Synthesis, Structure, Electrochemistry and Reactivity of the Bis(μ-σ-stannanediyl)dinickel Butterfly Cluster $[\{\{(SiMe_3)_2CH\}_2Sn–Ni(\eta^5\text{-}Cp)\}_2](Ni_2–Sn_2)$

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Addition of stannylene $[\{(SiMe_3)_2CH\}_2Sn{:}]$ (**2**) to the unbridged homobimetallic Ni–Ni bond of $[\{PEt_3Ni(\eta^5\text{-}Cp)\}_2]$ (**1**) gives the heterobimetallic, tetranuclear compound $[\{\{(SiMe_3)_2CH\}_2Sn–Ni(\eta^5\text{-}Cp)\}_2]$ (**3**) with a butterfly arrangement and leaves the Ni–Ni bond of **1** intact. Elimination of both PEt_3 ligands from the starting material **1** is observed, probably due to steric restraints. Compound **3** is formally related to the hypothetical *closo*-borane $B_4H_4^{2-}$. The Ni–Ni bond in **3** is only slightly elongated [2.454(3) Å] when compared to the starting material **1** [2.41(1) Å]. Compound **3** displays a butterfly arrangement with a hinge angle of 62.5°. An alternative route to **3** is by a direct reaction between nickelocene (**5**) and Lappert's stannylene $[\{(SiMe_3)_2CH\}_2Sn{:}]$ in 63% yield. Treating **3** with water results in the cleavage of an Ni–Sn bond and subsequent opening of the cluster cage of **3** to form the trinuclear compound $[(\eta^5\text{-}Cp)Ni\{Sn(CH(SiMe_3)_2\}_2OH]$ (**6**) having an Sn–OH–Sn bridge. The hydroxy proton in **6** can be exchanged by deuterium within a few minutes, as determined by ^{1}H-NMR spectroscopy, giving the monodeuterio product, $[D_1]$-**6**. Compound **6** is reactive towards acetonitrile, leading to cleavage of one Ni–Sn bond, elimination of one $[\{(SiMe_3)_2CH\}_2Sn{:}]$ unit, and formation of the organotin hydroxo complex $[\{(SiMe_3)_2CH\}_2(OH)Sn–Ni(\eta^5\text{-}Cp)(CH_3CN)]$ (**7**). In this complex, acetonitrile is coordinated to Ni via its σ lone pair, bearing the OH ligand in a terminal bonding mode to tin.

Introduction

Unbridged transition metal bonds (M−M) exhibit a high reactivity towards insertion and addition reactions of metal ligand fragments, especially when the M−M bond is polarized.[1] For complexes containing homo-metallic M−M bonds as in $L_xM{-}ML_x$-type dimers, usually little or no electronic polarization effects are available to enhance the reactivity of the particular M−M bond. Drastic reaction conditions are therefore often necessary to enhance the reactivity of these M−M bonds towards insertion or addition reactions. A unique way to activate homometallic M−M bonds and to increase their reactivity towards further reaction is to sterically overcrowd the ligand periphery L at each L_xM fragment. This results in a substantial weakening of M−M bonding, an increased reactivity, and consequently an easy homolytic scission of the M−M bond in such complexes.

We are interested in the reactivity of the dimer $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2]$ (**1**) containing an unbridged Ni−Ni bond.[2] Although the M−M bond in **1** is in the usual range for an Ni−Ni single bond and shows no significant elongation, **1** displays an unusually high reactivity with respect to a scission of its unbridged Ni−Ni bond.[2][3] This is a result of the sterically crowded situation at both Ni atoms of **1**, as revealed by X-ray crystallography and by ^{1}H-NMR spectroscopy in solution.[2] Rotation of the PEt_3 ligand around the Ni−Ni bond vector is restricted, even in solution, due to steric hindrance. This sterically encumbered ligand situation in **1** gives rise to cleavage of the Ni−Ni bond and insertion of a variety of low-valent main-group-element compounds.[2][3] For example, group-14 chloride $SnCl_2$, displaying carbenoid character, inserts into the Ni−Ni bond of **1** giving $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_2SnCl_2]$. Subsequent dehalogention leads to the stannio(IV) monochloride complex $[\{(\eta^5\text{-}Cp)Ni(PEt_3)\}_3SnCl]$.[2] In our work reported here, we set out to find new synthetic entries into Ni/Sn organometallics by direct insertion routes into the M−M bond of **1**. Such Ni/Sn organometallics might be valuable single-source target compounds in MOCVD processes for the preparation of Ni/Sn intermetallics, which recently gained interest with respect to the nature of intermetallic phases like NiSn and Ni_3Sn_2.[4] Further interest is in their use as single-source precursors in bimetallic silica-supported catalysts based on a combination of Ni−Sn, Pd−Sn and Pt−Sn, which up to now are only accessible from a mixture of Sn and M (M = Ni, Pd, Pt) molecular precursors.[5a] Such bimetallics have potential in CO oxidation reactions.[5a] In addition, Ni/Sn intermetallics have proven their catalytic properties as cyclohexane dehydrogenation catalyst.[5b]

A number of transition metal complexes of stannanediyls $:SnR_2$ are known so far, and have proven their versatility for coordination of transition metals.[6] We have choosen Lappert's bis{bis(trimethylsilylmethyl)tin} $[\{\{(SiMe_3)_2CH\}_2Sn\}_2]$ (**2**),[7] as candidate for introducing an organic

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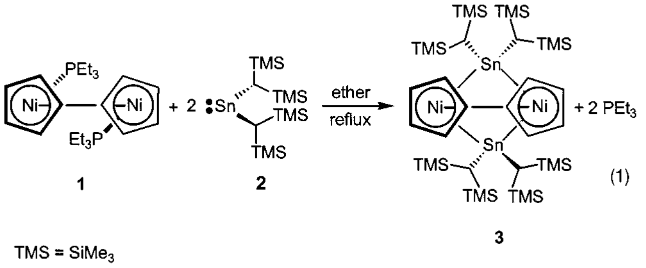
SnR_2 group into transition metal compounds under mild conditions. We have recently shown that addition of elemental Se and Te towards the unbridged Co−Sn bond of $[\{(SiMe_3)_2CH\}_2Sn-Co(\eta^2\text{-ethene})(\eta^5\text{-Cp})]$, derived from reaction of **2** with $[(Cp)Co(ethene)_2]$, leads to unique ternary Co/Sn/E organometallics.[8]

We describe here, our studies on the reactivity of Lappert's bis(stannanediyl) **2** towards the Ni−Ni bond of **1**, leading to the formation of a bimetallic Ni−Sn complex **3** with a *closo* cage structure; **3** is formed by the addition of subvalent SnR_2 fragments to the Ni−Ni bond of **1**. The electrochemistry of **3** and of its cage-opened product **6** is reported. In addition, the reactivity of **1** towards cage opening with water as a nucleophile and subsequent further reactivity of this product with acetonitrile is studied.

Results and Discussion

Reaction of $[\{(\eta^5\text{-Cp})Ni(PEt_3)\}_2]$ (1) with $[\{\{(SiMe_3)_2CH\}_2Sn\}_2]$ (2)

Over the course of several days, **1** does not react with **2** at ambient temperature in diethyl ether. However, reflux conditions in diethyl ether for 12 h led to a color change of the initially deep green reaction solution to brown. Workup by crystallization (from ether) gave brown-green crystals of **3** in 50% yield (Equation 1).



According to ^1H and ^{13}C NMR, **3** is diamagnetic and does not contain any signals corresponding to the PEt_3 ligands originally present in the starting complex **1**. This result is confirmed by mass-spectrometric studies which show the molecular peak of **3** at m/z = 1122, with a correct isotropic pattern corresponding to the composition Ni_2Sn_2 (Figure 1). Figure 1 clearly indicates that **3** is thermally robust, propably leaving the Ni_2Sn_2 metal core intact upon vaporization. This is of significance for further MOCVD applications of this compound.

Definitive proof of the spectroscopic data, especially the loss of the PEt_3 ligand came from a single-crystal X-ray investigation, which showed **3** to be indeed a dinickel complex (Figure 2).[9] Two $\{CH(SiMe_3)\}_2Sn$ fragments bridge two 15e-$\{(\eta^5\text{-Cp})Ni\}$ fragments, resulting in a tetrameric Ni_2Sn_2 metal core. The metal atoms show a butterfly arrangement with a hinge angle of 62.5(4)°. The two tin atoms display a distorted tetrahedral geometry with significantly compressed bond angles $\{Si(CH_3)_3\}_2HC-Sn-CH\{Si(CH_3)_3\}_2$, e.g. C6−Sn−C7 102.9(2)°. A characteristic feature of the structure of **3** is the Ni−Ni bond, which is only slightly elongated when compared to the Ni−Ni bond in the starting material **1**. [2.41(1) Å[2] vs. 2.454(3) Å]. Obviously, the steric repulsion upon addition of two $:SnR_2$ stannylene fragments to the Ni−Ni bond has only a minor impact on the geometry of **3**. The Ni−Sn bond length is well in accord with the Ni−Sn bond in $[(\eta^5\text{-Cp})Ni)\{(\mu\text{-}\eta^1\text{:}\eta^1\text{-}$

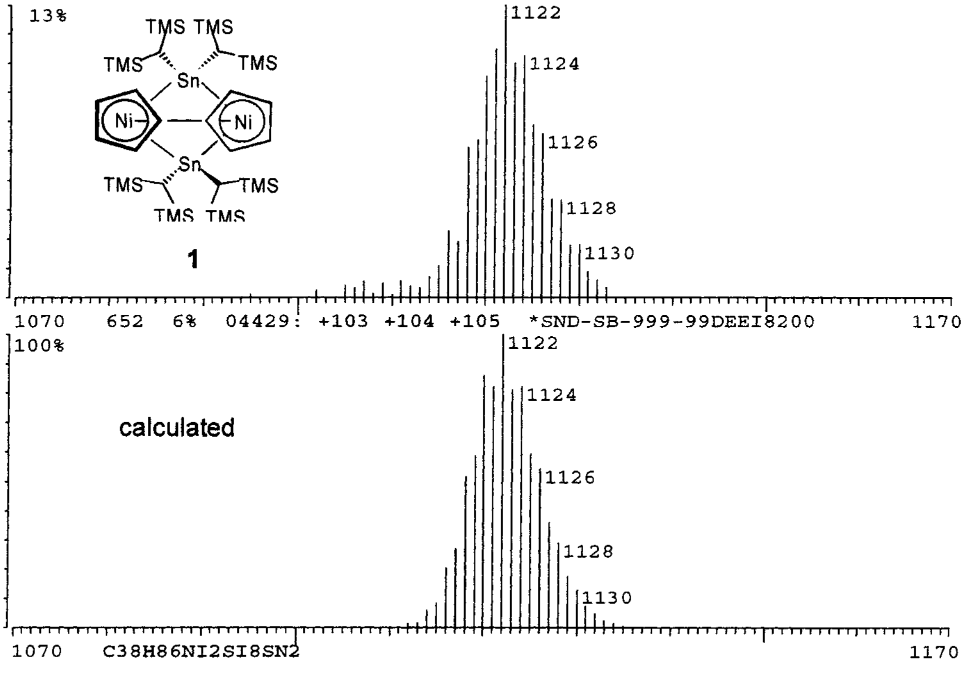


Figure 1. Top: experimental isotopic pattern of the molecular ion peak of **3**; bottom: calculated isotopic pattern for the molecular ion of composition $C_{38}H_{86}Ni_2Si_8Sn_2$

Cp){Sn(*N*(*t*Bu))$_2$SiMe$_3$}$_2$}] (**4**)[12] (Figure 3), containing a somewhat similar {(η^5-Cp)Ni−SnR$_3$} unit with a tetracoordinated Sn atom. The distance between the two tin atoms in **3** is 3.72 Å.

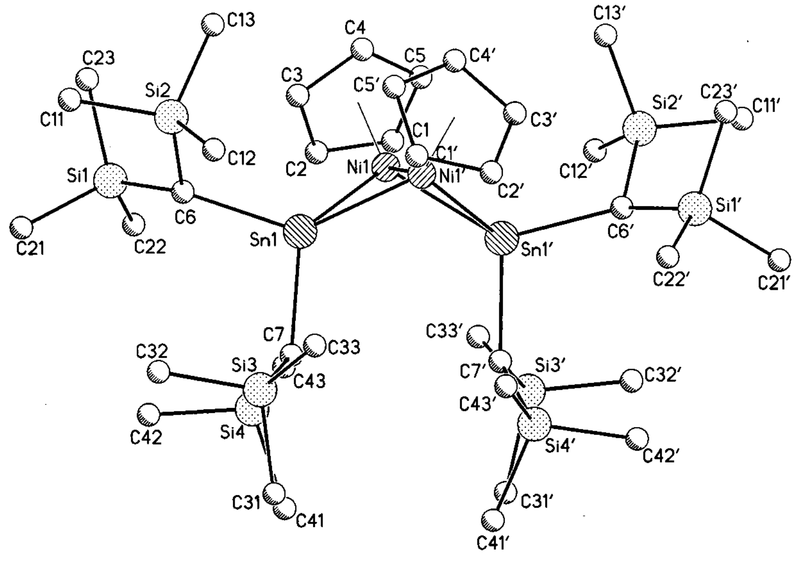
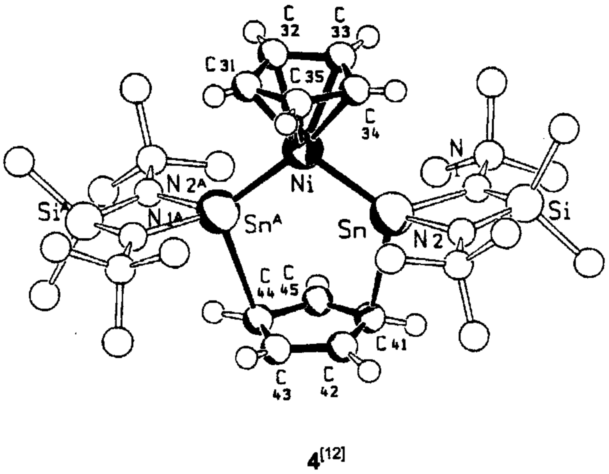


Figure 2. Molecular structure of **3** in the solid state; selected bond lengths [Å] and angles [°]: Sn−Ni 2.502, Ni−Ni 2.454, Sn−C7 2.208(6), Sn−C6 2.230(6), Ni−X1A (1B) 1.74; C6−Sn−C7 102.9(2), Ni−Sn−Ni′ 58.7(1), Sn−Ni−Sn′ 96.2(1)



4[12]

Figure 3. Molecular structure of **4** (reproduced from ref.[12] with permission)

Equation 1 represents a rare case of addition of stannylene fragments SnR$_2$ towards an unbridged M−M bond.[13][14] For electron bookkeeping sake, **3** formally represents a hetero-*closo* structure according to Wade's rules.[15] Taking into account that **3** does not contain any PEt$_3$ ligands (originally present in the starting material **1**), finding a direct synthesis to **3** was challenging. Stannylenes **:**SnR$_2$ are either able to react as donor or acceptor molecules due to their carbenoid character and the electron-accepting empty π orbitals on tin. Electron-rich metallocenes like nickelocene (**5**) offer either acidic metal sites or basic ligand sites, at which substitution chemistry may proceed (Figure 4). We therefore found that **5** reacts with **2** in ether, under reflux conditions, to give brown crystals of **3** in 65% (Equation 2).

In contrast to Equation 1, formation of **3** here proceeds by addition of two electronically unsaturated 15e-{CpNi} fragments, generated thermally from nickelocene, to give the tetranuclear Ni$_2$Sn$_2$ cluster **3**. Veith and Stahl reported a similar reaction of nickelocene with the N-donor-substituted, but more basic, stannylene [Sn(N*t*Bu)$_2$SiMe$_2$}] to yield **4**.[12] Consequently, this reaction resulted in an attack of this stannylene at the acidic Ni center and formal insertion of a stannanediyl fragment into the nickelocene sandwich structure. Obviously, the bis(silyl)stannylene [:Sn{CH(SiMe$_3$)$_2$}$_2$] (**2**) is basic enough to follow this reaction pathway.

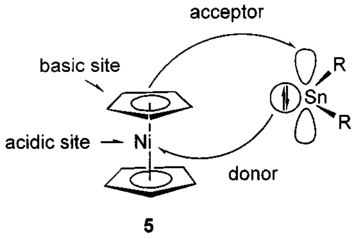
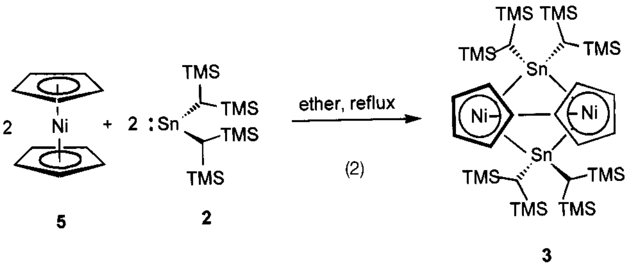


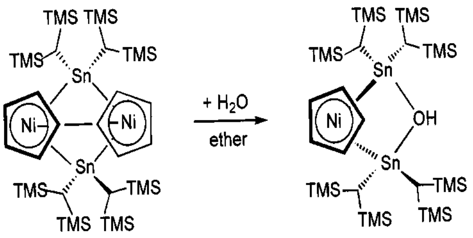
Figure 4. Different reaction sites of nickelocene with an amphiphilic Lewis acid/base stannylene ligand **:**SnR$_2$



With respect to the reactivity of **3**, we observed that if a mixture of **1** and **2** (Equation1) containing **3** is not directly crystallized from the initial reaction mixture, but still further purified by column chromatography (SiO_2, pentane), aside from **3**, a second compound **6** can be isolated in varying yields. The yield of **6** depends on the chromatography time and age of the stationary SiO_2 phase used. Older charges of SiO_2 containing higher water contents, consequently gave higher yields of **6**. Compound **6** was characterized by spectroscopic data (NMR, MS, and IR). In the mass spectrum, the molecular base-peak for **6** is found at m/z = 1016, showing a characteristic Sn/Ni atom isotopic ratio of 2:1 and an initial mass loss of m/z = [1016 − 17], owing to the loss of an OH unit. The OH grouping shows up in the IR spectrum with a sharp OH stretching absorption at $\tilde{\nu}$ = 3623 cm^{-1}.

The ^1H-NMR spectrum of **6** gives a characteristic broad OH proton resonance at δ = 1.46 with a $^{119}J_{Sn-H}$ coupling of 12 Hz, which characterizes the Sn−OH−Sn bridge in **6**. Unambigous proof of this assignment and the existence of such a bridging μ-OH ligand came from a deuterium exchange experiment.

Addition of N_2-saturated D_2O to a freshly prepared NMR sample of **3** in N_2-saturated C_6D_6 resulted in a substantial broadening of the initially very sharp OH signal after 5 min contact time, and complete disappearance of the OH proton resonance signal after 30 min, indicating the formation of **5**[OD] by H/D exchange. The remaining proton signals in the ^1H-NMR spectrum broaden significantly but do not change their chemical shifts and relative intensity ratios.



3 **6** (3)

To prove the assumption that **6** is not a direct reaction product of **1** and **2**, but is indeed formed by reaction of **3** with water, which must then be responsible for the Ni−Sn bond cleavage of the *closo* cluster **3**, a direct reaction of **3** with H_2O was conducted (Equation 3).

Stirring of an ethereal solution of **3** with a fourfold excess of N_2-saturated H_2O resulted in a color change from brown to red-brown within a few minutes. Workup furnished **6** as brown crystals in 63% yield. All spectroscopic data of **6** obtained by this independent route are in accord with the material obtained by chromatography of **3** on wet SiO_2 as described before. As a result of these experiments it is obvious that **3** is prone to the opening of the butterfly structure by oxidative addition of water. We found that **6** is also formed in a one-pot reaction by addition of excess water to a reaction mixture of **5** and **2** under reflux conditions, followed by subsequent crystallization of the crude material from ether.

A preliminary X-ray crystallographic study of **6** confirms the connectivity of the heavy-atom skeleton containing Sn and Ni, as well as the complete silicon/carbon framework. However, the μ-OH bridge could not be unambigously pinpointed due to the poor crystal quality of **6** obtained so far.[16]

Electrochemistry of 3 and 6

Figure 5 shows the cyclic voltammetric profiles exhibited by complexes **3** and **6** in dichloromethane solution. The dinickel complex **3** displays a rather complicated oxidation pathway (Figure 5, upper trace), in which only the first anodic step exhibits features of transient chemical reversibility (Figure 5, lower trace left). In contrast, the mononickel complex **6** undergoes a single oxidation process, chemically reversible in character on the cyclic voltammetric timescale (Figure 5, right trace).

Controlled potential coulometry (E_w = +0.5 V) showed that the oxidation of **6** involves the removal of one electron/molecule. The solution resulting from exhaustive oxidation

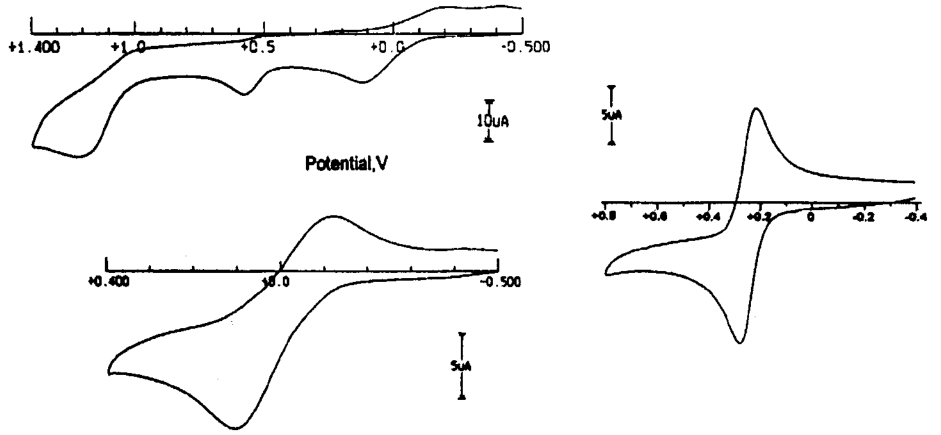


Figure 5. Cyclic voltammetric responses recorded at a platinum electrode in CH_2Cl_2 solutions containing $[Bu_4N][PF_6]$ (0.2 mol dm^{-3}) and **3** (9×10^{-4} mol dm^{-3}) (upper and lower left trace) or **6** (7×10^{-4} mol dm^{-3}) (right trace)

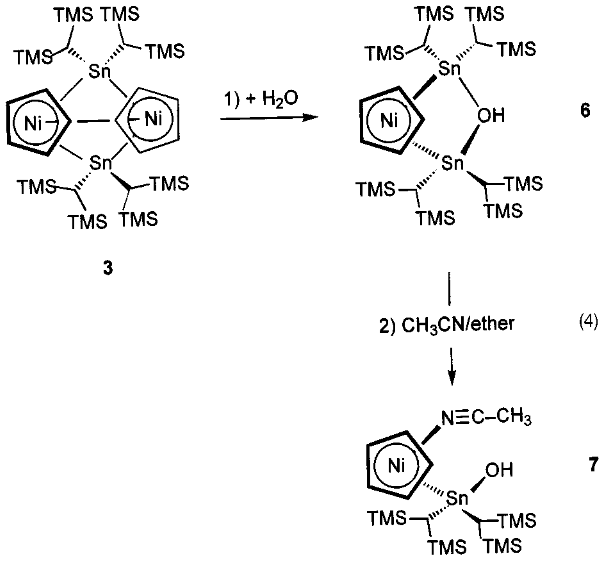
exhibits a cyclic voltammetric profile quite complementary to the original one, thus testifying the chemical reversibility of the redox change **6**/**6**$^+$ ($E^{\circ\prime} = +0.25$ V) also during the long times of macroelectrolysis.

The analysis of the cyclic voltammograms of **6** with the scan rate varying from 0.02 Vs^{-1} to 1.00 Vs^{-1} indicates that the anodic step is substantially reversible also from the electrochemical viewpoint, in that the peak-to-peak separation, particularly at slow scan rates, deviates slightly from the theoretical value of 60 mV.[17] For instance, at 0.05 Vs^{-1} it is equal to 70 mV, quite paralleling the value we obtain for the one-electron oxidation of ferrocene under the same experimental conditions ($E^{\circ\prime} = +0.38$ V). In this picture, the electrochemical reversibility suggests that no significant structural reorganization should accompany the electron removal from **6**.

As far as complex **3** is concerned, we limited our study to the first, partially reversible anodic step (at 0.05 Vs^{-1}, $i_{pc}/i_{pa} = 0.7$; $E^{\circ\prime} = -0.01$ V). Controlled potential coulometry ($E_w = +0.2$ V), even if affected by severe electrode-poisoning phenomena which required repeated cleaning of the electrode surface, seems to involve one electron/molecule. It is important to take into account that after completion of electrolysis a number of new waves appear, which testify the occurrence of framework-destroying processes, but none of this was attributable to the **6**/**6**$^+$ system. This means that the redox-induced cleavage of the cage of **3**, in spite of the unavoidable presence of traces of water in solution, follows a path different from that illustrated in Equation 3.

Reactivity of 6 Towards CH_3CN

The Sn−OH−Sn bridge in **6** is reactive, and can be opened by a nucleophilic attack, e.g. by acetonitrile. Addition of a large excess of CH_3CN to an ethereal solution of **6** results in a color change from brown-red to blood-red. Prolonged cooling (weeks) of this solution eventually results in brick-red rectangular-shaped crystals of **7** containing a terminal *Ni*-bonded $\{Sn\{CH(TMS)_2\}_2\}OH$ ligand, and a CH_3CN ligand according to spectral data (see Experimental Section) (Equation 4). The OH stretching frequency of **7** at $\tilde{\nu} = 3624$ cm^{-1} is well in accord with the one observed for **6**.



The molecular structure of **7** in the solid state was determined by X-ray crystallography[9] and displays a two-legged piano-stool geometry at the Ni center (Figure 6), with a trigonal planar structure at Ni as its most prominent feature. The tin atom is coordinated in a strongly distorted tetrahedral environment. The Sn−O bond length [2.017(2) Å] points towards an Sn=O π-bond contribution as it is discussed for $[\{SnR_2(OH)\}_2(\mu\text{-}O)]$ containing a μ-Sn−O−Sn bridge, and two terminal Sn−OH groups [2.032(5) Å].[18] In contrast to **7**, organotin hydroxides often have a bridging OH as in **6** or $[Sn(\mu\text{-}OH)(phenyl)_3]_\infty$.[19] Besides $[\{SnR_2(OH)\}_2(\mu\text{-}O)]$,[18] tris(tropolone)tin hydroxide[20] and $[\{CH(SiMe_3)_2\}_2Sn(H)(OH)]$,[21] **7** represents another rare case of a compound having a terminal OH functionality.

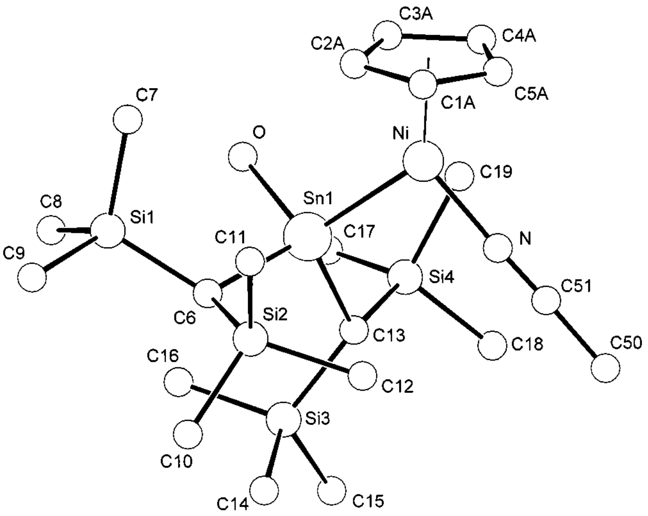


Figure 6. Molecular structure of **7** in the solid state; selected bond lengths [Å] and angles [°]: Ni−Sn 2.472(1), Ni−N 1.829(3), Sn−C13 2.209(3), Sn−C6 2.203(3), Sn−O 2.017, N−C51 1.138(5); C13−Sn−C6 109.3, O−Sn−Ni 109.6(1), C13−Sn−O 102.0(1), O−Sn−C6 102.5(2), C13−Sn−Ni 112.0(2), C6−Sn−Ni 119.6(1), N−Ni−Sn 93.7(1)

Conclusion

Bulky SnR_2 fragments are able to add to the Ni−Ni bond of **2**, forming the tetranuclear Ni_2Sn_2 cluster **3** with a *closo* cage structure. However, steric demands require that both PEt_3 ligands are eliminated in this addition/elimination-type reaction. A novel feature in this complex is the bulky R_2Sn-bridged Ni−Ni bond which is without precedent so far. Compound **3** displays reactivity towards cage opening with H_2O, leading to the trinuclear μ-OH bridged complex **6**. SnR_2 elimination and cleavage of the μ-OH bridge in **3** can be achieved by reaction with acetonitrile. The free coordination site generated by this cleavage is occupied by a σ-donor N→Ni dative bond of the CH_3CN

ligand to the Ni atom. The fact that **3** can be obtained in high yield under mild conditions and is prone to cage opening of its Ni_2Sn_2 skeleton offers some useful features for further studies. It can be envisaged that addition of various nucleophiles other than H_2O are also able to open a synthetic useful pathway into new Ni−Sn organometallics by the cage-opening reaction route of **3**.

The 1:1 Ni/Sn stoichiometry of **3**, as well as its promising evaporation characterictics (10^{-2} Torr/100°C, without decomposition) make **3** an outstanding candidate as single-source precursor to intermetallic nanostructured binary Ni/Sn phases[4][22] by MOCVD techniques. Very recently we have shown that the presence of the bulky mixed hydrocarbyl/organosilyl ligand $\{CH(SiMe_3)_2\}$ in volatile organo-bimetallic main-group complexes is in no way detrimental towards a succesful MOCVD application of organometallic complexes containing this ligand.[23]

Experimental Section

General: All reactions were carried out under dry nitrogen with standard Schlenk techniques. Compounds **1** and **2** were prepared according to published procedures.[2][6] − Microanalyses were performed by the microanalytical laboratory of the Chemistry Department of the University−GH Essen. − All solvents were dried appropriately and were stored under nitrogen. − The NMR spectra were recorded with a Bruker AC 300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C) and referenced against the remaining protons of the deuterated solvent. NMR samples were prepared by vacuum transfer of solvents onto the appropriate amount of solid sample, followed by flame sealing of the NMR tube. − MS spectra were recorded with a MAT 8200 instrument using standard conditions (EI, 70 eV) and the fractional sublimation technique for compound inlet. − Materials and apparatus for electrochemistry and coupled EPR spectroscopy have been described elsewhere.[24] − Either a BAS 100 A or a BAS 100 W were used in cyclic voltammetric measurements. The potential values reported refer to the saturated calomel electrode (SCE).

Synthesis of $[\{\{(SiMe_3)_2CH\}_2Sn{-}Ni(\eta^5\text{-}Cp)\}_2]$ (3)

A: By Reaction of 1 and 2: To a solution of 700 mg (1.44 mmol) of **1**, dissolved in 100 mL of diethyl ether, was added 1.26 g (1.44 mmol) of dimeric stannanediyl $[\{Sn\{CH(SiMe_3)_2\}_2\}_2]$ (**2**). This solution was refluxed for 24 h resulting in a color change from green-brown to brown. After removal of all volatiles in vacuum, the remaining solid was dissolved in pentane and this solution was filtered. Crystallization at −30°C during the course of several days gave brown crystals of **3** (0.73 mmol, 51%). − MS (EI, 70 eV, T_{vap} = 140°C); m/z (%): 1122 (40) [M^+], 963 (30), [M^+ − $CH(SiMe_3)_2$], 685 (15) [M^+ − $Sn\{CH(SiMe_3)_2\}_2$]. − ^{1}H NMR ($[D_6]$benzene): δ = 5.30 (s, Cp, 10 H), 2.46 (s, CH, 4 H), 0.32 [s, ^{1}J(Si,H) = 6.0 Hz, $SiMe_3$, 72 H]. − $\{^1H\}^{13}C$ NMR ($[D_6]$benzene): δ = 89.12 (s, Cp), 7.91 (s, CH), 5.95 (s, $SiMe_3$) − $C_{38}H_{86}Ni_2Si_8Sn_2$ (1122.58): calcd. C 40.64, H 7.70; found C 40.90, H 7.65.

B: By Reaction of 4 and 2: To a solution of **4** (1.0 g, 5.30 mmol), dissolved in 150 mL of ether, was added 2.32 (2.65 mmol) of $[\{Sn\{CH(SiMe_3)_2\}_2\}_2]$ (**2**). This solution was refluxed for 3 d. Evaporation of all volatiles in vacuum and recrystallisation of the crude residue from pentane gave 1.94 g (1.73 mmol, 64%) of brown crystals of **3**.

Synthesis of $[(\eta^5\text{-}Cp)Ni(\mu\text{-}OH)\{Sn(CH(Si(CH_3)_3)_2)_2\}_2]$ (6): A fourfold excess of N_2-saturated H_2O was added a solution of **3** in diethyl ether {prepared from 0.571 mmol of $[\{Sn\{CH(SiMe_3)_2\}_2\}_2]$ (**2**) and 1.14 mmol of **4**}. After stirring the initial brown solution for about 5 min, a color change to bright red was observed. Additional stirring for 2 h, followed by vacuum removal of all volatiles and recrystallization of the crude residue from diethyl ether at −30°C, gave 368 mg (0.363 mmol, 64%) of **6**. − MS (EI, 70 eV, T_{vap} = 130°C); m/z (%): 1016 (20) [M^+], 999 (10) [M^+ − OH] 857(30), [M^+ − $CH(SiMe_3)_2$], 697(100), [M^+ − $[CH(SiMe_3)_2]_2$]. − IR (KBr): $\tilde{\nu}$ = 3623 cm^{-1} (s) (OH), 2949 (s), 2898 (s), 1402 (s), 1250 (s), 839 (br.), 784 (br.) (all tms), 1348 (s), 1315 (s), 1294 (s), 1139 (s), 959 (s) [all Cp]. − ^{1}H NMR ($[D_6]$benzene): δ = 5.23(s, Cp, 5 H), 1.46 [br. s, $^{2}J(^{119}Sn,H)$ = 12 Hz, OH, 1 H], 0.67 (s, CH, 4 H), 0.42 (s, $SiMe_3$, 36 H), 0.24 (s, $SiMe_3$, 36 H). − $\{^1H\}^{13}C$ NMR ($[D_6]$benzene): δ = 88.4 [s, $^{2}J(^{119}Sn,C)$ = 19 Hz, Cp], 20.66 (s, CH), 5.17 [s, ^{3}J(Sn,C) = 15 Hz, $SiMe_3$], 4.29 [s, $^{3}J(^{119}Sn,C)$ = 15 Hz, $SiMe_3$]. − $C_{33}H_{82}NiOSi_8Sn_2$ (1015.79): calcd. C 39.00, H 8.14, found C 39.06, H 8.15.

Synthesis of $[(\eta^5\text{-}Cp)(CH_3CN)Ni{-}Sn(OH)\{CH(Si(CH_3)_3)_2\}_2]$ (7): A fourfold excess of N_2-saturated H_2O was added to a solution of **3** in 50 mL of diethyl ether {prepared from 0.571 mmol of $[\{Sn\{CH(SiMe_3)_2\}_2\}_2]$ (**2**) and 1.14 mmol of **4**}. After stirring of the initial brown solution for about 5 min, a color change to bright red was observed. After additional stirring for 2 h, 25 mL of ether was removed under vacuum and replaced by 20 mL of acetonitrile. This solution was filtered and stored for two weeks at −20°C whereupon 730 mg (0.72 mmol, 79%) of brick-red crystals of **7** could be isolated, co-crystallized with 220 mg (0.25 mmol) of **1**. These two compounds were then separated mechanically. − ^{1}H NMR ($[D_6]$benzene): δ = 5.29 (s, Cp, 5 H), 1.48 (br. s, J = 24 Hz, OH, 1 H), 0.78 (s, $C{-}CH_3$, 3 H), 0.43 (s, $SiMe_3$, 36 H). − $\{^1H\}^{13}C$ NMR ($[D_6]$benzene): δ = 94.48 (s, C_{Sp}), 88.58 [s, Cp, ^{2}J(Sn,C) = 14.3 Hz], 20.88 [s, CH, $^{1}J(^{119}Sn,C)$ = 117 Hz, ^{1}J(Si,C) = 39.0 Hz], 5.36 [s, $SiMe_3$, ^{3}J(Sn,C) = 16 Hz]. − IR (KBr): $\tilde{\nu}$ = 3624 cm^{-1} (OH), 3220, 2271, 1371 (CH_3CN), 2947, 2923, 2894, 1249, 1015, 841, 663, 608, 521 (all tms), 3088, 2961, 2835, 1400, 1346, 1292, 1242, 1108, 779 (all Cp).

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[1] [1a] D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41. − [1b] S. Friedrich, H. Memmler, L. H. Gade, W.-S. Li, M. McPartlin, *Angew. Chem.* **1994**, *106*, 705; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 676. − [1c] S. Friedrich, L. H. Gade, I. J. Scowen, M. McPartlin, *Angew. Chem.* **1996**, *108*, 1440; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1338. − [1d] S. Friedrich, L. H. Gade, I. S. Scowen, M. McPartlin, *Organometallics* **1995**, *14*, 5344. − [1e] D. Selent, R. Beckhaus, J. Pickart, *Organometallics* **1993**, *12*, 2857. − [1f] L. H. Gade, *Angew. Chem.* **1996**, *108*, 2226; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2089. − [1g] G. Jansen, M. Schubert, B. Findeis, L. H. Gade, I. J. Scowen, M. Mc. Partlin, *J. Am. Chem. Soc.* **1998**, *120*, 7239.

[2] U. Denninger, J. J. Schneider, G. Wilke, R. Goddard, C. Krüger, *Inorg. Chim. Acta* **1993**, *213*, 129.

[3] J. J. Schneider, U. Denninger, J. Hagen, C. Krüger, D. Bläser, R. Boese, *Chem. Ber.* **1997**, *130*, 1433.

[4] G. Schwitzgebel, R. Mildenberger, *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 1742.

[5] [5a] J. Arana, P. Ramirez de la Piscina, J. Llorca, J. Sales, N. Homs, *Chem. Mater.* **1998**, *10*, 1333. − [5b] A. Onda, T. Komatsu, T. Yashima, *J. Chem. Soc., Chem. Commun.* **1998**, 1507.

[6] [6a] J. D. Cotton, P. J. Davidson, D. E Goldberg, M. F. Lappert, K. M. Thomas, *J. Chem. Soc., Chem. Commun*. **1974**, 893. − [6b] J. D. Cotton, P. J. Davidson, M. F. Lappert, *J. Chem. Soc., Dalton. Trans.* **1976**, 2275. − [6c] C. Pluta, K. R. Pörschke, R. Mynott, P. Betz, C. Krüger, *Chem. Ber.* **1991**, *124*, 1321. − [6d] W. E. Piers, R. M. Whittal, G. Ferguson, J. F. Gallagher, R. D. J. Froese, *Organometallics* **1992**, *11*, 4015. − [6e] J. Krause, K. H. Haack, K.-R. Pörschke, B. Gabor, R. Goddard, C. Pluta, K. Seevogel, *J. Am. Chem. Soc.* **1996**, *118*, 804. − [6f] F. Schager, K. Seevogel, K.-R. Pörschke, M. Kessler, C. Krüger, *J. Am. Chem. Soc*. **1996**, *118*, 13075. − [6g] M. F. Lappert, R. S. Rowe, Coord. *Chem. Rev.* **1990**, *100*, 267. − [6h] P. B. Hitchcock, M. F. Lappert, S. A. Thomas, A. J. Thorne, *J. Organomet. Chem.* **1986**, *315*, 27. − [6i] P. B. Hitchcock, M. F. Lappert, M. C. Misra, *J. Chem. Soc., Chem. Commun.* **1985**, 863. − [6j] P. B. Hitchcock, M. F. Lappert, S. A. Thomas, A. J. Thorne, A. J. Carthy, N. J. Taylor, *J. Organomet. Chem*. **1986**, *315*, 27. − [6k] M. Weidenbruch, A. Stilter, K. Peters, H. G. von Schnering, *Chem. Ber*. **1996**, *129*, 1565. − [6l] M. Weidenbruch, A. Stilter, K. Peters, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1996**, *14*, 365. − [6m] M. Weidenbruch, A. Stilter, W. Saack, K. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1998**, *560*, 125. − [6n] D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, *J. Chem. Soc., Chem. Commun.* **1976**, 261. − [6o] M. Weidenbruch, H. Kilian, K. Peters, H. G. von Schnering, H. Marsmann, *Chem. Ber.* **1995**, *128*, 983. − [6p] M. Veith, L. Stahl, V. Huch, *J. Chem. Soc., Chem. Commun.* **1990**, 359. − [6q] M. Veith, *Angew. Chem.* **1975**, *87*, 287; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 263; *Z. Naturforsch, Teil B*, **1978**, *33*, 7.

[7] [7] P. J. Davidson, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1973**, 317. − [7b] P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1976**, 2268. − [7c] J. D. Cotton, P. J. Davidson, M. F. Lappert, *J. Chem. Soc., Dalton. Trans.* **1976**, 2275.

[8] J. J. Schneider, J. Hagen, D. Bläser, C. Krüger, R. Boese, *Angew. Chem*. **1997**, *109*, 771; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 739.

[9] **Crystal Structure Analysis of 3:** Nicolet-Siemens R3 four-circle diffractometer with Mo-K_α radiation at 293 K. $C_{38}H_{86}Ni_2Si_8Sn_2 \cdot 1/2C_4H_{10}O$ (1159.65), crystal dimensions 0.47 × 0.38 × 0.31 mm, cell dimensions of the monoclinic system $a = 15.327(8)$, $b = 15.989(8)$, $c = 24.631(3)$ Å, $\beta = 94.56(4)°$, $V = 6017(5)$ Å^3, space group $C2/c$ with $Z = 4$, $D_x = 1.280$ g m^{-3}, $\mu = 1.620$ mm^{-1}, empirical absorption correction on ψ scans with Siemens-XEMP programme (V.4.20.2), min/max transmission 0.628/0.966, R_{int} before/after correction 0.0699/0.0206, 5461 intensities collected ($2\Theta_{max} = 55°$), 5315 unique [$R_{int}(F^2) = 0.0433$], 3907 observed [$F_o^2 \geq 2\sigma(F^2)$], structure solution (direct methods) with Siemens-SHELXS-86[10] and refinement (240 parameters, H atoms as riding groups, 1.2-fold isotropic U values, 1.5-fold for methyl groups of the corresponding C atoms) with SHELXL-97−1, $R1 = 0.0465$, $wR2$ (all data) = 0.1250, GoF = 1.046, $w^{-1} = \sigma^2(F_o^2) + (0.0718\ P)^2 + 0.1022\ P$, where $P = (F_{o,max}^2 + 2F_c^2)/3$, residual electron density 0.656 eÅ^{-3}. The atoms of a diethyl ether molecule C51, C52 and O50 are disordered around the cell origin, and were treated with half occupancy. − **Crystal Structure Analysis of 7:** Siemens SMART diffractometer (Mo-K_α radiation), T = 293 K; structure solution by heavy-atom method (SHELXS-86[10]) and structure refinement by SHELXL-93;[11] monoclinic, space group $P2_1/c$; lattice constants $a = 13.8547(14)$, $b = 12.0522(8)$; $c = 19.132(3)$ Å, $\beta = 99.350(8)°$, $V = 3152.2(6)$ Å^3, $Z = 4$, μ(Mo-K_α) = 1.554 mm^{-1}, crystal size 0.70 × 0.67 × 0.53 mm; $\theta_{max} = 27.46°$; 7203 independent reflections, 7768 measured of which 5942 were considered observed with $I > 2\sigma(I)$; residual electronic density 0.614 and −1.266 e/Å^3. 257 parameters (C, N, Ni, O and Si anisotropic). The Cp ring (C1a−C5a) is disordered. Individual positions could be resolved with occupancy factors of 1/2 (50%). Positions of the H atoms were calculated for idealized positions ($d_{C-H} = 0.980$ Å); $R_1 = 0.0398$; $wR^2 = 0.1245$. − Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102667 (**7**) and -114509 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

[10] G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Solution*, Universität Göttingen, **1986**.

[11] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, Universität Göttingen, **1993**.

[12] M. Veith, L. Stahl, *Angew. Chem*. **1993**, *105*, 123; *Angew. Chem. Int. Ed. Engl.* **1993**, *33*, 1731.

[13] C. J. Cardin, D. J. Cardin, H. E. Page, J. M. Power, *J. Chem. Soc., Chem. Commun*. **1984**, 609.

[14] [14a] Addition of stannanediyls **:**SnR_2 to unbridged M−M bonds is reported in: D. E. Westerberg, B. R. Sutherland, J. C. Huffmann, K. G. Caulton, *J. Am. Chem. Soc.* **1988**, *110*, 1642. − [14b] For an example of two $Sn\{CH(SiMe_3)_2\}_2$ fragments bridging two transition metal centers see: W. E. Piers, R. M. Whittal, G. Ferguson, J. F. Gallagher, R. D. J. Froese, *Organometallics* **1992**, *11*, 4015.

[15] K. F. Purcell, J. C. Kotz, *Inorganic Chemistry* W. B. Saunders, Philadelphia, **1977**.

[16] R. Boese, D. Bläser, J. J. Schneider, unpublished results, Universität Essen **1997**.

[17] E. R. Brown, J. R. Sandifer in *Physical Methods of Chemistry, Electrochemical Methods* (Eds.: B. W. Rossiter, J. F. Hamilton), Wiley, New York, **1986**, vol. 2, chapter 4.

[18] M. A. Edelman, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1990**, 1116.

[19] C. Glidewell, D. C. Lilles, *Acta Crystallogr., Sect. B* **1978**, *34*, 129.

[20] J. J. Park, D. M. Collins, J. C. Hoard, *J. Am. Chem. Soc*. **1970**, *92*, 3636.

[21] F. Schager, R. Goddard, K. Seevogel, K. R. Pörschke, *Organometallics* **1998**, *17*, 1546.

[22] T. T. Kodas, M. Hampden-Smith in *The Chemistry of Metal CVD* (Eds.: T. T. Kodas, M. J. Hampden-Smith), VCH, Weinheim, **1994**.

[23] [23a] J. J. Schneider, J. Hagen, G. Heinemann, J. Bruckmann, C. Krüger, *Thin Solid Films* **1997**, *304*, 144. − [23b] I. S. Chuprakov, K. H. Dahmen, J. J. Schneider, J. Hagen, *Chem. Mater.* **1998**, *10*, 3467.

[24] P. Barbaro, C. Bianchini, F. Laschi, S. Midollini, S. Moneti, G. Scapacci, P. Zanello, *Inorg. Chem.* **1994**, *33*, 1622.

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