Hydrostannylation

DOI: 10.1002/ange.200805595

Reactions of Tin(II) Hydride Species with Unsaturated Molecules**

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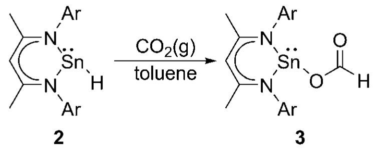
Dedicated to Professor Joachim Sauer on the occasion of his 60th birthday

SnH_2 has been prepared and characterized in an argon matrix.[1] At elevated temperature, SnH_2 changed to an insoluble solid of unknown structure. Terphenyl and β-diketiminate ligands have been used for the preparation of substituted tin(II) hydrides. The terphenyl derivatives exist in the solid state as dimeric structures,[2] whereas the β-diketiminate species incorporates a terminal tin(II) hydride with very weak intermolecular interactions.[3] Until recently, reactions of organotin hydrides were based on tin(IV) precursors. Di- and triorganotin hydrides, of composition R_2SnH_2 and R_3SnH, with a formal oxidation state of Sn^{IV} undergo a rich variety of chemical transformations.[4] The most commonly used reagent of this class of compounds is tributyltin hydride, which is widely used as a reducing agent in organic and inorganic chemistry.[5] To our knowledge, there are no hydrostannylation reactions described using tin(II) hydride. Herein, we report the first hydrostannylation reactions of carbon dioxide, ketones, aldehydes, alkynes, and carbodiimides with [LSnH] (**2**, L = HC{CMeN(2,6-iPr$_2$C$_6$H$_3$)}$_2$).

We have previously reported the synthesis of **2** from the reaction of the corresponding tin(II) chloride, [LSnCl] (**1**),[6] with one equivalent of $AlH_3{\cdot}NMe_3$ in toluene.[3] Preparation of **2** from $AlH_3{\cdot}NMe_3$ resulted in the formation of the expected product contaminated with small amounts of the starting material [LSnCl] (**1**), which , when it was used in hydrostannylation reactions, led to products containing chlorine. Furthermore, when contaminated with chlorine, **2** was unstable and decomposed in an inert atmosphere within four days. Therefore, a different method of preparation was required. Treatment of [LSnCl] (**1**) with potassium triisobutylborohydride in toluene at −10 °C afforded the tin(II) hydride **2** in high yield. The crude reaction product was recrystallized from n-hexane and obtained as pure yellow crystals which were characterized by ^1H ($\delta = 13.96$ ppm) and ^{119}Sn ($\delta = -4.45$ ppm, $^1J(^{119}Sn,^1H) = 64$ Hz) NMR spectroscopy. The chemical shift for ^{119}Sn of **2** given in ref. [3] is that of [LSnCl].

Carbon dioxide is a readily accessible atmospheric gas that could be a useful feedstock for organic compounds.[7] The kinetic and thermodynamic stability of carbon dioxide present significant challenges in designing efficient chemical transformations. Reactions of metal hydrides with carbon dioxide to generate metal formate species are well known for transition metal hydrides and alkali metal hydrides.[8] However, for group 14 metal hydrides there are only a few reports on the hydrogenation of carbon dioxide using silicon(IV) hydride[9] or tin(IV) hydride.[10] The reaction of carbon dioxide and silicon(IV) hydride requires a transition metal catalyst. Herein, we report on the synthesis of a stannylene formate [LSn−O−C(O)H] (**3**), by the reaction of **2** with carbon dioxide at room temperature without any catalyst in quantitative yield (Scheme 1).



Scheme 1. Preparation of **3**. Ar = 2,6-iPr$_2$C$_6$H$_3$

Stannylene formate **3** is a colorless solid, which is soluble in benzene, THF, n-hexane, and n-pentane and shows no decomposition on exposure to air. It was characterized by multinuclear NMR and IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ^1H NMR spectrum of **3** exhibits an upfield shifted singlet ($\delta =$ 8.97 ppm) which can be assigned to the CH proton and is flanked by satellite peaks attributable to Sn ($^3J(^{119}Sn,^1H) =$ 52 Hz). The ^{119}Sn NMR signal of **3** appears at $\delta = -360$ ppm, which is very different from that for the starting compound **2**. The IR spectrum shows two bands at 2700 and 1641 cm^{-1}, which are assigned to the C−H and C=O stretching frequencies.

Colorless compound **3** crystallizes in the triclinic space group $P\bar{1}$, with two monomers in the asymmetric unit from saturated n-hexane solution at −32 °C after two days. Coordination around the tin center has a distorted tetrahedral geometry with one lone pair (Figure 1).[11]

The carbonyl group and its transformation to other functional groups is very important in organic chemistry.[12] There are numerous reports on hydrostannylation of compounds with carbonyl groups using tin(IV) hydride.[13] Herein, we demonstrate for the first time the hydrostannylation of a variety of carbonyl compounds, such as 2-benzoylpyridine, 2,2,2-trifluoroacetophenone, and ferrocene carbaldehyde, using tin(II) hydride **2**.

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[**] Support of the Deutsche Forschungsgemeinschaft is highly acknowledged.

Supporting Information for this article, containing experimental synthetic details and physical data, is available on the WWW under http://dx.doi.org/10.1002/anie.200805595.

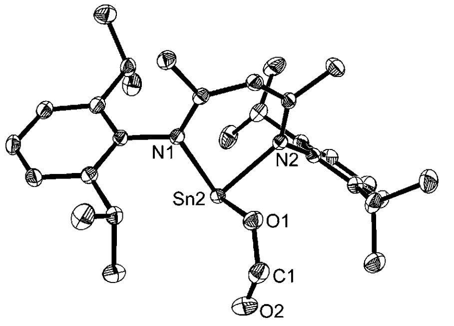
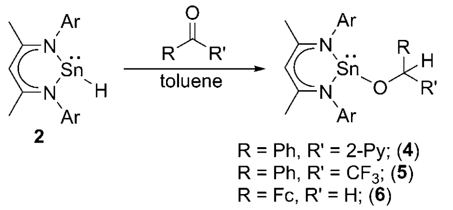


Figure 1. Molecular structure of **3**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn2–O1 2.1353(15), O1–C1 1.299(2), C1–O2 1.209(3), Sn2–N1 2.1655(17), Sn2–N2 2.1752(15); Sn2-O1-C1 116.40(13), O1-C1-O2 126.78(18), N1-Sn2-N1 86.42(6).

Ketone insertion into the tin–hydrogen bond of various complexes is well established.[14] Although **2** displayed no reactivity toward acetone at room temperature, it reacted cleanly with aromatic ketones. Treatment of **2** with 2-benzoylpyridine and 2,2,2-trifluoroacetophenone led quantitatively to the stannylene alkoxides **4** and **5**, respectively (Scheme 2). The ^{1}H NMR spectrum of **4** exhibits an upfield shifted singlet ($\delta = 6.28$ ppm) which can be assigned to the quaternary CH proton. The ^{119}Sn NMR resonance signal of **4** appears at $\delta = -286$ ppm. Compound **4** crystallized in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 2).[11]



Scheme 2. Preparation of **4**, **5**, and **6**. Ar = 2,6-iPr$_2$C$_6$H$_3$

Compound **5** has one CF$_3$ group and gives rise to interesting NMR spectra. The ^{1}H NMR spectrum of **5** exhibits a quartet ($\delta = 5.15$ ppm) which corresponds to the quaternary CH proton. The ^{19}F NMR signal is a doublet ($\delta = -76.29$ ppm) with a coupling constant of 7.3 Hz and is flanked by Sn satellite peaks ($^4J(^{119}\text{Sn},^1\text{H}) = 42$ Hz). The four isopropyl groups of **4** and **5** give rise to four different resonances, and the two methyl groups in the backbone exhibit two different signals in the proton NMR spectra. Future study is planned to generate enantiomerically pure secondary alcohols by using organocatalysts.

Ferrocene moieties are important in organometallic chemistry, with respect to electrochemistry[15] and material science, because bridging ferrocenophanes undergo polymerization and generate organometallic polymers with high molecular weight.[16] The reaction of **2** with ferrocene carbaldehyde generated bimetallic tin(II) alkoxide **6** (Scheme 2).

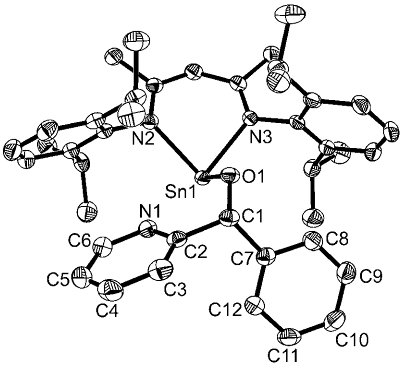


Figure 2. Molecular structure of **4**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.0414(15), Sn1–N2 2.2420(16), Sn1–N3 2.2632(18); N2-Sn1-O1 99.99(6), N2-Sn1-N3 82.10(6).

Compound **6** is an orange solid, which is soluble in benzene, THF, n-hexane, and n-pentane and shows no decomposition on exposure to air. It was characterized by multinuclear NMR and IR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis (Figure 3).[11] The ^{1}H NMR spectrum of **6** exhibits a singlet ($\delta = 4.81$ ppm), which can be assigned to the CH$_2$ protons and is flanked by Sn satellite peaks ($^3J(^{119}\text{Sn},^1\text{H}) = 13.5$ Hz). The ^{119}Sn NMR signal of **6** appears at $\delta = -262$ ppm.

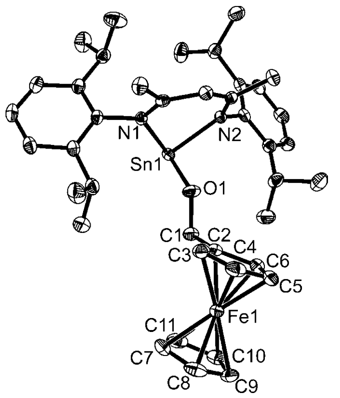
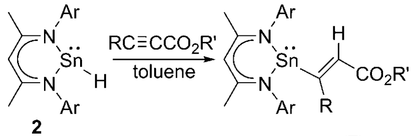


Figure 3. Molecular structure of **6**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.0253(13), Sn1–N1 2.1834(14), Sn1–N2 2.1894(14); Sn1-O1-C1 129.13(11), N1-Sn1-O1 87.89(6), N1-Sn1-N2 85.10(5).

The hydrostannylation of olefins and alkynes has been established for nearly 50 years and follows either a polar or a free-radical pathway, depending on substituents and conditions.[17] In contrast to this result, the present hydrostannylation reaction of alkynes with **2** proceeds without any catalyst, although alkyne insertion into transition metal–hydride bonds is well established.[18]

Compound **2** reacts with MeC≡CCO$_2$Et and MeO$_2$CC≡CCO$_2$Me at room temperature to form stannylenes **7** and **8**

(Scheme 3), respectively. The ^{1}H NMR spectrum of **7** shows a broad resonance ($\delta = 6.64$ ppm), which can be tentatively assigned to the vinyl proton. The IR spectrum of this compound exhibits a strong band at 1686 cm^{-1}, which can be tentatively assigned to the carbonyl group. The crystal structure of **7** (Figure 4)[11] reveals a *cis* orientation of the tin and hydrogen atom across the double bond and crystallizes in the triclinic space group $P\bar{1}$. In solution, only one isomer is detected, indicating that **7** is obtained by 1,2-*syn*-addition of **2** to the alkyne, which results in the transfer of the hydrogen atom and stannylene across the carbon–carbon triple bond.



2

R = Me, R' = Et; (**7**)
R = CO$_2$Me, R' = Me; (**8**)

Scheme 3. Preparation of **7** and **8**. Ar = 2,6-iPr$_2$C$_6$H$_3$

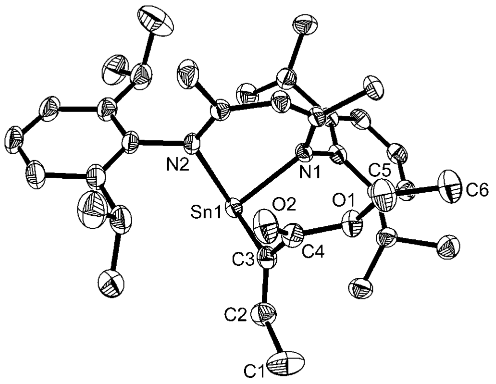
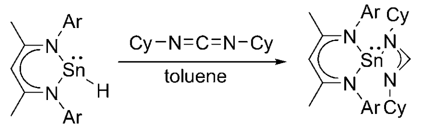


Figure 4. Molecular structure of **7**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity reasons.Selected bond lengths [Å] and angles [°]: Sn1–C3 1.942(8), C3–C2 1.335(4), C4–O2 1.2101(3), Sn1–N1 2.1990(19), Sn1–N2 2.199(2); Sn1-C3-C2 114.13(19), Sn1-C3-C4 127.37(13), N2-Sn1-N2 86.31(8).

Compound **2** reacts with $MeO_2CC{\equiv}CCO_2Me$ in toluene at room temperature to form both the *E* and *Z* stannylene-substituted alkenes in a 1:0.7 ratio (calculated by integration of all ^{1}H resonance peaks as well as the ^{119}Sn resonance). The ^{1}H NMR spectrum of **8** exhibits two singlets ($\delta = 6.93$ and 6.27 ppm), which are situated between Sn satellite peaks with two different coupling constants (21.6 and 23.5 Hz). The ^{119}Sn NMR signals of the two isomers appear at $\delta = -132$ and -211 ppm, respectively.

The reaction of **2** with compounds containing C–N multiple bonds was studied by its reaction with dicyclohexyl carbodiimide (DCC) (Scheme 4). This reaction proceeded rapidly and quantitatively at room temperature to give the spirocyclic compound **9**, which contained the four- and six-membered heterocycles of composition C_3N_2Sn and CN_2Sn. In the ^{1}H NMR of **9**, the CH proton of the four-membered ring gives rise to a singlet ($\delta = 8.30$ ppm) and other resonances as expected while the ^{119}Sn NMR signal appears at $\delta = -175$ ppm.



2 **9**

Scheme 4. Preparation of **9**. Ar = 2,6-iPr$_2$C$_6$H$_3$

In summary, a number of reactions of [LSnH] (**2**) with compounds containing unsaturated C–O, C–C, and C–N bonds resulted in simultaneous hydrogen and {LSn} transfer to the organic substrates. Compounds **3**–**9** represent a unique new class of stannylene compounds with an electron lone pair on tin(II) that is suitable for complexation with transition metal fragments. Moreover, most of these compounds are stable to air and moisture.

Received: November 16, 2008

Keywords: alkynes · carbonyl compounds · hydrides · hydrostannylation · tin

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