Radicals

A Mechanistic Study on Reactions of Group 13 Diyls LM with Cp*SbX₂: From Stibanyl Radicals to Antimony Hydrides

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Abstract: Oxidative addition of Cp*SbX₂ (X = Cl, Br, I; Cp* = C₅Me₅) to group 13 diyls LM (M = Al, Ga, In; L = HC(C(Me)N(Dip)₂) yields elemental antimony (M = Al) or the corresponding stibanylgallanes [L(X)Ga]SbX(Cp*) (X = Br, I) and -indanes [L(X)In]SbX(Cp*) (X = Cl, Br, I). 1 and 2 react with a second equivalent of LGa to eliminate decamethyl-1,1'-dihydrofulvalene (Cp*)₂ and form stibanyl radicals [L(X)Ga]Sb' (X = Br, I), whereas analogous reactions of 5 and 6 with Ln selectively yield stibanes [L(X)In]₂SbH (X = Cl, Br, I) by elimination of 1,2,3,4-tetramethyldifluorvalene. The reactions are proposed to proceed via formation of [L(X)₃M]SbCp* as reaction intermediate, which is supported by the isolation of [L(Cl)In]₂SbCp* (11, Cp* = C₅H₅). The reaction mechanism was further studied by computational calculations using two different models. The energy values for the Ga- and the In-substituted model systems showing methyl groups instead of the very bulky Dip units are very similar, and in both cases the same products are expected. Homolytic Sb–C bond cleavage yields van der Waals complexes from the as-formed radicals ([L(Cl)M]Sb' and Cp*), which can be stabilized by hydrogen atom abstraction to give the corresponding hydrides, whereas the direct formation of Sb hydrides starting from [L(Cl)M]SbCp* via concerted β-H elimination is unlikely. The consideration of the bulky Dip units reveals that the amount of the steric overload in the intermediate I determines the product formation (radical vs. hydride).

Introduction

Monovalent group 13 metal compounds of the general type RM (R = Cp*, L, others; Cp* = C₅Me₅, L = HC(C(Me)N(Dip)₂)) have been extensively studied over the last decade due to their interesting structures and unusual chemical reactivity.¹ These compounds not only serve as powerful two-electron reduction reagents, but also as potential Lewis bases or Lewis acids due to their reactivity in oxidative addition reactions originating from the M-centered (M = Al, Ga, In) electron lone pair (HOMO) as well as from the formally large variety of main group-metal-hydrogen [7] as well as C–N bonds, [8] and bond activation reactions of a large variety of organic compounds. [9] Their reactivity in oxidative addition reactions originates from the M-centered (M = Al, Ga, In) electron lone pair (HOMO) as well as from the formally large variety of main group-element-hydrogen [7] as well as C–N bonds, [8] and bond activation reactions of a large variety of organic compounds. [9] Their reactivity in oxidative addition reactions originates from the M-centered (M = Al, Ga, In) electron lone pair (HOMO) as well as from the formally large variety of main group-element-hydrogen [7] as well as C–N bonds, [8] and bond activation reactions of a large variety of organic compounds. [9] Their reactivity in oxidative addition reactions originates from the M-centered (M = Al, Ga, In) electron lone pair (HOMO) as well as from the formally large variety of main group-element-hydrogen [7] as well as C–N bonds, [8] and bond activation reactions of a large variety of organic compounds. [9]
Reactions of EX$_3$ (E = As, Sb, Bi; X = halide, amide, alkoxide) with gallanediyl LGa typically occur with the insertion of LGa into the E–X bond (oxidative addition) followed by the elimination of LGaX$_2$. The outcome led to a variety of compounds with unusual bonding properties, that is, Ga-substituted dipnictides $[L(X)Ga]_2E$ ($E$ = As, Sb, Bi; $X$ = halide, amide, alkoxide) with $E$–E double bonds,[16] tetrasila- and tetrabismabicyclo[1.1.0]butane analogues $[L(X)Ga]_2E$ ($E$ = Sb, Bi; $X$ = Cl, NMe$_3$) with a central $E_2$ core,[17] as well as gallapnictenes $[L(X)Ga]E$. [19] Based on the isolation of several carbene-stabilized stibinidenes $^{56}$CAAC-Sb$[Ga(X)L]$(X = halide, amide, alkoxide) and $^{57}$Dipp$-[Ga(X)L]$(IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidine), the reactions were confirmed to proceed with the intermediate formation of Ga-substituted ptcntinidenes $[L(X)Ga]E$.[18] In addition, reactions of LGa with [CP*$Sb$]$_4$ yielded (LGa)$_2Sb$$_4$,[14] whereas those with $[CP*SbCl]$$_2$ and $[CP*BiI]$_2$ produced $Sb$- and $Bi$-centered radicals $[L(Cl)Ga]_2Sb$$_2$ (A) and $[L(I)Ga]Sb$$_2$ (B) (Scheme 1),[20] respectively. The formation of radicals A and B is accompanied by liberation of a centered Cp* radical through a sterically induced homolytic C–E bond breakage of the precursor. $[L(Cl)Ga]_2Sb$$_2$ and $[L(I)Ga]_2Sb$$_2$ are both rare examples of neutral pnictogen-centered radicals, which are stable in solution and in the solid state.[21]

Recently, the same synthetic approach was extended to heteroleptic Sb-centerd radicals of the type $[[L(Cl)Ga](R)]Sb$$_2$ (R = Bi[N(Dip)CH$_2$]$_2$, 2,6-Mes$_2$C$_6$H$_3$, N(SiMe$_3$)Dip; Mes = 2,4,6-Me$_3$C$_6$H$_3$) (Scheme 1).[22] The influence of the ligand R on the electronic properties of the resulting radicals was thoroughly investigated. A strong dependence on the steric demand of the cyclopentadienyl substituent and the E–E double bond, [16] tetrastiba- and tetrabismabicyclo[1.1.0]butane analogues $[L(X)Ga]_2E$$_4$ (E = As, Sb, Bi; X = halide, amide, alkoxide) was first observed in reactions of LGa with CP*AsCl$_2$, which was subsequently confirmed to proceed with the intermediate formation of Ga-substituted ptcntinidenes $[L(X)Ga]E$.[19] In contrast, the analogous reaction with $[CP*AsCl]$_2 (CP* = C$_5$(4- Bu$_3$C$_6$H$_3$)$_5$) containing the bulkier CP* ligand proceeded with As–C bond rupture to form the As-centered radical $[L(Cl)Ga]_2As$ $_2$ (D) and the stable CP*$_2$ radical.[24]

To determine the general applicability of this synthetic approach for group 15-centered radicals, we investigated the influence of the halide substituents in CP$^*$SbX$_2$ ($X$ = F, Cl, Br, I), as well as the influence of the group 13 diyl LM (M = Al, Ga, In) on the formation of antimony-centered radicals. In order to gain a deeper understanding of the reaction mechanism, the reactions of CP$^*$SbX$_2$ with LM were performed stepwise with different amounts of LM, which was furthermore studied by replacing the CP* ligand in CP$^*$SbCl$_2$ with the less sterically demanding CP ligand. In addition, computational calculations on the reaction mechanism were performed.

**Results and Discussion**

The influence of different cyclopentadienyl substituents on the reaction mechanism was already shown in reactions with CP$^*$EX$_3$ ($E$ = As, Sb, Bi) and CP$^*$AsCl$_2$.[20, 21, 24] To further study the effect of the halide substituent X in CP$^*$SbX$_2$ on the product formation and the role of the group 13 metal M in LM, we systematically studied reactions of different group 13 diyls LM (M = Al, Ga, In) with four CP$^*$SbX$_2$ derivatives ($X$ = F, Cl, Br, I).

**Variation of the halide substituent X in CP$^*$SbX$_2$**

CP$^*$SbF$_2$[20] and CP$^*$SbCl$_2$[25, 26] were synthesized according to literature methods. CP$^*$SbBr$_2$ was reported to be formed in the reaction of CP$^*$Br with Sb powder.[22] However, both CP$^*$SbBr$_2$ and hitherto unknown CP$^*$Sb$_2$ were synthesized via more convenient salt metathesis reactions of KCp$^*$ with SbX$_3$. CP$^*$Sb$_2$ was structurally characterized by single-crystal X-ray diffraction (Figure S50 in Supporting Information). CP$^*$Sb$_2$ ($X$ = F, Cl, Br, I) were then reacted with one equivalent of LGa. For CP$^*$SbF$_2$, an immediate reduction was observed under various conditions with formation of LGaF$_2$.[28] In contrast, reactions of CP$^*$SbCl$_2$, CP$^*$SbBr$_2$, and CP$^*$Sb$_2$ yielded $[L(X)Ga]Sb$$_2$(CP*) ($X$ = Cl E[20] Br 1, I 2). 1 and 2 were isolated as orange crystals suitable for X-ray diffraction (Scheme 2).

1 and 2 were further reacted with one equivalent of LGa, yielding stibanyl radicals $[L(Br)Ga]_2Sb$$_2$ (3) and $[L(I)Ga]_2Sb$$_2$ (4) in good yields. The observation of decamethyl-1,1'-dihydrofulvalene in the $^1$H NMR spectrum strongly indicates the initial liber-

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**Scheme 1.** Homo- and heteroleptic Gallium-substituted heavy group 15 element-centered radicals formed upon homolytic Sb–C bond breakage.

**Scheme 2.** Reactions of LGa with CP$^*$SbX$_2$. Yields in parentheses.
ation of a Cp* radical during formation of 3 and 4, which subsequently dimerized. 3 and 4 were also directly formed in reactions of Cp*SbX₂ (X = Br, I) with two equivalents of LGa, whereas the same reaction with Cp*SbF₂ only yielded LGaF₂,[28] with no radical species observed even at low temperatures (−80 °C). Remarkably, reactions with Cp*SbBr₂ and Cp*SbI₂ are complete within 24 h, whereas that of Cp*SbCl₂ takes about seven days for completion.[20] These findings highlight the decreasing Sb–X bond strength with increasing atomic number of the halogen atom X. 3 and 4 were isolated in moderate yields as red crystals from deep red solutions upon storage at −30 °C (Scheme 1). In contrast to A and 3, crystals of radical 4 are accessible from benzene and toluene solutions. They can be easily separated from minor side products such as LGaX₂, distibene [(LX)Ga]₂Sb₂, and gallastibene [(L(X)Ga)]SbGaL, which are formed in about 10% yield each as estimated by in situ ¹H NMR spectroscopy.

Compounds 1 and 2 are stable in the solid state at ambient temperature under argon atmosphere, but slowly decompose in solution to give LGaX₂ and Cp*₂ as was confirmed by ¹H NMR spectroscopy, as well as elemental antimony as was proven by EDX analysis. The respective ¹H and ¹³C NMR spectra illustrate the asymmetric substitution at the Sb center, showing eight doublets and four septets that correspond to the CHMe₃ and CHMe₂ protons of the Dip groups, respectively. The C₅Me₃ protons appear as a single resonance at room temperature, indicative of fast sigmatropic shifts. The molecular structures of 1 (Figure 1) and 2 (Figure S43), which were determined by single-crystal X-ray diffraction,[29] show Ga–Sb bond lengths of 2.7058(5) Å (1) and 2.6567(5) Å (2), comparable to that of E (2.6979(2) Å). The Cp* ligands are coordinated to the Sb center in a κ¹ fashion with Sb–C bond lengths of 2.2441(16) Å (1) and 2.243(4) Å (2).

Radicals 3 and 4 are stable in the solid state and in solution at ambient temperature under argon atmosphere, but immediately decompose upon exposure to air and moisture. As is typical for paramagnetic species, their ¹H NMR spectra exhibit only broad resonances between −0.5 and 8 ppm. Based on the Evans method,[30] effective magnetic moments μₑff of 1.62 μ₀ (3) and 1.64 μ₀ (4) were determined, which confirm a paramagnetic character due to the presence of a single unpaired electron (S = 1/2). A variable-temperature (VT) ¹H NMR study showed no signs of dimerization upon cooling solutions of 3 and 4 down to −80 °C. IR spectra do not reveal any absorption bands in the expected region for Sb–H moieties (1750–1900 cm⁻¹).[20] The electronic structures of 3 and 4 were also examined by EPR spectroscopy; the X-band EPR spectra of 3 and 4 are displayed in Figure 2 alongside with that of A.[20] The complicated, yet well resolved super-hyperfine pattern of the spectra is consistent with >80% spin population at the Sb center with significant unpaired spin distributed to the Ga ligands (≈8% to each).[20] No significant differences between the EPR spectra are observed. The high-field region of the EPR spectra offers a limited selection of transitions, allowing a thorough comparison where no differences in the gₐ, Aₐ(Sb) or Aₐ(Ga)-values of A, 3, and 4 can be distinguished. No resolved ¹³Cl hyperfine was observed for the Cl atom in A.[20] Despite the larger hyperfine coupling constants of 79.4, 81Br and 121I values of 3, 4 can be distinguished. No resolved ¹³Cl hyperfine was observed for the Cl atom in A.[20] Despite the larger hyperfine coupling constants of 79.4, 81Br and 121I, in comparison to Cl (≥5x),[31] no further hyperfine splittings are observed, indicating minimal unpaired spin on the halides. The EPR parameters of Sb-centered radicals are very sensitive to the complexes’ electronic structure, which may be influenced by geometry and secondary factors such as steric demand. The remarkable similarities between the EPR spectra of A, 3, and 4 indicate that they have nearly identical local Sb p-orbital radical character and electronic structures. Therefore, the halide has minimal, if any direct influence on the electronics of the Sb radical center.

![Figure 1. Molecular structure of 1. Hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.](Image 56x124 to 282x323)

![Figure 2. X-band (≈ 9.63 GHz) EPR spectra of A, 3, and 4 in frozen toluene collected at 15 K. The asterisk at g ≈ 2 indicates a < 1% organic radical impurity. The inset is an expansion of the high-field region on g-scale, corrected for slight shifts due to differences in microwave frequencies (±0.005 GHz). Spectrometer conditions: 100 kHz modulation frequency, 6 G modulation amplitude, 81.92 ms conversion time, 81.92 ms time constant, 4096 points. The spectrum of A is a replication of a previously published measurement collected under the same conditions, except for a 20.48 ms time constant.](Image 314x191 to 539x374)
The molecular structures of 3 (Figure S44) and 4 (Figure 3) were determined by single-crystal X-ray diffraction. 3 and 4 show two-coordinated Sb centers, which adopt a bent geometry with Ga-Sb-Ga angles of 107.026(15)° (3) and 107.314(17)° (4) as summarized in Table 1. Due to the larger atomic radii of Br and I compared to Cl, these values are slightly larger compared to the Ga-Sb-Ga angle of A (104.890(10))°.[20] This trend is also reflected by the increasing Ga–X bond lengths (A 2.2028(7) Å, 2.1623(9) Å; 3 2.3554(6) Å, 2.3556(6) Å; 4 2.5789(5) Å, 2.5745(5) Å). In addition, the X1-Ga1···Ga2-X2 torsion angles (A 41.36(3)°, 3 34.52(2)°, 4 32.75(2)°)[20] steadily decrease with increasing atomic number of the halide. The Sb–Ga bond lengths observed for radicals A (2.5899(4) Å, 2.5909(3) Å, 3 (2.5930(5) Å, 2.5849(4) Å), and 4 (2.5833(5) Å, 2.5936(5) Å) are virtually identical and agree with the values observed for similar Sb compounds containing [L(X)Ga] ligands.[16–19,22]

### Table 1. Central bond lengths [Å] and angles [°] of \([\text{L(X)Ga/Sb/X}][\text{Cp*}](\text{E, 1, 2), [L(X)In/Sb/X}][\text{Cp*}](\text{5–7), [L(X)Ga/Sb}][\text{X}][\text{Cp*}](\text{A, 3, 4, and [L(X)In/Sb}][\text{X}][\text{Cp*}](\text{B, 8, 9; X = Cl, Br, I.})

|        | \([\text{L(X)Ga/Sb/X}][\text{Cp*}](\text{E, 1, 2), [L(X)In/Sb/X}][\text{Cp*}](\text{5–7), [L(X)Ga/Sb}][\text{X}][\text{Cp*}](\text{A, 3, 4, and [L(X)In/Sb}][\text{X}][\text{Cp*}](\text{B, 8, 9; X = Cl, Br, I.})
|--------|------------------|------------------|------------------|------------------|------------------|------------------|
|        | \text{E} | \text{1} | \text{2} | \text{5} | \text{6} | \text{7} |
| Ga–Sb  | 2.6979(2) | 2.7058(5) | 2.6567(5) | In–Sb | 2.8317(3) | 2.8333(3) | 2.8340(2) |
| Ga–N   | 1.9571(13) | 1.9573(13) | 1.9592(15) | In–N  | 2.1530(10) | 2.1546(10) | 2.1654(13) |
| Sb–C   | 2.2381(16) | 2.2441(16) | 2.243(4)  | Sb–C  | 2.2325(12) | 2.2365(12) | 2.2429(16) |
| Ga–Sb–C | 106.83(4) | 107.60(4) | 110.72(9) | In-Sb-C | 102.58(3) | 103.16(3) | 104.50(4) |
| Ga-Sb–X | 93.614(13) | 94.09(7)  | 98.216(12) | In-Sb-X | 90.58(9)  | 90.59(5)  | 91.29(5)  |
| N-Ga–N | 95.47(5)  | 95.53(5)  | 96.56(9)  | N-In-N  | 89.09(4)  | 89.24(4)  | 89.80(5)  |
| X-Sb–C | 94.68(5)  | 94.84(4)  | 98.51(10) | X-Sb-C  | 97.08(3)  | 97.09(3)  | 96.73(4)  |
|        | \text{A} | \text{4} | \text{5} | \text{8} | \text{9} |
| Ga–Sb  | 2.5899(4) | 2.5849(4) | 2.5833(5) | In–Sb | 2.7348(5) | 2.7384(5) | 2.7250(4) |
| Ga–N   | 1.9558(19) | 1.9594(19) | 1.9653(5) | In–N  | 2.143(3)  | 2.161(3)  | 2.166(3)  |
| Ga–Sb–Ga | 104.890(10) | 107.026(15) | 107.314(17) | In-Sb-In | 101.78(2) | 100.94(2) | 98.60(2)  |
| N-Ga–N | 95.78(8)  | 95.84(11) | 96.09(13) | N-In-N  | 89.57(11) | 90.21(12) | 89.83(11) |
|        | \text{B} | \text{9} |
|        | 95.69(8) | 95.73(11) | 95.58(12) | In-Sb-In | 89.06(11) | 90.14(11) |

[a] The syntheses and solid-state structures of A and E were reported previously; [b] Identical values due to special position.[16]
The molecular structures of 5–7 (Figure 4, Figures S45, S46 in Supporting Information) reveal the presence of rare Sb–In bonds with virtually identical bond lengths of 2.8317(3) Å (5), 2.8333(3) Å (6), and 2.8340(2) Å (7), that are comparable to those reported for [R₂SbInR’₂] (2.824–2.934 Å; x = 2, 3; R = Me, SiMe₃; R’ = Me, Et, tBu, CH₂SiMe₃).[32] The Cp* ligands adopt a κ¹-coordination with Sb–C bond lengths of 2.2325(12) Å (5), 2.2365(12) Å (6), and 2.2429(16) Å (7).

Reactions of Cp*SbX₂ (X = Cl, Br) with two equivalents of Lin (Scheme 3), as well as treatment of either 5 or 6 with one equivalent of Lin at ambient temperature all produce orange solutions over the course of several hours. Crystallization from solutions in hexane yielded pale yellow crystals, which were identified as In-substituted antimony hydrides [L(X)In]₂SbH (X = Cl, Br 9). The reactions proceed without formation of significant amounts of side products as was proven by ¹H NMR spectroscopy. In contrast, no clean reactions were observed with Cp*SbF₂ and Cp*SbI₂ such that neither hydrides nor radical species could be isolated. However, an in situ monitoring of Cp*Sbl₂ with Lin by ¹H NMR spectroscopy revealed trace amounts of [L(lin)₂SbH due to the appearance of a resonance at –2.56 ppm (Figure S31). A comparable resonance was not found in the reaction of Lin with Cp*SbF₂. The formation of 8 and 9 is astonishing as it raises the question about the origin of the Sb-bound hydrogen atom. The observation of the reaction progress by in situ ¹H NMR spectroscopy revealed a simultaneous production of 1,2,3,4-tetramethylfulvene, which was identified by its characteristic methylene proton resonance at 5.34 ppm.[33] Interestingly, a similar fulvene elimination/E-H (E = P, As) bond formation reaction was observed upon the phosphine coordination of Cp*-substituted bridged pentelidene complexes.[34]

¹H and ¹³C NMR spectra of compounds 8 and 9 show the expected resonances of the β-diketiminate ligand. The Sb–H resonances are found at higher field (8 – 3.42 ppm, 9 – 3.07 ppm) compared to Dmp₂SbH (5.18 ppm) (Dmp = 2,6-Mes₂C₆H₃),[30] [O(Me₅SiNDip)₂]₂SbH (11.34 ppm)[36] and [L(Cl)Ga]Sb(H)Cp* (2.73 ppm).[20] A similar shift was only reported for [Me₃N(H)₂B]₂SbH (2.48 ppm),[37] which contains two electropositive B-based substituents at Sb. The presence of the Sb–H moieties was further proven by IR spectroscopy, which featured characteristic bands at 1846 and 1848 cm⁻¹ for 8 and 9, respectively. These values are in accordance to the reported values of antimony hydrides.[20, 35–37] The molecular structures of 8 (Figure 5) and 9 (Figure S47) were determined by single-crystal X-ray diffraction.

Unfortunately, the Sb-bound hydrogen atoms could not be located on the electron density map, which could possibly be due to a two-fold disorder of the hydride ligand relative to the In-Sb-In plane. Nevertheless, its existence was unambiguously proven by ¹H NMR and IR spectroscopy. The Sb–In bond lengths of the two independent moieties of 8 (molecule 1: 2.7348(5) Å, 2.7384(5) Å; molecule 2: 2.7382(5) Å, 2.7472(5) Å) compare well to those of 9 (2.7250(4) Å, 2.7347(3) Å), but are

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**Scheme 3.** Reactions of Lin with Cp*SbX₂. Yields in parentheses.

**Figure 4.** Molecular structure of 6. Hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.

**Figure 5.** Molecular structure of 8. Hydrogen atoms were omitted for clarity. Displacement ellipsoids are drawn at 50% probability level.
considerably shorter than those of 5–7. The same trend is observed for A, 3, and 4 in comparison to E, 1, and 2 (Table 1), which can be either explained by a stronger backdonation from the electron-rich Sb in the [L(X)M]_2Sb motives or by enhanced dispersion forces between the Dip groups of the β-diketiminate ligands. The In-Sb-In angles (8 molecule 1: 101.775(15), molecule 2: 100.943(15); 9 98.602(11)) are comparable yet slightly sharper than those in A, 3, and 4, presumably due to the decreased steric bulk of the [L(X)In] ligands compared to [L(X)Ga] (see below).

Investigation of the reaction mechanism

To provide an explanation for the observed radical (LGa) versus the hydride formation (LIn), the underlying reaction mechanism was studied in more detail. Similar to the analogous reactions of antimony trihalides SbX₃ with LGa, we propose a mechanism that includes a sequential two-fold insertion of LM into the Sb–X bonds of Cp*SbX₂, which initially yields [L(X)M]Sb(X)Cp* (compounds E, 1, 2, 5, 6, 7), followed by a short-lived intermediate of the type [L(X)M]₂SbCp* (I). Although such an intermediate could neither be isolated nor observed by in situ ¹H NMR spectroscopy, the high degree of steric congestion in I likely leads to the liberation of the most labile ligand in the system, namely ¹-Cp*. This step proceeds via two potential pathways: a) Sb–C bond homolysis with the formation of radical [L(X)Ga]₂SbC₄ and Cp* or b) synchronous or asynchronous β-H elimination with the formation of hydride [L(X)In]₂SbH and 1,2,3,4-tetramethylfulvene (Scheme 4).

In order to detect proposed intermediates such as I, LM was reacted with CpSbCl₂, which contains the sterically less demanding Cp (Cp = C₅H₅) substituent. Reactions with one equivalent of LGa yielded [L(Cl)Ga]Sb(Cl)Cp (10), while reactions with two equivalents of LGa gave [L(Cl)Ga]₂SbCp (11) (Scheme 5). These results support the proposed reaction mechanism. Unfortunately, similar reactivities were not observed for LAl and LIn, instead, dark insoluble materials were obtained with different solvents and reaction temperatures. 10 and 11 were isolated as colourless and yellow crystals, respectively, which are stable in the solid state, but decompose in solution (see below). The ¹H and ¹³C NMR spectra of 10 show the expected resonances of the corresponding ligands (L, Cp) in a 1:1 ratio and appear overall very similar to those of insertion compounds E, 1, 2, 5, 6, and 7. Compound 11 shows several broad resonances in the ¹H NMR spectrum at ambient temperature due to dynamic processes, which became sharper upon cooling to –60°C. Two distinct signals of the γ-CH protons of both magnetically inequivalent β-diketiminate ligands and four resonances corresponding to the C₅H₅ protons were observed under these conditions (Figure S35). The solid-state structures of 10 (Figure S48) and 11 (Figure 6) feature k¹-coor...
dinated Cp ligands at Sb with Sb–C bond lengths of 2.221(3) Å (10) and 2.2396(12) Å (11), which are in good agreement with the Cp*-substituted complexes E, 1, 2, 5, 6, and 7. The Ga–Sb bond lengths (10 2.6453(5) Å; 11 2.6472(5) Å, 2.6352(5) Å) lie within the expected range,16–19,22 while the Ga-Sb-Ga bond angle in 11 (106.838(13)°) is similar to those in radicals 3 and 4,26 but considerably wider than that in [L(Cl)Ga]2SbDip (97.603(7)°).24

11 is unstable in solution and decomposes slowly at ambient temperature but much faster at elevated temperature (60 °C), yielding stibanyl radical A and LGa(Cl)Cp as side product (12) in moderate yields (Scheme 5, Figure S49). The formation of A shows the tendency of homolytic Sb–C cleavage of cyclopentadienyl-substituted stibanes and supports the proposed mechanism (Scheme 4). However, the formation of 12 shows that besides homolytic pathways, heterolytic/polar pathways are also accessible depending on the nature of the ligand.

Furthermore, the origin of the observed radical versus hydride selectivity was investigated by quantum chemical calculations. 13 and 14 were chosen as model systems with methyl groups instead of the very bulky Dip units (Scheme 6). These models allow to separate electronic influences from steric effects. In the first step, the two possible reaction pathways (homolytic bond cleavage (pathway a) in Scheme 6), while the second step is the hydrogen atom abstraction from the Cp* radical by the antimony radical (pathway c) in Scheme 6). The computed energy profile for this reaction yielded a curve (right side of Figure 8) with a flat area for large Sb–H distances, a transition state at about 2.1 Å, as open-shell singlets using the UB3LYP function. This procedure provides reliable geometries and energies for singlet-state diradicals of large systems with diradical character where high-level ab initio calculations are not feasible.16

In order to calculate the homolytic bond cleavage (pathway a) in Scheme 6), the distance between the antimony and the carbon atom was fixed at given values and all other parameters were optimized by means of B3LYP-D3BJ. The resulting data are depicted in Figure 7.

An enlargement of the distance d(Sb–C) leads to a curve showing a sharp energy increase in the first part followed by a flat area in the second part. The first part corresponds to the cleavage of the Sb–C bond, while the second part represents the van der Waals complexes (15 and 16) between the two radicals ([L(Cl)M]2Sb and Cp*). These diradicals are minima and about 30 kcal mol⁻¹ higher in energy than the corresponding intermediates 13 and 14. In the case of the β-H elimination (pathway b) in Scheme 6), a relaxed surface scan of the Sb–H bond length was applied, where the distance between the antimony and the hydrogen atom was held constant at certain values. The obtained curves (Figure 8, right) show that the energy values raise to over 65 kcal mol⁻¹ at a 1.75 Å Sb–H distance for 13 and 14, which is slightly larger than an expected Sb–H hydride distance (1.7 Å). This shows that 13 and 14 fail to form the corresponding van der Waals complexes between the antimony hydride and 1,2,3,4-tetramethylfulvene (17 and 18). Here, the β-H elimination does not occur for 13 and 14, hence an alternative pathway for the formation of the hydride must be considered. One possibility is a stepwise mechanism: the first step is the formation of the diradicals 15 and 16 (pathway a) in Scheme 6), while the second step is the hydrogen atom abstraction from the Cp* radical by the antimony radical (pathway c) in Scheme 6). The computed energy profile for this reaction yielded a curve (right side of Figure 8) with a flat area for large Sb–H distances, a transition state at about 2.1 Å.

$$\Delta E = kT \ln \left( \frac{n}{n_0} \right)$$
and a very steep part representing the formation of the Sb–H bond. The energy of the van der Waals complexes 17 and 18 is about 16 kcal mol$^{-1}$ higher than that of the corresponding intermediates 13 and 14.

The following conclusions can be drawn for the model systems 13 and 14. The cleavage of the Sb–C bond is accompanied by high energetic effort. The diradicals can be stabilized by hydrogen atom abstraction yielding the corresponding hydrides, whereby the activation energy for this process is very low. The direct formation of the hydrides starting from the intermediates 13 and 14 via a concerted β-H elimination is unlikely. The energy values for the Ga- and the In-substituted systems are very similar, and in both cases the same products are expected.

Figure 8. Left: Energy profile for the decrease of the Sb–H bond in the intermediates 13 and 14 (blue: M = Ga; red: M = In). Right: Energy profile for the hydrogen atom abstraction from the Cp* radical by the antimony radical yielding the van der Waals complexes 17 and 18 (blue: M = Ga; red: M = In).

A completely different picture emerges if the homolytic Sb–C bond cleavage (pathway a) and the subsequent hydrogen atom abstraction from the Cp* radical by the antimony radical (pathway c) are considered for the Dip-substituted systems (Figure 9). Due to the high steric overload in the Ga-substituted intermediate 1a, the radicals A and Cp* are more stable by ca. 11 kcal mol$^{-1}$ than the intermediate 1a. For the subsequent hydrogen atom abstraction reaction, an activation energy of 19.2 kcal mol$^{-1}$ is required. Hence, this abstraction does not occur, but a dimerization of the Cp* radical is observed. Consequently, radical A remains in solution. In the case of the In-substituted intermediate 1b, the radicals F and Cp* are less stable than 1b and the subsequent hydrogen atom abstraction, with an activation energy of about 10 kcal mol$^{-1}$, can occur, leading to the hydrides 8 and 1,2,3,4-tetramethylfulvene. These findings lead to the following conclusion: the driving force for the Sb–C bond homolysis is the steric overload in the intermediate I. The higher the steric overload at the antimony atom, the higher the activation barrier for the subsequent hydrogen atom abstraction. In the case of the Ga-substituted system, the H-atom abstraction does not occur, hence only the radical is observed. The higher steric overload in the Ga-substituted intermediate I was assessed by comparing the buried volume calculations$^{34(1)}$ of the [L(Cl)Ga] and [L(Cl)In] ligands. In the case of [L(Cl)Ga] ($V_{bur} = 35.3\%$), the Sb center in [L(Cl)(M)Sb] is by about 13% more encumbered in comparison to [L(Cl)In] ($V_{bur} = 28.6\%$) (Figure S51).

Conclusions

A systematic study on reactions of Cp*SbX$_2$ with different amounts of LM were performed to gain a deep understanding on the reaction mechanism of these reactions and on the influence of the halide substituents as well as the group 13 metal. The reactions proceeded stepwise; first with the formation of

Figure 9. Reaction of the intermediates 1a-b to the radicals [L(Cl)(M)Sb] (A and F) and the hydrides [L(Cl)(M)SbH] (8 and 19) calculated by means of B3LYP-D3BJ. The indicated free-energies ($\Delta$G) are given in kcal mol$^{-1}$.
the corresponding mono-insertion products [LXM]SbX2Cp* (M = Ga, In; X = Cl, Br, I), followed by the formation of either Ga-substituted stibanyl radicals [LXGa]Sb or In-substituted stibanes [LInSb]SbCl containing the sterically less demanding Cp substituent. Computational calculations gave more insights into the underlying reaction mechanism, suggesting that the formation of [LInSb]SbCl proceeds via a hydrogen atom abstraction from Cp* by intermediate [LInSb]Sb radicals, rendering this process a stepwise β-H elimination that is mainly controlled by the steric environment.

**Experimental Section**

**General Procedures:** All manipulations were performed under an atmosphere of purified argon using standard Schlenk and glovebox techniques. Solvents were dried using a MBraun Solvent Purification System and were carefully degassed. Karl Fischer titration of the dry solvents show water levels less than 3 ppm. Deuterated solvents were prepared according to slightly modified literature procedures.

**Instrumentation:** 1H (300, 500, 600 MHz) and 13C{1H} (75, 126, 151 MHz) NMR spectra were recorded using a Bruker Avance DPX-300, Bruker Avance DRX-500 or Bruker Avance III HD spectrometer and the spectra were referenced to internal 2,2-dimethyl-2-silapentane-5-sulfonic acid (DSS). Microanalyses were performed at the Elemental Analysis Laboratory of the University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FTIR spectrometer equipped with a single reflection ATR sampling module, which is placed in a glovebox.

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