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$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3(H_2O)Sn\}W(CO)_5]^+CB_{11}H_{12}^-$: Aqua Complex of a Transition-Metal-Bound Organotin(II) Cation versus an Ammonium-Type Structure

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The molecular structures of the intramolecularly coordinated tungstenpentacarbonyl organostannylene complexes 2,6-$(Me_2NCH_2)_2C_6H_3(Cl)SnW(CO)_5$ and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3\text{-}(H_2O)SnW(CO)_5]^+(CB_{11}H_{12})^-$ are reported. The latter compound is an aqua complex in which the water molecule replaces one of the two N→Sn coordination sites. The coordination of the water molecule is accompanied by proton transfer to the nitrogen atom. DFT calculations reveal this to be the thermodynamically most-stable structure.

Introduction

The synthesis of organometallic cations R_3E^+ of Group 14 elements [structure (a) in Figure 1] is a current topic of intensive research.[1] These analogues of carbenium ions that possess high electrophilicity have found applications in synthesis and catalysis.[1,2] On the other hand, and despite some early pioneering work on cyclopentadienyl- and *N*-isopropyl-2-(isopropylamino)troponimine-substituted RSn^{II+} and cyclophane-stabilized RGe^{II+} cations,[3] the chemistry of the organometallic as well as the inorganic divalent cations of Group 14 elements is yet to be explored in depth and remains a challenge for chemists. Concepts on how to stabilize such low-valent cations are shown in Figure 1 [structures (b)–(e)]. Recent milestones in this field came from the research groups led by Jutzi, Power, Driess, and Müller, who reported the synthesis of two-coordinate Si^{II} or Ge^{II} cations stabilized by sterically encumbered *β*-diketiminate ligands or by Power-type terphenyl anions.[4] Finally, the research in this field reached a temporary height with the work of Baines et al. on N-heterocyclic carbene- and cryptand-stabilized Ge^{II} cations.[5] Notably, already Rausch et al. reported (η^5-pentamethylcyclopentadienyl)-tin(II) tetrakis(pentafluorophenyl)borate to be an effective co-catalyst for Ziegler–Natta olefin polymerization, which demonstrates that low-valent Group 14 element cations are not only of academic interest but also have potential for application in valuable industrial processes.[6] Interestingly, we are aware of only three reports dealing with completely characterized transition-metal-coordinated divalent cations of Group 14 elements, namely *trans*-$[(MeCN)(dppe)_2WGe(\eta^1\text{-}Cp^*)][B(C_6F_5)_4]$,[7] $[L(OTf)Ge]W(CO)_5$ (L = NPhC(Me)CHC(Me)NPh)[8] and $[(Ph_2PCH_2CH_2PPh_2)_2WSnC_6H_3\text{-}2,6\text{-}Mes_2]PF_6$.[9]

For any group 14 element cation a high electrophilicity is to be expected, which in turn implies easy formation of (f)-type (Figure 1) aqua complexes provided that contact with air and moisture is allowed. Once such a complex is formed one has to consider the possibility that the base D deprotonates the coordinated water molecule to give an onium-substituted transition-metal-coordinated organoelement(II) hydroxide of type (g) (Figure 1).

As part of a comprehensive study on intramolecularly coordinated heteroleptic organostannylenes of the type RSn(L)X (L = lone pair, transition-metal fragment; X = electronegative substituent such as halide, SPh, PPh_2) that contain the N,C,N- and O,C,O-coordinating pincer-type ligands $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ and $[4\text{-}t\text{Bu-}2,6\text{-}\{P(O)(OiPr)_2\}_2C_6H_2]^-$,[7] we report here attempts to synthesize the corresponding cationic species RSn^+ and $[RSnW(CO)_5]^+$ that contain a σ-bonded aryl group. We failed for the former but succeeded in the isolation of the latter, as its aqua complex, and learned that in the solid state, it represents an intermediate between the (f)- and (g)-type structures. DFT calculations were applied to rationalize the results obtained.

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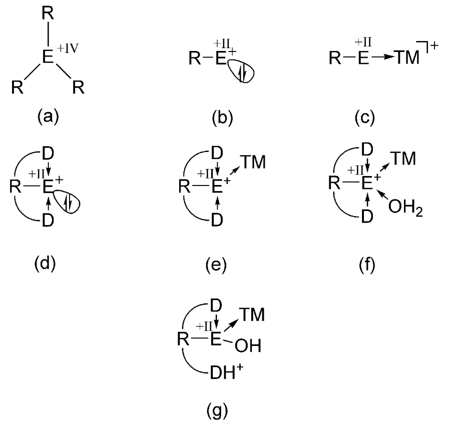
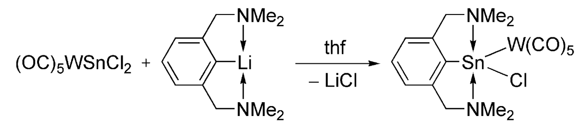


Figure 1. Organometallic cations with group 14 elements with the oxidation number (a) +IV and (b) +II; stabilization of a group 14 element cation in the oxidation state +II by (c) coordination to a transition metal or (d)intramolecular coordination; (e) combination of both possibilities; (f) formation of an aqua complex; (g) onium-substituted transition-metal-coordinated organoelement(II) hydroxide. (R: organic backbone; E: group 14 element; TM: transition metal; D: donor group such as NMe_2, PPh_2, OMe; SMe).

Results and Discussion

The reaction of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SnCl$[10] with $AgCB_{11}H_{12}$ gave quantitative precipitation of elemental silver and organotin(IV) compounds that were not analyzed further. However, no reaction at all was observed between $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SnCl$ and $NaCB_{11}H_{12}$. Apparently, silver salts, in general, are not suitable for nucleophilic reactions with Sn^{II} compounds,[11] whereas sodium carboranate is not reactive enough. Consequently, we prepared the tungstenpentacarbonyl organostannylene complex $2,6\text{-}(Me_2NCH_2)_2C_6H_3(Cl)SnW(CO)_5$ (**1**) according to Scheme 1.



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Scheme 1. Synthesis of compound **1**.

Compound **1** is a pale yellow solid with a sharp melting point that is very soluble in common organic solvents such as benzene, dichloromethane and tetrahydrofuran. Single crystals of its thf solvate **1**·0.5thf suitable for X-ray diffraction analysis were obtained by recrystallization from thf/pentane. The molecular structure of **1**·0.5thf is shown in Figure 2, selected bond lengths and bond angles are given in Table 1.

The tin atom is five-coordinate and shows a distorted square-pyramidal configuration in which the C(1), N(1), N(2) and W(1) atoms occupy the equatorial positions and the Cl(1) atom occupies the axial position of the square pyramid. In comparison to the parent organostannylene $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SnCl$,[10] complex **1** shows a widening of the C(1)–Sn(1)–Cl(1) angle by approximately 14° to 103.89(10)° and a shortening of the Sn(1)–C(1) and Sn(1)–Cl(1) bond lengths to 2.127(4) and 2.4098(10) Å, respectively. The Sn(1)–N(1) and Sn(1)–N(2) distances fall in the narrow range between 2.543(3) and 2.5526(3) Å, and, most interestingly, they are not shorter than the corresponding distances in $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SnCl$ [2.525(8), 2.602(8) Å].

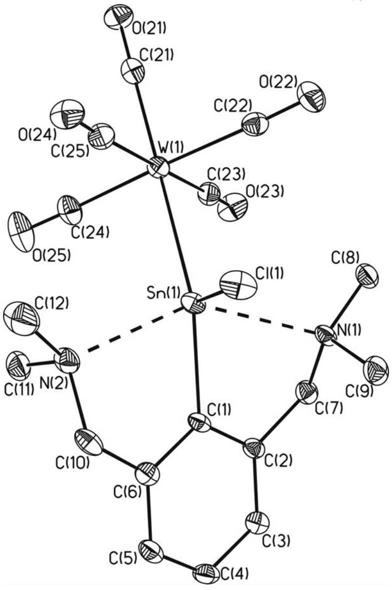


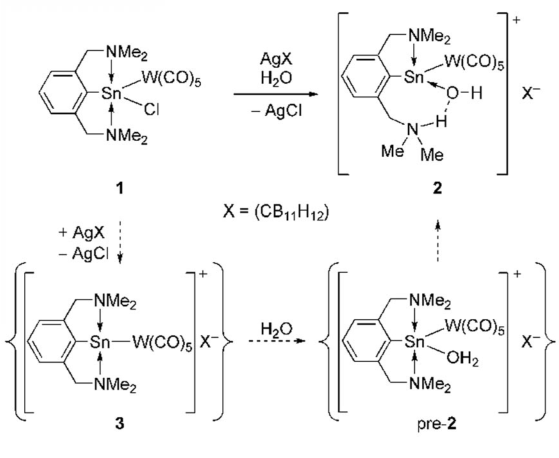
Figure 2. Molecular structure of compound **1**.

Table 1. Selected measured (X-ray) and calculated (B3LYP) bond lengths [Å] and bond angles [°].

	1 (X = Cl)		**2** (X = O)		**3**
	X-ray	B3LYP	X-ray	B3LYP	B3LYP
Sn(1)–W(1)	2.7630(3)	2.860	2.7117(3)	2.779	2.750
Sn(1)–C(1)	2.127(4)	2.170	2.150(3)	2.195	2.139
Sn(1)–X(1)	2.4098(10)	2.474	2.017(2)	2.094	
Sn(1)–N(1)	2.543(3)	2.707	2.264(2)	2.393	2.606
Sn(1)–N(2)	2.5526(3)	2.601			2.606
W(1)–C(21)	1.989(5)	2.022	1.983(4)	2.042	2.054
O(1W)–H(1W)			1.67(3)	1.662	
O(1W)–H(2W)			0.69(3)	0.971	
N(2)–H(1W)			0.99(3)	1.063	
C(1)–Sn(1)–W(1)	146.12(9)	145.7	135.95(8)	138.7	180
C(1)–Sn(1)–X(1)	103.89(10)	99.4	90.25(10)	89.2	
X(1)–Sn(1)–W(1)	109.99(3)	114.9	120.79(6)	119.3	
N(1)–Sn(1)–N(2)	143.66(11)	142.7			146.7
N(1)–Sn(1)–X(1)	90.45(7)	90.8	100.28(9)	99.9	
N(2)–Sn(1)–X(1)	88.48(8)	86.9			

The ^1H NMR spectrum of compound **1** in C_6D_6 shows, in addition to the signals for the aromatic protons, an AB-type resonance at $\delta = 3.16$ ppm for the diastereotopic CH_2 protons and a broad singlet for the methyl protons. In particular, the latter indicates some nonrigidity, such as Sn–N and/or Sn–Cl bond dissociation of compound **1** in solution, but this was not investigated further. The ^{13}C NMR spectrum reveals two signals at $\delta = 200.2$ and 199.2 ppm, which indicates the presence of *cis* and *trans* CO groups in the $W(CO)_5$ moiety. The ^{119}Sn NMR spectrum shows a single resonance at $\delta = 140$ ppm flanked by $^1J(^{119}Sn\text{-}^{183}W)$ satellites of 1186 Hz. The latter are somewhat smaller than those found for {4-*tert*-Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2$C$_6$H$_2$}ClSnW(CO)$_5$ (1366 Hz)[12] and W(CO)$_5$SnX$_2$thf (X = Cl, Br) (1440-1610 Hz).[13]

The treatment of complex **1** with AgCB$_{11}$H$_{12}$ in toluene yielded the organostannylidenium tungstenpentacarbonyl carboranate [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$(H$_2$O)SnW(CO)$_5$]$^+$-(CB$_{11}$H$_{12}$)$^-$ (**2**) as the aqua complex (Scheme 2). It is likely that in the first reaction step, the water-free intermediate **3** is formed, which, as a rather strong Lewis acid, complexes a water molecule to give pre-**2** and finally **2** (see results from DFT calculations).



Scheme 2. Synthesis of compound **2** and a proposed reaction pathway for its formation (X = CB$_{11}$H$_{12}$).

Single crystals of the toluene solvate **2**·C$_7$H$_8$ suitable for X-ray diffraction analysis were obtained by recrystallization from toluene. The molecular structure of **2**·C$_7$H$_8$ is shown in Figure 3, selected bond lengths [Å] and angles [°] are given in Table 1.

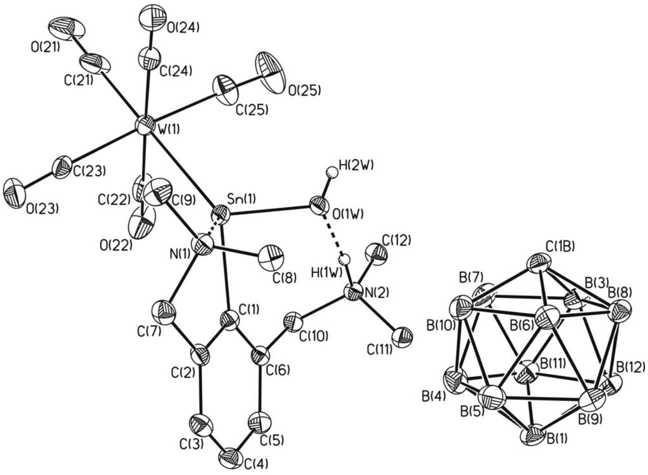


Figure 3. Molecular structure of compound **2**.

The Sn(1) atom in compound **2** is four-coordinate and exhibits a rather strongly distorted tetrahedral configuration (average bond angle 107.69°) with bond angles that vary between 79.21(10)° [C(1)–Sn(1)–N(1)] and 135.95(8)° [C(1)–Sn(1)–W(1)]. The Sn(1)–W(1) distance [2.7117(4) Å] in **2** is 0.0509 Å shorter than that in **1**, and this hints at an increased π-acceptor strength of the tin atom. The intramolecular Sn(1)–N(1) distance of 2.264(2) Å is shorter as well, whereas the Sn(1)–C(1) bond [2.150(3) Å] is slightly longer. Most remarkably, the second N→Sn coordination is broken and replaced by a H$_2$O→Sn interaction with a Sn(1)–O(1W) distance of 2.017(2) Å. This distance is even shorter than the corresponding Sn–O distance of 2.0330(2) Å reported for the monoorganotin tribromide aqua complex [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnBr$_3$(H$_2$O)].[14] The coordinated water molecule is stabilized by an intramolecular nonsymmetrical O···H–N hydrogen bridge with O(1W)–H(1W) and N(2)–H(1W) distances of 1.61(3) and 1.05(3) Å, respectively.

The structure of the cation **2** can be seen as a snapshot along the path of a Brønsted acid–base reaction in which the aqua acid [{(CO)$_5$W}2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnOH$_2$]$^+$ (pre-**2**) reacts intramolecularly with an amine base (Scheme 2). This reaction resembles those of previously reported [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnBr$_3$(H$_2$O)] and [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$Sn(O$_2$CCF$_3$)$_3$(H$_2$O)][14,15] and seems to be a general property of organotin halides that contain amine-functionalized organic substituents.

Examples for other cationic organotin aqua complexes that show longer Sn–O(water) distances are [Me$_3$Sn(H$_2$O)$_2$]-N(SO$_2$CH$_3$)$_2$ [2.327(3), 2.254(2) Å],[16] [Me$_3$Sn(H$_2$O)$_2$]-N(SO$_2$CF$_3$)$_2$ [2.306(3), 2.335(3) Å][17] and [Bu$_3$Sn(H$_2$O)$_2$]-[C$_5$(CO$_2$Me)$_5$] [2.295(4), 2.326(5) Å].[18] The Sn–O(water) distances in the related neutral aqua complexes [MePh$_2$Sn-(OCOCF$_3$)(H$_2$O)]·18-crown-6 [2.483(5) Å],[19] *m*-(Ph$_2$Cl-SnCH$_2$CH$_2$)-15-benzocrown-5 [2.469(4) Å],[20a] Ph$_2$I(H$_2$O)-SnCH$_2$Sn(I)(Ph)–CH$_2$-16-crown-5 [2.440(3) Å][20b] and Ph$_2$I-(H$_2$O)SnCH$_2$Sn(I)(Ph)-CH$_2$-19-crown-6 [2.516(3) Å][20c] are even longer.

The ^{1}H NMR spectrum of compound **2** shows two singlets at δ = 2.61 and 3.97 ppm, which are assigned to the NCH$_3$ and the CH$_2$ protons, respectively. Both resonances are high-frequency shifted relative to those in compound **1** and indicate stronger N→Sn coordination but also equivalence of both the N-methyl and methylene groups. The broad signal at δ = 7.72 ppm in the ^{1}H NMR spectrum of **2** indicates the presence of a water molecule that is coordinated to the tin atom. The ^{11}B{^{1}H} NMR spectrum of **2** shows three distinct 1:5:5 resonances, typical for the free [1-CB$_{11}$H$_{12}$]$^-$ anion, and proves the ionic character of **2**. The ^{119}Sn NMR spectrum of **2** displays a sharp signal at δ = –8.4, which is low-frequency shifted relative to that of compound **1**.

DFT Calculations

In order to obtain more insight into the bonding situation in compounds **1** and **2** and to learn about the process of formation of the aqua complex **2**, DFT calculations were performed. The latter were also used to support the refinement of the X-ray data of **2**, with respect to the position of the proton H(1W), and to predict the structure of the cation [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnW(CO)$_5$]$^+$ (**3**).

The calculated minimum-energy structures of **1** and **2** correlate sufficiently well with the structures determined by single-crystal X-ray diffraction analysis (Figure 4, Table 1). The correlation of the bond angles is rather good. However, the Sn–E (E = C, N, O, Cl, W) distances are overestimated in each case, which is a known phenomenon with DFT calculations.[21]

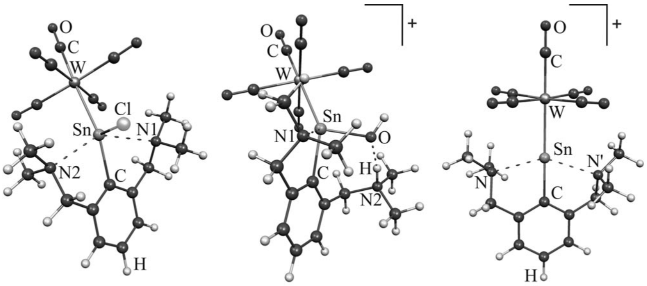


Figure 4. Calculated structures of **1**, **2** and the hypothetical cation **3** (Molekel representation[22]). The C–Sn–W angles are 145.7°, 138.7° and 180°, respectively.

The calculated molecular structure of the hypothetical (not yet isolated) cation $[2,6\text{-}(Me_2NCH_2)_2C_6H_3SnW(CO)_5]^+$ (**3**) exhibits a C(1)–Sn(1)–W(1) angle of 180°, which leads to C_2 symmetry. This hints at sp hybridization of the tin atom, which in turn suggests that attack of nucleophiles such as water to be an easy process. The Sn(1)–W(1) and Sn(1)–C(1) bond length of 2.750 Å and 2.054 Å, respectively, are shorter than the corresponding bond lengths in **1** and **2**. The N···Sn distance of 2.61 Å is comparable to that in **1**. Furthermore, the bond length W(1)–C(21) [C(21) is part of the *trans* CO bond] increases continuously in the series **1**, **2** and **3**. These structural parameters hint at an increasing but yet weak back donation from tungsten to tin. Additionally, a change from fivefold to fourfold coordination takes place, and the electronegativity of the substituents increases from chlorine in **1** to oxygen in **2**. Both facts cause a higher cationic character of the central tin atom in the latter compound and favour slight back-bonding towards the tungsten atom. NBO calculations prove this increasing cationic character. The tin atom in **1** and **2** show NBO charges of 1.42 and 1.63, respectively. However, no significant evidence for strong back donation was found by analyzing the molecular orbitals (plots of selected molecular orbitals are shown in the Supporting Information).

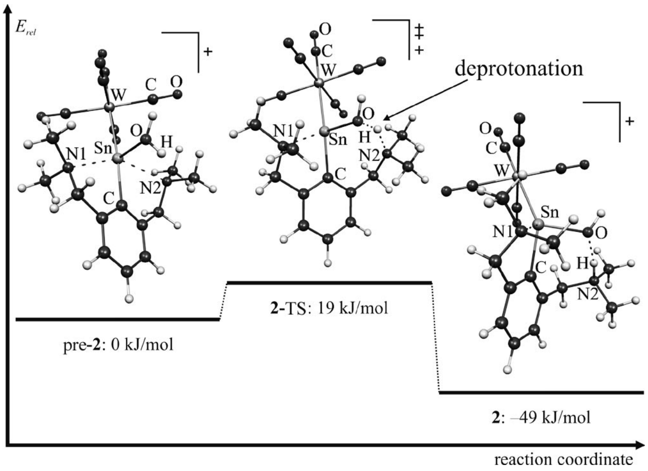


Figure 5. The intermolecular deprotonation forming **2** (Molekel representation[22]).

In order to support the proposed reaction mechanism, the thermodynamics of the last reaction step was calculated. The results are illustrated in Figure 5. The counterion $(CB_{11}H_{12})^-$ was omitted in these calculations. Indeed, **2** is approximately 49 kJ/mol lower in energy than pre-**2**. This shows that the thermodynamically favoured product has been formed. The transition state is by 19 kJ/mol higher in energy than pre-**2**, which in turn means that the activation energy E_a can easily be provided, even at low temperatures (Table 2).

Table 2. Total (SCF) and zero-point (ZPE) energies of the calculated compounds and transition state.

	SCF [Hartree]	ZPE [Hartree]
1	–1675.79768	–1675.45832
pre-**2**	–1291.76520	–1291.40287
2-TS	–1291.75863	–1291.39579
2	–1291.78704	–1291.42141
3	–1215.32006	–1214.98171

Notably, this reaction is accompanied by a decrease in the C(1)–Sn(1)–W(1) angle by 31.5° and by an almost complete proton transfer from the oxygen to the nitrogen atom.

Conclusions

In this report, we have shown that transition-metal-bound intramolecularly coordinated organostannylene cations are accessible from appropriate precursors by reaction with the silver salt of the noncoordinating carboranate anion $[CB_{11}H_{12}]$–. The cation is rather electrophilic and prone to coordinate a water molecule. The coordination of the latter is in turn supported by a hydrogen bridge with the nitrogen atom of one of the two dimethylaminomethyl moieties. Thus, the structure actually observed in the solid state is an intermediate along the path $[(CO)_5WSn^+(R)(H_2O)] \rightarrow [(CO)_5WSn(R)OH + H^+]$, in which the proton is intramolecularly trapped by the nitrogen atom of a dimetylaminomethyl group. This suggests that organic substrates such as aldehydes, ketones, esters and alcohols might also be able to coordinate to the tin atom and thus be activated for further reactions. Further studies in this direction are under way.

Experimental Section

General Methods: Solvents were dried by standard methods and distilled prior to use. All moisture- and air-sensitive reactions were carried out in an argon atmosphere by using standard Schlenk techniques. $(CO)_5WSnCl_2$ was prepared according to the literature.[13] Elemental analyses were performed on an LECO-CHNS-932 analyzer. The ^1H, ^{13}C and ^{119}Sn NMR spectra were acquired on Bruker DRX400 and Bruker DPX300 FT NMR spectrometers with broad band decoupling of ^{119}Sn at 149.21 or 111.92 MHz and of ^{13}C at 100.61 MHz, by using an external and internal deuterium lock. The ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR chemical shifts δ are given in ppm and referenced to external Me_4Sn (^{119}Sn), Me_4Si (^{13}C, ^{1}H) and $BF_3{\cdot}OEt_2$ (^{11}B). Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) by using an acetonitrile mobile phase. Pressure in the mass analyzer region was usually about 4–10.5 mbar. The ions showed the expected isotopic pattern.

Synthesis of $2,6\text{-}(Me_2NCH_2)_2C_6H_3(Cl)SnW(CO)_5$ (1): A solution of $2,6\text{-}(Me_2NCH_2)_2C_6H_3Li$ (0.2 g, 1 mmol) in hexane (20 mL) was added dropwise to an in situ generated thf solution of $(CO)_5WSnCl_2$ (0.63 g, 0.1 mmol). After stirring the mixture for 20 h at room temperature, the solvent was evaporated, and the residue was suspended in toluene (40 mL). After filtration from LiCl, the solvent was evaporated in vacuo, and the residue was washed with pentane to afford **1** as pale yellow solid. Yield: 0.55 g (85%). M.p. 168–170 °C. $C_{17}H_{19}ClN_2O_5SnW$ (M_w = 669.3): C 30.51, H 2.86; found C 30.40, H 2.65. Monoisotopic M_w = 668. Positive-ion ESI-MS: m/z (%) = 674 (5) $[M - Cl + CH_3CN]^+$, 633 (5) $[M - Cl]^+$, 577 (5) $[M - Cl - 2CO]^+$, 311 (60) $[M - Cl - W(CO)_5]^+$. ^{1}H NMR (C_6D_6, 500.13 MHz): δ = 2.19 (s, 12 H, NCH_3), 3.16 (AB, 4 H, CH_2N), 6.77 (d, 2 H, ArH), 7.09 (t, 1 H, ArH) ppm. ^{13}C NMR (C_6D_6, 125.77 MHz): δ = 45.8 (br. s, N*C*H_3), 64.7 (*C*H_2N), SnC_6H_3 124.1 (C3,5), 130.1(C4), 144.1 (C2,6), 153.7 (C1), 199.2 [*C*O^{eq}, $^{1}J(^{13}C, ^{182}W)$ = 154 Hz, $^{2}J(^{13}C, ^{119}Sn)$ = 55 Hz], 200.2 [*C*O^{ax}, $^{1}J(^{13}C, ^{182}W)$ = 159 Hz, $^{2}J(^{13}C, ^{119}Sn)$ = 71 Hz] ppm. ^{119}Sn NMR (C_6D_6, 186.49 MHz): δ = 140 [$^{1}J(^{119}Sn, ^{182}W)$ = 1186 Hz] ppm.

Synthesis of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3(H_2O)SnW(CO)_5]^+(CB_{11}H_{12})^-$ (2): The solid $AgCB_{11}H_{12}$ (0.08 g, 0.25 mmol) was added to a toluene solution (20 mL) of **1** (0.17 g, 0.25 mmol), and the mixture was stirred for 12 h. The resulting suspension was filtered from AgCl, and the mother liquor was concentrated and left to crystallize at 4 °C to give 0.162 g (80%) of **2** with a m.p. of 125 °C (decomposition). Prior to elemental analyses a sample of **2** was kept for several hours at vacuum (0.01 Torr) in order to remove the solvate toluene. $C_{18}H_{33}B_{11}N_2O_6SnW$ (M_w = 794.93): calcd. C 27.20, H 4.18; found C 27.40, H 4.35. Monoisotopic M_w = 794. Positive-ion ESI-MS: m/z (%) = 633 (5) $[M - H_2O - CB_{11}H_{12}]^+$, 311 (100) $[M - W(CO)_5 - H_2O - CB_{11}H_{12}]^+$. Negative-ion ESI-MS: m/z (%) = 143 (100) $[CB_{11}H_{12}]^-$. ^{1}H NMR ([D$_8$]thf, 300.13 MHz): δ = 2.21 (1 H, CH), 2.61 (s, 12 H, CH_3), 3.94 (4 H, CH_2), 7.34 (d, 2 H, Ar), 7.45 (t, 1 H, Ar), 7.58 (br. s, 2 H, H_2O) ppm. ^{13}C NMR ([D$_8$]thf, 75.63 MHz): δ = 45.2 (*C*H_3), 50.7 (*C*H), 64.4 (*C*H_2), SnC_6H_3, 124.9 (C4), 127.8 (C3,5), 128.6 (C2,6), 144.1 (C(1)), 197.7 [*C*O^{eq}, $^{1}J(^{13}C, ^{182}W)$ = 154 Hz], 197.6 (*C*O^{ax}) ppm. ^{11}B NMR ([D$_8$]thf): δ = –5.12 [s, 1B, B(12)], –11.24 [s, 5 B, B(2–6)], –13.97 [s, 5 B, B(7–11)] ppm. ^{119}Sn NMR ([D$_8$]thf, 111.95 MHz): δ = –8.4 ppm.

Crystallography: Intensity data for the colourless (**1**) und light yellow (**2**) crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α (0.71073 Å) radiation at 173(1) K. The data collection covered almost the whole sphere of reciprocal space with 3 (**1**) and 4 (**2**) sets at different k angles with 287 (**1**) and 424 (**2**) frames with ω rotation (Δ/ω = 1°) at two times 25 s (**1**) and 20 s (**2**) per frame. The crystal-to-detector distance was 3.4 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. On analyzing the duplicate reflections, there was no indication of any decay. The structure was solved by direct methods SHELXS97[16] and successive difference Fourier syntheses. Refinement applied was with full-matrix least-squares methods SHELXL97.[17] The H atoms were placed in geometrically calculated positions by using a riding model U_{iso} constrained at 1.2 times U_{eq} for non-methyl and at 1.5 times U_{eq} for methyl groups of the carrier C atom. Solvent molecules thf (**1**) and toluene (**2**) were refined isotropically with an occupancy of 0.5. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the International Tables for X-ray Crystallography.[18] The figures were created by SHELXTL.[19] Crystallographic data are given in Table 3, selected bond lengths and angles in Table 1. CCDC-748835 (**1**) and CCDC-748836 (**2**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data for **1** and **2**.

	1·0.5thf	**2**·2toluene
Empirical formula	$C_{19}H_{23}ClN_2O_{5.5}SnW$	$C_{25}H_{41}B_{11}N_2O_6SnW$
Formula mass [g mol^{-1}]	705.38	887.05
Temperature [K]	173(1)	173(1)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Crystal size [mm]	0.20 × 0.20 × 0.18	0.20 × 0.18 × 0.18
Space group (no.)	*Pbca* (61)	$P\bar{1}$ (2)
a [Å]	17.5570(6)	10.6446(8)
b [Å]	13.6661(6)	12.0609(9)
c [Å]	19.2460(6)	16.1023(15)
α [°]	90	76.307(4)
β [°]	90	89.682(4)
γ [°]	90	66.672(4)
V [Å^3]	4617.8(3)	1835.3(3)
Z	8	2
Density (calculated) [g cm^{-3}]	2.029	1.605
Absorption coefficient [mm^{-1}]	6.209	3.850
F(000)	2688	864
θ range [°]	2.95–27.48	3.19–27.50
Index ranges	$-22 \le h \le 22$	$-13 \le h \le 13$
	$-17 \le k \le 17$	$-13 \le k \le 15$
	$-24 \le l \le 24$	$-20 \le l \le 20$
Reflections collected	41906	24382
Completeness of θ_{max} [%]	99.9	99.5
Independent reflections/R_{int}	5284/0.049	8374/0.039
Data/restraints/parameters	5284/0/268	8374/0/507
Goodness of-fit on F^2	0.870	0.594
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0277$	$R_1 = 0.0263$
	$wR_2 = 0.0375$	$wR_2 = 0.0407$
R indices (all data)	$R_1 = 0.0597$	$R_1 = 0.0597$
	$wR_2 = 0.0390$	$wR_2 = 0.0448$
Largest diff. peak and hole [e Å^{-3}]	0.906 and –2.172	0.959 and –0.841

Computational Details: All calculations were performed with the Gaussian 03, Revision E.01,[23] suite of programs. Full density functional theory (DFT) calculations were carried out with the B3LYP functional[24] and the 6-31+G(d) basis set[25] for all non-metal atoms. The tin and tungsten atoms were described with the Stuttgart ECP basis sets.[26] Starting coordinates were achieved from the crystal coordinates. Additional harmonic vibrational frequency analyses were realized on the same theoretical level to determine the nature of stationary points on the potential energy surface. Thereby the minima showed no imaginary frequencies, whereas the transition-state showed one imaginary frequency, which is in accordance with the process of deprotonation. All calculations were done without symmetry restrictions. To determine the correct symmetry of **3**, an additional C_2-symmetry restricted calculation was executed. No change in energy was detected. All calculated total (SCF) and zero-point (ZPE) energies are listed in Table 2, standard orientations can be found in the Supporting Information. In order to perform natural bond orbital analyses (NBO), the built-in NBO-3.1 subroutines of the Gaussian 03, Revision B.01,[27] program package were used.

Supporting Information (see footnote on the first page of this article): Computational studies on compounds **1**, **2**, the hypothetical cation **3**, pre-**2** and 2-**TS** (Tables S1–S6) and selected molecular orbitals of the hypothetical cation **3** (Figure S1) are presented.

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