1.15.

As a continuation of our work within this field of chemistry, we now report on the facile synthesis, structural characterization and catalytic activity studies of two novel *C,N*-chelated organotin(IV) monocarba-*closo*-dodecaborates.

2. Results and Discussion

2.1 Synthesis

The reaction of $L^{CN}R_2SnCl$ (R = *n*-Bu (**1**) and Ph (**2**)) with one equivalent of $AgCB_{11}H_{12}$ (Ag·**3**) in THF gave the desired ionic organotin(IV) species $[L^{CN}(n\text{-Bu})_2Sn]^+[CB_{11}H_{12}]^-$ (**4**) and $[L^{CN}Ph_2Sn]^+[CB_{11}H_{12}]^-$ (**5**), respectively, in a very high yield (85 and 88 %, respectively) after the work-up (Scheme 1). Despite all effort, we were not successful in obtaining single crystals of either **4** or **5**. Both compounds are presumably reactive towards water and should be stored under an inert atmosphere (the instability issues are further discussed below in the NMR spectroscopy characterization paragraph). The unprecedented reactivity of other target species (*i.e.* $[L^{CN}(n\text{-Bu})Sn]^{2+}[CB_{11}H_{12}]_2^-$, $[(L^{CN})_2Sn]^{2+}[CB_{11}H_{12}]_2^-$ and $[L^{CN}Sn]^{3+}[CB_{11}H_{12}]_3^-$) towards the THF (which started to polymerize) thwarted the isolation of these compounds. The use of a different solvent within the synthesis is not possible because of solubility issues.
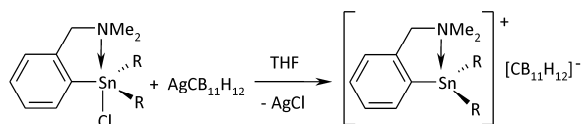
Scheme 1: Synthesis of triorganotin(IV) catalysts **4** and **5** (R = *n*-Bu or Ph).

### 2.2 NMR spectroscopy investigation of 4, 4a and 5

The ^1H NMR spectra of **4** and **5** (recorded in THF-d_8) display somewhat broadened signals with appropriate multiplicity and integral intensity due to the *n*-Bu or Ph and L^{CN} moieties that are bound to the central tin atom. The resonances of aromatic protons (H(6)) are accompanied by characteristic tin satellites with reasonable $^{119}Sn\text{-}^1H$ coupling constants of 61 and 60 Hz, respectively, which is in line other triorganotin compounds bearing the L^{CN} substituent.[10] A characteristic set of broad resonances (similar to that recorder for the starting Ag·**3** in THF-d_8) attributable to the $CB_{11}H_{12}$ anion is observed in the region of 2.19 to 1.05 ppm for both compounds. In the case of **4**, some of these signals are overlapped by resonances of the *n*-Bu moieties and residual THF signal by coincidence.

$^{11}B\{^1H\}$ NMR spectra of **4** and **5** exhibit a typical pattern of 3 signals at ca. -7.4, -13.9 and -17.0 ppm, respectively, in a 1:5:5 ratio which is usually observed for the parent $CB_{11}H_{12}$ anion.[11] The dichotomy between ^1H and $^{11}B\{^1H\}$ chemical shifts may be explained on the basis of weak $CB_{11}H_{12}$ cage-tin interactions in THF-d_8 as discussed similarly in the literature for Ag·**3**.[12]

All signals in the ^{13}C NMR spectra of **4** and **5** are in perfect agreement with expected patterns for respective compounds. All relevant carbon resonances of the L^{CN} and *n*-Bu or Ph substituents are accompanied by tin satellites with appropriate

$^nJ(^{117/119}Sn,^{13}C)$ coupling constants (see Experimental for detailed assignment of all resonances and the $^nJ(^{117/119}Sn,^{13}C)$ values).[10] Quite broad resonance of the C_{cage} is found at 51.5 ppm for both **4** and **5**.[11b]

The most valuable data regarding the structure (*i.e.* the vicinity of the tin atom) of **4** and **5** in solution simply arose from the ^{119}Sn NMR spectra. We assume the presence of triorganotin(IV) cations of the type $[L^{CN}R_2Sn]^+$ while the $[CB_{11}H_{12}]^-$ moieties act as very weakly coordinating anions making thus these species of ionic nature in solution. This conclusion is based on the observed ^{119}Sn NMR chemical shift value of 35.2 ppm (in THF-d_8) found for **4**, which is shifted to higher frequencies when compared to starting **1** ($\delta(^{119}Sn)$ = -57.4 ppm in THF-d_8). Similar change of chemical shift value towards higher frequencies was reported earlier for purely ionic $[L^{CN}(n\text{-Bu})_2Sn]^+[Ti_2Cl_9]^-$ (broad resonance at 185.6 ppm in C_6D_6)[13] or $L^{CN}(n\text{-Bu})_2SnOTf$ ($\delta(^{119}Sn)$ = -1.0 ppm in C_6D_6) where we postulated a partial dissociation of the latter complex.[9b] The same trend is observed for the ^{119}Sn NMR chemical shift value in the case of **5** ($\delta(^{119}Sn)$ = -111.9 ppm in THF-d_8) which is shifted by ca. 66 ppm to higher frequencies with respect to starting **2** ($\delta(^{119}Sn)$ = -178 ppm in THF-d_8). In general, the ionization phenomenon has been described for structurally related *N,C,N*- or *O,C,O*-chelated organotin(IV) compounds as well.[14]
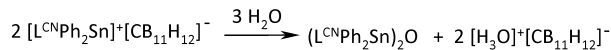
Scheme 2: Hydrolysis of **5**.

The expected instability of **4** and **5** towards water was studied by NMR techniques, too. The hydrolysis of **5** led to the formation of corresponding hexaorganodistannoxane $(L^{CN}Ph_2Sn)_2O$ (Scheme 2) which was identified on the basis of its ^1H, ^{13}C and ^{119}Sn NMR spectra.[15] The second presumed decomposition product, $[H_3O]^+[CB_{11}H_{12}]^-$, could be thus plausibly formed as demonstrated by us earlier.[16] Surprisingly, we observed the expected hexaorganodistannoxane $(L^{CN}(n\text{-}Bu)_2Sn)_2O$ only as a very minor decomposition product[14] within the hydrolysis of **4** while an unknown species ($\delta(^{119}Sn)$ = -43.1 ppm in THF-d_8) bearing presumably the $L^{CN}(n\text{-Bu})_2Sn$ fragment was identified by the multinuclear NMR spectroscopy as the major one. Further NMR investigation showed that the unknown species may be an adduct of $L^{CN}(n\text{-Bu})_2SnOH$ and $[H_3O]^+[CB_{11}H_{12}]^-$ complex which may arise due to the dihydrogen bonding and/or interaction *via* hydrogen bonding of either nitrogen atom of the pendant arm or oxygen atom of the OH group. All these possible interactions lead to the decrease of the electron density at the central tin atom which is reflected in the observed downfield shift in the ^{119}Sn NMR spectrum. Furthermore, this species exhibits reasonable signals in ^1H and ^{11}B (see the Experimental part). Unfortunately, all attempts to grow single crystals failed and thus no sc-XRD analysis could be performed.

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View Article Online
DOI: 10.1039/C7NJ05058E

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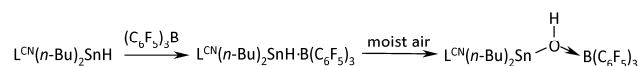
Scheme 3: Plausible formation of **4a** as a model compound with a Sn-O(H)···B linkage.

On the other hand, our hypothesis is further supported by the comparison of its multinuclear NMR spectra to that of an adduct of $L^{CN}(n\text{-}Bu)_2SnOH$ and $B(C_6F_5)_3$ ($\delta(^{119}Sn)$ = -19.3 ppm in C_6D_6) which was isolated as a product of decomposition of the original $L^{CN}(n\text{-}Bu)_2SnH \cdot B(C_6F_5)_3$ species (Scheme 3).[17] Thus, $L^{CN}(n\text{-}Bu)_2SnO(H) \cdot B(C_6F_5)_3$ (**4a**, Fig. 1) exhibits one set of somewhat broadened signals attributable to L^{CN} and n-Bu moieties and a very broad signal of the bridging OH unit at 4.03 ppm in its ^1H NMR spectrum measured in C_6D_6. Similarly, quite broad resonances are found for L^{CN} and n-Bu substituents in the ^{13}C NMR spectrum in which a characteristic spectral pattern consisting of doublets of multiplets arises due to the presence of pentafluorophenyl moieties. Very broad resonance at 14.2 ppm is observed in the $^{11}B\{^1H\}$ NMR spectrum of **4a**. Such chemical shift value is consistent with that reported for compounds of the type $L \cdot BR_3$.[18] Finally, the above mentioned ^{119}Sn NMR chemical shift of -19.3 ppm clearly reflects the presence of the $L^{CN}(n\text{-}Bu)_2SnOH$ within the adduct.

2.3 Solid-state structures of 4a, 6 and 7

Compound **4a** consists of the nearly perfectly trigonal bipyramidal triorganotin(IV) fragment where the carbon substituents are located in the equatorial plane and intramolecularly coordinated nitrogen atom from the pendant amino group and oxygen atom of the O(H) group found in the axial positions (Fig. 1). Very strong coordination of the nitrogen group (Sn1-N1 = 2.414(2) Å), when compared to other triorganotin(IV) species bearing the same ligand (~2.50 Å),[10b,d,19] is most probably the reason of Sn-O distance elongation (Sn1-O1 = 2.3010(17) Å) in comparison to standard bonds of the tin atom to the oxygen bridge being < 2.15 Å. Similar type of elongation is observed in the case of the B-O separation where the interatomic distance O1-B1 of 1.520(3) Å is usually attributed to the donor-acceptor connection than for a covalent bond (~1.35 Å) or the only SnO(H)···B fragment containing structure reported within the Cambridge Structural Database which is the diorganotin(IV) complex with two phenylboronato(1-) ligands (B-O = 1.482 Å).[20] On the other hand, the B1-O1-Sn1 angle of 145.92(14)° found in **4a** is about 25° larger than reported in the literature.
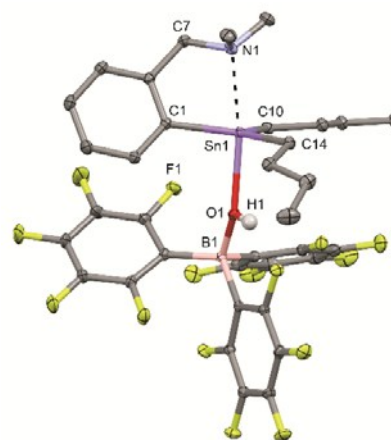

Fig. 1: Molecular structure of **4a** (ORTEP presentation, 50% probability level). Hydrogen atoms, except of the OH group, and the *n*-hexane solvent molecule are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-O1 2.3010(17), Sn1-N1 2.414(2), Sn1-C14 2.137(2), Sn1-C1 2.126(2), Sn1-C10 2.138(2), O1-B1 1.520(3), O1-Sn1-N1 169.29(7), C14-Sn1-O1 85.46(8), C14-Sn1-N1 97.33(9), C14-Sn1-C10 116.19(9), C1-Sn1-O1 93.46(8), C1-Sn1-N1 76.33(8), C1-Sn1-C14 122.94(10), C1-Sn1-C10 120.77(9), C10-Sn1-O1 94.20(8), C10-Sn1-N1 93.82(8), B1-O1-Sn1 145.92(14).

The structure of **6** is composed of trimethylbenzylammonium cation and 1-carba-*closo*-dodecaborate anion (Fig. S2). Two structurally related compounds with quarternized nitrogen atom and $CB_{11}H_{12}^-$ anion have been already reported in the literature. These include the methylimidazolium[21] and *n*-butylpyridinium[22] cations. Significant parameters for both reported compounds are very close to that of **6**. The identity of **6** has been further confirmed by the multinuclear NMR spectroscopy. Thus the multinuclear NMR spectra of **6** are in absolute agreement with the structure established by the sc-XRD techniques (see the Experimental part for detailed assignment of all resonances).

Very rich structural chemistry of organotin(IV) oxides, hydroxides, alkoxides and carbonates is dominated by aggregation of species to higher oligomers *via* oxygen bridges - more than 330 structures reported up to now.[23] Such aggregation is mostly pronounced in cases of diorganotin(IV) alkoxides, where a ladder- or stairs-like structures[24] formed by a four-membered Sn-O-Sn-O rings are mutually interconnected to tetra-, hexa- or octanuclear arrangements.[25] In cases of diorganotin(IV) carbonates, alkoxy- or oxo-carbonates, the mononuclear arrangements were reported for complexes containing ligands with two adjacent donor arms,[26] dinuclear species for ligands with one additional donor,[27] trinuclear ones for compounds containing bulkier ligands such as *t*-Bu,[28] while decanuclear[29] and polymeric[30] aggregates contain smaller benzyl or methyl groups. Immediate neutral carbonato decanuclear mixed mono- and diorganotin cluster[(*t*-Bu)$_2$Sn(OH)OSnR(OH)$_2$OC(OSn(*t*-Bu)$_2$OH)$_2$(O)SnR(OH)(H$_2$O)]$_2$, here R is 2,6-Mes$_2$C$_6$H$_3$, was isolated from the reaction mixture of organotin oxides and hydroxides which were bubbled with CO$_2$, and has a U-shape structure due to the presence of bulky ligands.[31]

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[(*n*-Bu)$_{20}$Sn$_{10}$O$_2$(OMe)$_6$(CO$_3$)$_2$]$^{2+}$·2[CB$_{11}$H$_{12}$]$^-$ complex (**7**), which crystallized from a residual methanolic solution recovered from the reactor after a catalytic run using **4** as a catalyst, has a hybrid structure with the central tetranuclear 4-4-4 Sn-O-Sn-O tricyclic moiety which interconnects two trinuclear 4-4 bicyclic fragments *via* two carbonato ligands (Fig. 2). The almost co-planar arrangement of all the rings further consists of ten di-*n*-butyltin(IV), four oxo and six methoxy moieties. The overall 2+ charge is compensated by two CB$_{11}$H$_{12}^-$ clusters used for stabilization of organotin and other main group metal species in the ionic form.[32] To the best of our knowledge, there are no cationic species reported in above mentioned series of stannoxane, tin(IV) alkoxide or carbonate complexes. There are four different types of the tin atom in **7**, where all of them being five-coordinate with the shape of a deformed trigonal bipyramid with the largest deviation from the ideal angles found for O6-Sn4-O8 (149.3(3) °) and O6-Sn4-O8i (144.8(3) °), respectively. These as well as other values found for interatomic distances and angles are in line with previously published work within the series of similar di- or triorganotin(IV) oxo-compounds mentioned *vide supra*.
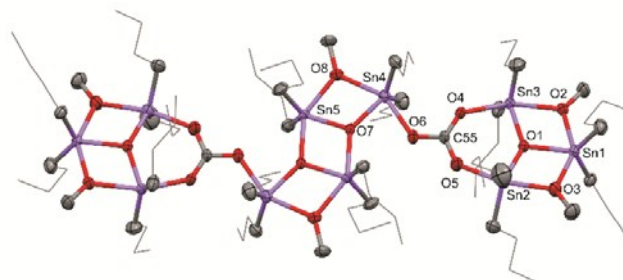

Fig. 2: Molecular structure of **7** (ORTEP presentation, 30% probability level). Hydrogen atoms and two CB$_{11}$H$_{12}^-$ anions are omitted for clarity. Selected interatomic distances [Å]: Sn1-O1 2.080(8), Sn1-O2 2.140(10), Sn1-O3 2.117(10), Sn2-O1 2.024(9), Sn2-O4 2.106(11), Sn2-O2 2.165(10), Sn5-O7 2.037(7), Sn5-O7a 2.131(8), Sn5-O8 2.179(9), Sn3-O1 2.048(9), Sn3-O5 2.158(9), Sn3-O3 2.199(9), Sn4-O7 1.999(8), Sn4-O6 2.178(10), Sn4-O8 2.219(9).

In general, the formation of **7** during the catalytic run may be seen as a proof of a presence of a presumably key catalytically active species and/or intermediate within the direct synthesis of DMC from CO$_2$ and methanol. Thus, the presence of several carbonate and methoxy ligands in the skeleton of **7**, two and six respectively, can be directly perceived as a reminiscence of the formation of DMC. Interestingly, and from a structural point of view, the composition of **7** shows strong similarities to the deca-tin complex, (*n*-Bu$_2$SnO)$_6$[(n-Bu$_2$SnOCH$_3$)$_2$(CO$_3$)]$_2$,[29a] isolated under similar reaction conditions (mixture of CO$_2$/CH$_3$OH, *P* 200 bar, *T* = 150 ° C, using *n*-Bu$_2$Sn(OCH$_3$)$_2$ as tin precursor) and whose the implication has recently been underlined for the direct carbonation of primary alcohols.[6] Therefore, these polynuclear compounds could even be qualified as dormant species. However and at the present stage of our knowledge, the mechanism leading to the formation of **7** from **4** remains still indeterminate. Based on previous studies, several hypotheses and leads can be advanced:

(i) The central tetranuclear moiety can be reasonably constructed by the condensation of *n*-Bu$_2$SnO and *n*-Bu$_2$Sn(OCH$_3$)$_2$.[33] The resulting distannoxane could then in turn react with CO$_2$ to lead to a complex bearing two terminal hemicarbonate ligands and whose the structure has already been described.[34]

(ii) The trinuclear carbonato moieties may be derived from the condensation of *n*-Bu$_2$Sn(OCH$_3$)$_2$ with (n-Bu$_2$Sn)$_2$OCO$_3$ which can be prepared from *n*-Bu$_2$SnO under supercritical CO$_2$ conditions.[35]

(iii) Hydrolysis of *n*-Bu$_2$Sn(OCH$_3$)$_2$ leads to the formation of *n*-Bu$_2$SnO.

From another point of view, one can pinpoint the loss of the L^{CN} ligands within the catalytic run which may be explained by the well-known phenyl group migration process that is feasible under the relatively harsh reaction conditions.[36] Nevertheless, the ^{1}H, ^{11}B and ^{119}Sn NMR spectra of **7** correspond quite well to the structure established by the sc-XRD analysis (see Experimental part for detailed assignment of all resonances).
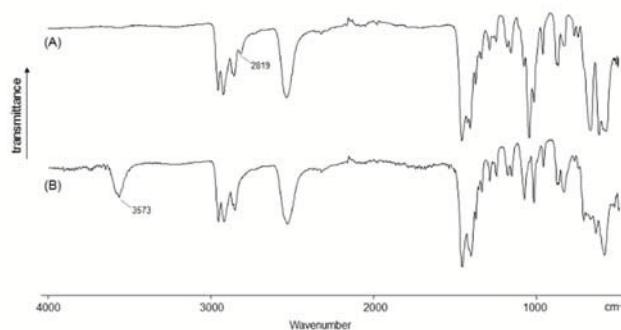

Fig. 3: FT-IR spectra of **7** (A) and its evolution after one hour of exposure to ambient air (B).

Under exposure to the ambient air, **7** undergoes a hydrolysis rapidly which can be monitored by FT-IR spectroscopy. Over time several modifications are clearly observed changing the initial IR fingerprint (Fig. 3). In particular, after one hour, a new absorption band of high intensity is observed at 3573 cm^{-1} (spectrum B, attributed to ν_{OH}) while the band at 2819 cm^{-1} (ν_{OC-H}), assigned to the -OCH$_3$ units of **7** (spectrum A), disappeared completely. Thus, we assume the transformation of all -OCH$_3$ moieties in favor of −OH groups. A representation of the plausibly resulting species is shown in Scheme 4. This hypothesis is experimentally corroborated by the elemental analysis carried out on crystals of **7**, subjected several hours to ambient air. The results support satisfactorily the suggested formula (% found: C = 34.90; H = 7.31. Calcd. for C$_{84}$H$_{210}$O$_{16}$B$_{22}$Sn$_{10}$ (2901.49): C = 34.77; H = 7.29). However, the hydrolysis causes the irreversible deterioration of the crystals. Thus, and despite several attempts, it was not possible to confirm by sc-XRD analysis the structure of the hydrolysis product.

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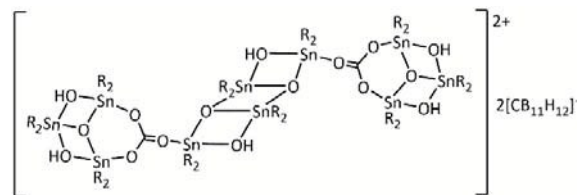
Scheme 4: Possible molecular representation of the hydrolysis product of **7** (R = *n*-Bu).

2.4 Evaluation of DMC synthesis

Both ionic organotin(IV) species **4** and **5** were employed as potential catalysts or catalyst precursors within the direct synthesis of DMC from methanol and carbon dioxide (Table 1). Surprisingly, only **4** (or better say its active form **7**) turned out to be catalytically active within such synthesis which was proved by the stoichiometry of $n_{DMC}/n_{Sn(cat)}$ being 1.5 (the $n_{Sn(cat)}$ represents the amount of starting **4** in moles used in a catalytic run). The reproducibility of the carbonation reaction was satisfactorily verified by repeating the procedure four times, and with three distinct batches of precursor.[37] The reaction was also tested using undistilled and undried methanol leading to a decrease in precursor activity. A DMC: Sn molar ratio of 0.9 was then recorded. On the other hand, only traces of DMC were detected by GC techniques when **5** was used. The inactivity of **5** may be regarded to the presumably expected loss of both L^{CN} and/or Ph substituents during the catalytic run which may be explained by the above mentioned phenyl group migration.[38] This loss of organic groups was confirmed by NMR spectroscopy as well as sc-XRD analysis of the by-product **6**. Unfortunately, however, the nature of the tin-based residue still remains in doubt.

Table 1. Summary of results of direct synthesis of DMC from CO_2 and methanol using compounds **4** and **5** as catalyst precursor ($P_{(CO2)}$ = 200 bar, T = 150 °C, reaction time 24 hours).

Complex	Solvent	CO₂ used (g)	n_{DMC} (mmol)[a]	$n_{Sn(cat)}$ (mmol)	$n_{DMC}/n_{Sn(cat)}$
4	MeOH (20 mL)	37.5	1.7	1.10	1.5
5	MeOH (20 mL)	32.3	traces	1.17	-

[a] Determined by GC using diethyl carbonate (DEC) as external standard.

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3. Conclusions

We have expanded the family of known (*C,N*-chelated) organotin(IV) complexes that are able to catalyze the direct synthesis of DMC from methanol and carbon dioxide. Further investigations involving the possibility of reusing the catalytically active species recovered from the reactor in subsequent runs are in progress now. In general, an increase of an ionic character of the catalytically active organotin(IV) species leads to higher yield of the desired DMC as discussed *vide supra*. This was also demonstrated in this paper since the use of the ionic catalyst precursor **4** enabled obtaining of the highest $n_{DMC}/n_{Sn(cat)}$ ratio of 1.5 among all organotin(IV)-based catalysts used by us so far. From this point of view, presumably better results regarding the yield of DMC (*i.e.* significant increase of the $n_{DMC}/n_{Sn(cat)}$ ratio) may be achieved by the use of mono- and/or dialkyltin(IV) cationic species (with appropriate counter anion(s)) which synthesis is an subject of our current interest.

4. Experimental section

4.1 General remarks

All reactions were carried out under an inert atmosphere of argon using standard Schlenk techniques. **1**[39], L^{CN}(*n*-Bu)$_2$SnH,[13] **2**[40] and Ag·**3**[41] were prepared according to published procedures. All reagents (B(C$_6$F$_5$)$_3$) and solvents (methanol, hexane, THF, methanol-d$_4$, C$_6$D$_6$ and THF-d$_8$) were obtained from commercial sources (Sigma-Aldrich or VWR). THF was dried with the help of solvent purification system PureSolv MD 7 supplied by Innovative Technology, Inc., degassed and then stored under an argon atmosphere over a potassium mirror. C$_6$D$_6$ and THF-d$_8$ were distilled from sodium benzophenone ketyl prior to use.

4.2 NMR spectroscopy

The NMR spectra were recorded from solutions in THF-d$_8$, C$_6$D$_6$ or methanol-d$_4$ on a Bruker Ascend™ 500 spectrometer (equipped with *Z*-gradient 5mm Prodigy cryoprobe) at frequencies 500.13 MHz for ^{1}H, 160.48 MHz for ^{11}B{^{1}H}, 125.76 MHz for ^{13}C{^{1}H} and 186.50 MHz for ^{119}Sn{^{1}H} at 295 K. The solutions were obtained by dissolving of approximately 40-60 mg of each compound in 0.6 ml of deuterated solvent. The values of ^{1}H chemical shifts were calibrated to residual signals of THF-d$_8$ (δ(^{1}H) = 3.58 ppm), C$_6$D$_6$ (δ(^{1}H) = 7.16 ppm) or methanol-d$_4$ (δ(^{1}H) = 3.31 ppm). The ^{11}B chemical shift values are referred to external BF$_3$·OEt$_2$ (δ(^{11}B) = 0.0 ppm). The values of ^{13}C chemical shifts were calibrated to signals of THF-d$_8$ (δ(^{13}C) = 67.57 ppm), C$_6$D$_6$ (δ(^{13}C) = 128.4 ppm) or methanol-d$_4$ (δ(^{13}C) = 49.1 ppm). The ^{119}Sn chemical shift values are referred to external neat tetramethylstannane (δ(^{119}Sn) = 0.0 ppm). Positive chemical shift values denote shifts to the higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. The unambiguous attribution of the resonances in the ^{1}H and ^{13}C{^{1}H} NMR spectra was provided by standard 2D NMR techniques. See also the supplementary data file for the NMR numbering of

prepared compounds (Fig. S1) and graphical presentation of their NMR spectra.

4.3 Crystallography

The X-ray data for colorless crystals of **4a** and **7**, respectively, were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK$_\alpha$ radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[42] The absorption was corrected by integration methods.[43] Structures were solved by direct methods (Sir92)[44] and refined by full matrix least-square based on F^2 (SHELXL-97).[45]

The data for structure of **6** were collected on a Bruker APEX-II CCD diffractometer at 150 K using Oxford Cryostream low-temperature device with MoK$_\alpha$ radiation (λ = 0.71073 Å), the TRIUMPH curved crystal monochromator, and the ϕ and χ scan mode. Data reductions were performed with SAINT v8.34A program package. The absorption was corrected by SADABS-2014/5. Structures were solved by ShelXT and refined by XL[46] and Olex2 software.[47]

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors H$_{iso}$(H) = 1.2 U$_{eq}$(pivot atom) or of 1.5U$_{eq}$ for the methyl moiety with C-H = 0.96, 0.97, 1.1 and 0.93 Å for methyl, methylene, and hydrogen atoms in BH, CH groups in carborane cages and aromatic rings moiety, respectively. Hydrogen atom of the OH group in **4a** was placed according to a maximum found on the Fourier difference electron density map. Carbon atoms in the carborane cages were assigned to the maxima with shortest separations to another five maxima in the icosahedron. Crystals of **7** were of a poor quality, several disordered *n*-butyl groups were found within this structure having no influence on the composition of the model. Some of them were split into two positions. Remaining ones were treated with ISOR instruction.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre (no. 1590298 (**6**), 1590299 (**7**) and 1590300 (**4a**)). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

4.4 IR spectroscopy

The FT-IR spectra were recorded at ambient temperature on a Bruker Vector 22 equipped with a Specac Golden Gate™ ATR device (Specac Ltd., Orpington, UK) in the wave number range of 4000–500 cm^{-1} (twelve scans at a spectral resolution of 4 cm^{-1}).

4.5 Synthesis

Preparation of [L^{CN}(n-Bu)$_2$Sn]$^+$[CB$_{11}$H$_{12}$]$^-$ (4)

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The synthesis was carried out under the exclusion of light. $L^{CN}(n$-Bu$)_2$SnCl (805 mg, 2.00 mmol) was dissolved in THF (20 mL) and solution of AgCB$_{11}$H$_{12}$ (502 mg, 2.00 mmol) in THF (15 mL) was added dropwise. AgCl precipitated immediately. The reaction mixture was filtered and the filtration cake was washed with THF (2x 10 mL). THF filtrates were combined and the volatiles were removed *in vacuo*. The oily residue was washed with hexane (15-20 mL) in order to induce precipitation of the title compound. After filtration, the off-white solid was dried *in vacuo* giving pure **4**. Yield 867 mg (85%). M. p. 74-75 °C. ^{1}H NMR (THF-d_8, 295 K, ppm): 7.60 (d, 1H, H(6), $^3J(^1$H, ^{1}H) = 6.4 Hz, $^3J(^{119}$Sn, ^{1}H) = 61 Hz); 7.43-7.30 (m, 3H, H(3-5)); 3.94 (s, 2H, NCH$_2$); 2.59 (s, 6H, N(CH$_3$)$_2$); 2.12 (br, 1H, C$_{cage}$H); 1.72-1.62 (br, 4H, α-CH$_2$); 1.60-1.50 (br m, 4H, β-CH$_2$); 1.41 (m, 4H, γ-CH$_2$); 0.90 (t, 6H, δ-CH$_3$, $^3J(^1$H, ^{1}H) = 7.3 Hz); broad BH resonances with overall integral intensity of 11 display a typical pattern ranging from 2.05 to 1.05 ppm and some of them are overlapped by resonances of the *n*-Bu moieties and residual THF signal by coincidence. ^{11}B{^{1}H} NMR (THF-d_8, 295 K, ppm): -7.4 (br s, 1B, B(12)); -13.9 (br s, 5B, B(7-11)); -17.0 (br s, 5B, B(2-6)). ^{13}C{^{1}H} NMR (THF-d_8, 295 K, ppm): 144.2 (C(2), $^2J(^{119/117}$Sn, ^{13}C) = 33Hz); 138.7 (C(1), $^1J(^{119/117}$Sn, ^{13}C) = 618/590 Hz); 137.4 (C(6), $^2J(^{119/117}$Sn, ^{13}C) = 42 Hz); 131.2 (C(4)); 129.3 (C(5), $^3J(^{119/117}$Sn, ^{13}C) = 60 Hz); 128.4 (C(3), $^3J(^{119/117}$Sn, ^{13}C) = 51 Hz); 66.4 (CH$_2$N, $^nJ(^{119/117}$Sn, ^{13}C) = 26 Hz); 51.5 (br, C$_{cage}$H); 46.3 (NMe$_2$); 29.0 (β-C, $^2J(^{119/117}$Sn, ^{13}C) = 30 Hz); 27.8 (γ-C, $^3J(^{119/117}$Sn, ^{13}C) = 91 Hz); 17.4 (α-C, $^1J(^{119/117}$Sn, ^{13}C) = 452/433 Hz); 13.9 (δ-C).^{119}Sn{^{1}H} NMR (THF-d_8, 295 K, ppm): 35.2 (br). Elemental analysis (%): found: C, 42.7; H, 8.5; N, 2.5. Calcd. for C$_{18}$H$_{42}$NB$_{11}$Sn (510.14): C, 42.38; H, 8.30; N, 2.75.

Hydrolysis of 4

The sealed NMR tube containing the THF-d_8 solution of **4** was opened in the air and several drops of water were added. After staying overnight at ambient temperature, the NMR spectra were recorder again. ^{1}H NMR (THF-d_8, 295 K, ppm): 7.70 (br d, 1H, H(6), $^3J(^1$H, ^{1}H) = 7.0 Hz Hz, $^3J(^{119}$Sn, ^{1}H) ≈ 62 Hz); 7.32-7.23 (br m, 3H, H(3-5)); 4.08 (br, 1H, OH); 3.79 (s, 2H, NCH$_2$); 2.45 (s, 6H, N(CH$_3$)$_2$); 2.08 (br, 1H, C$_{cage}$H); 1.61 (br, 4H, α-CH$_2$); 1.38-1.32 (br m, 8H, β- and γ-CH$_2$); 0.90 (t, 6H, δ-CH$_3$, $^3J(^1$H, ^{1}H) = 7.1 Hz); broad BH resonances with overall integral intensity of 11 display a typical pattern ranging from 2.05 to 1.05 ppm and some of them are overlapped by resonances of the *n*-Bu moieties and residual THF signal by coincidence. ^{11}B{^{1}H} NMR (THF-d_8, 295 K, ppm): -7.5 (br s, 1B, B(12)); -13.8 (br s, 5B, B(7-11)); -16.8 (br s, 5B, B(2-6)). ^{119}Sn{^{1}H} NMR (THF-d_8, 295 K, ppm): -43.1.

Preparation of $L^{CN}(n$-Bu$)_2$SnOH·B(C$_6$F$_5$)$_3$ (4a)

$L^{CN}(n$-Bu$)_2$SnH (368 mg, 1.00 mmol) was reacted with (C$_6$F$_5$)$_3$B (95%, 539 mg, 1.00 mmol) in benzene (20 mL) at ambient temperature overnight providing presumably [$L^{CN}(n$-Bu$)_2$Sn]$^+$[(C$_6$F$_5$)$_3$BH]$^-$ (not isolated). Upon its contact with moist air overnight, the title compound was isolated as colorless crystals in high yield after crystallization from diethyl ether/hexane mixture of solvents. M.p. 145-146 °C. ^{1}H NMR (C$_6$D$_6$, 295 K, ppm): 7.57 (d, 1H, H(6), $^3J(^1$H, ^{1}H) = 6.6 Hz, $^3J(^{119}$Sn,

^{1}H) = 62 Hz); 6.98 (m, 2H, H(4,5)); 6.63 (d, 1H, H(3), $^3J(^1$H, ^{1}H) = 6.6 Hz); 4.03 (br, 1H, OH); 2.62 (s, 2H, NCH$_2$); 1.31 (s, 6H, N(CH$_3$)$_2$); 1.25 (br, 4H, α-CH$_2$); 1.18 (br m, 4H, β-CH$_2$); 1.11 (br, 2H, γ-CH$_2$); 0.98 (br, 2H, γ-CH$_2$); 0.84 (t, 6H, δ-CH$_3$, $^3J(^1$H, ^{1}H) = 7.3 Hz). ^{11}B{^{1}H} NMR (C$_6$D$_6$, 295 K, ppm): 14.2 (br). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 295 K, ppm): 148.8 (d of m, C$_6$F$_5$, $^1J(^{19}$F, ^{13}C) = 252 Hz); 145.0 (br d, C$_6$F$_5$, $^1J(^{19}$F, ^{13}C) = 261 Hz); 142.2 (br, C(2), $^2J(^{119/117}$Sn, ^{13}C) could not be read); 138.8 (d of m, C$_6$F$_5$, $^1J(^{19}$F, ^{13}C) = 252 Hz); 137.0 (br, C(1), $^1J(^{119/117}$Sn, ^{13}C) could not be read); 135.4 (br, C(6)); 131.2 (C(4)); 127.0 (br, C(3); 64.4 (br, CH$_2$N); 113.8 (br, C$_6$F$_5$); 44.4 (br, NMe$_2$); 28.5 (br, β-C); 26.8 (br, γ-C); 16.4 (br, α-C, $^1J(^{119/117}$Sn, ^{13}C) could not be read); 13.1 (δ-C); resonance of the C(4) is overlapped by the signal of C$_6$D$_6$ by coincidence. ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 295 K, ppm): -19.3.

Preparation of [L^{CN}Ph$_2$Sn]$^+$[CB$_{11}$H$_{12}$]$^-$ (5)

5 was prepared according to the procedure described for **4** using L^{CN}Ph$_2$SnCl (885 mg, 2.00 mmol) and AgCB$_{11}$H$_{12}$ (502 mg, 2.00 mmol). Off-white powder. Yield 968 mg (88%). M.p. 142-144 °C. ^{1}H NMR (THF-d_8, 295 K, ppm): 7.92 (br, 1H, H(6), $^3J(^{119}$Sn, ^{1}H) ≈ 60 Hz); 7.81 (br d, 4H, *o*-Ph, $^3J(^{119}$Sn, ^{1}H) ≈ 64 Hz); 7.63-7.48 (br m, 8H, L^{CN} and Ph moieties); 4.04 (s, 2H, CH$_2$N); 2.22 (s, 6H, NMe$_2$); 2.11 (br, 1H, C$_{cage}$H); broad BH resonances with overall integral intensity of 11 display a typical pattern ranging from 2.05 to 1.10 ppm and some of them are overlapped by resonances of the residual THF signal by coincidence. ^{11}B{^{1}H} NMR (THF-d_8, 295 K, ppm): -7.3 (br s, 1B, B(12)); -13.8 (br s, 5B, B(7-11)); -16.9 (br s, 5B, B(2-6)). ^{13}C{^{1}H} NMR (THF-d_8, 295 K, ppm): 144.9 (C(2), $^2J(^{119/117}$Sn, ^{13}C) = 38 Hz); 138.0 (C(6), $^2J(^{119/117}$Sn, ^{13}C) = 49 Hz); 137.1 (*o*-Ph, $^2J(^{119/117}$Sn, ^{13}C) = 47 Hz); 136.3 (br, *i*-Ph, $^1J(^{119/117}$Sn, ^{13}C) could not be read); 133.9 (br, C(1), $^1J(^{119/117}$Sn, ^{13}C) could not be read); 132.4 (br, C(4)); 132.3 (br, *p*-Ph); 130.9 (*m*-Ph, $^3J(^{119/117}$Sn, ^{13}C) = 71 Hz); 130.2 (C(5), $^3J(^{119/117}$Sn, ^{13}C) could not be read); 129.1 (C(3), $^3J(^{119/117}$Sn, ^{13}C) = 60 Hz); 65.8 (CH$_2$N, $^nJ(^{119/117}$Sn, ^{13}C) = 30 Hz); 51.5 (br, C$_{cage}$H); 46.6 (NMe$_2$). ^{119}Sn{^{1}H} NMR (THF-d_8, 295 K, ppm): -111.9. Elemental analysis (%): found: C, 48.4; H, 6.4; N, 2.4. Calcd. for C$_{22}$H$_{34}$NB$_{11}$Sn (550.12): C, 48.03; H, 6.23; N, 2.55.

Isolation of [BnNMe$_3$]$^+$[CB$_{11}$H$_{12}$]$^-$ (6)

Single crystals of **6** were obtained from a methanolic solution of the reaction mixture which was collected from the reactor after the catalytic run where **5** was employed as a catalyst. M.p. 220-222 °C. ^{1}H NMR (methanol-d_4, 295 K, ppm): 7.60-7.50 (m, 5H, H$_{arom.}$); 4.52 (s, 2H, CH$_2$N); 3.11 (s, 6H, NMe$_2$); 2.19 (br, 1H, C$_{cage}$H); unresolved BH resonances with overall integral intensity of 11 display a typical pattern ranging from 2.05 to 1.05. ^{11}B{^{1}H} NMR (THF-d_8, 295 K, ppm): -7.5 (br s, 1B, B(12)); -13.8 (br s, 5B, B(7-11)); -16.6 (br s, 5B, B(2-6)). ^{13}C{^{1}H} NMR (methanol-d_4, 295 K, ppm): 134.0 (*o*-C$_{arom.}$); 132.1 (*p*-C$_{arom.}$); 130.4 (*m*-C$_{arom.}$); 129.0 (*i*-C$_{arom.}$); 70.6 (pseudo t, CH$_2$N, $^1J(^{14}$N, ^{13}C) = 3 Hz); 53.1 (pseudo t, NMe$_2$, $^1J(^{14}$N, ^{13}C) = 4 Hz); 52.2 (br, C$_{cage}$H). Elemental analysis (%): found: C, 45.4; H, 10.0; N, 4.5. Calcd. for C$_{11}$H$_{28}$NB$_{11}$ (293.26): C, 45.05; H, 9.62; N, 4.77.

Isolation of [(n-Bu)$_{20}$Sn$_{10}$O$_2$(OMe)$_6$(CO$_3$)$_2$]$^{2+}$·[CB$_{11}$H$_{12}$]$_2$$^-$(7)

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Single ingle crystals of **7** were grown from a methanolic solution which was recovered from the reactor after a catalytic run using **4** as a catalyst. M. p. > 220 °C (dec.). ^{1}H NMR (THF-d_8, 295 K, ppm): 2.72 (br, 18H, OCH$_3$); 2.10 (br, 2H, C$_{cage}$H); 1.65 (br m, 20H, α-CH$_2$); 1.49-1.38 (m, 40H, β- and γ-CH$_2$); 0.95 (t, 60H, δ-CH$_3$, $^{3}J(^{1}$H, ^{1}H) = 7.0 Hz); broad BH resonances with overall integral intensity of 22 display a typical pattern ranging from 2.05 to 1.05 ppm and some of them are overlapped by resonances of the *n*-Bu moieties and residual THF signal by coincidence. ^{11}B{^{1}H} NMR (THF-d_8, 295 K, ppm): -7.6 (br s, 2B, B(12)); -13.9 (br s, 10B, B(7-11)); -17.0 (br s, 10B, B(2-6)). ^{119}Sn{^{1}H} NMR (THF-d_8, 295 K, ppm): -164.3 (s, 2Sn); -177.2 (s, 2Sn); -207.6 (s, 4Sn), -211.8 (s, 2Sn). IR (ATR, selected bands, cm^{-1}): 2956 v(C−H), 2924 v(C−H), 2857 v(C−H), 2819 v(OC−H), 2535 v(B−H), 1461, 1426, 1409, 1377, 1048, 1019, 964, 870, 836, 670, 619, 580. Elemental analysis (%): found: C, 35.84; H, 7.48. Calcd. for C$_{90}$H$_{222}$B$_{22}$O$_{16}$Sn$_{10}$ (2985.65): C, 36.21; H, 7.49.

4.6 High-pressure experiments

Safety Warning: Experiments involving pressurized gases can be hazardous and must only be conducted with suitable equipment and following appropriate safety considerations.[48] General procedure for reactions of methanol with carbon dioxide: The reaction was carried out in a 125 mL stainless steel reactor equipped with a magnetic stirrer. The reactor was purged with argon and a 20 mL solution of the appropriate *C,N*-chelated organotin(IV) species (**4** and **5**) in anhydrous methanol was introduced by syringe. Then, CO$_2$ was admitted to the desired amount (see Table 1). The reaction temperature (150 °C) was controlled by an internal thermocouple. After a reaction time of 24 hours the reactor was cooled down to 0°C, the pressure was gently released and the liquid phase was transferred to a Schlenk tube. Trap-to-trap distillation under *vacuum* at ambient temperature allowed separation of volatile compounds that were quantitatively analyzed by GC (DEC external standard, Fisons 8000, J&W Scientific DB-WAX 30 m capillary column, FID detector). Tin-based residue was firstly characterized by IR and multinuclear NMR spectroscopy.

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