

DOI: 10.1002/zaac.202200014

Reactivity of the stibinidene complex $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2(\text{thf})]$

Lena Rummel,^[a] Michael Seidl,^[a] Alexey Y. Timoshkin,^[b] and Manfred Scheer*^[a]

Stibinidene complexes are rare and highly sensitive low-valent main group compounds, which have not been studied extensively for their reaction behavior so far. In the reaction with GaCl_3 , the stibinidene complex $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2(\text{thf})]$ (**1**) shows a dimerization to $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2]_2$ (**2**) and yields the anionic double-chlorinated compound $[\text{Cl}_2\text{Sb}\{\text{Cr}(\text{CO})_5\}_2]^-$ (**3**) in the reaction with different ionic nucleophiles. When using neutral

nucleophiles (such as amines, isocyanides and phosphines) as reaction partners, tetrahedral complexes of the type $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2\text{Nu}]$ (**4**: $\text{Nu} = \text{NH}_2\text{Mes}$; **5**: $\text{Nu} = \text{CN}(\text{dmp})$; **6**: $\text{Nu} = \text{PPh}_3$; **7**: $\text{Nu} = \text{PPh}_2\text{H}$) are formed which can be used in subsequent reactions. All of these products are among the first of their type to be synthesized and isolated.

Introduction

Since the first synthesis of a stable carbene in 1988 by the group of Bertrand^[1] and the subsequent synthesis of the first N-heterocyclic carbene (NHC) by *Arduengo et al.* a few years later,^[2] low-valent main group compounds have been the target of major research activities. In the field of low-valent pnictogen compounds, the first stable nitrene ($\text{R}-\text{N}$) was synthesized only in 2012.^[3] Its heavier homologues, the phosphinidenes ($\text{R}-\text{P}$), are considered to be very reactive and are often stabilized, e.g. by transition metal fragments in order to use them for synthetic purposes. Their coordination modes range from η^1 to μ_4 .^[4] Phosphinidene complexes also exhibit various interesting properties such as a small HOMO-LUMO gap and unusually high downfield shifts in the ³¹P NMR spectrum as well as special reaction behaviors.^[5,6]

Going further down the periodic table, arsinidene complexes are already more uncommon and their reaction behavior and applications are not as well-studied as for their lighter homologues. Stibinidene and bismuthinidene complexes, on the other hand, have been scarce and their features were barely examined. This changed in recent years when new systems to stabilize the stibinidenes and bismuthinidenes were developed. The most significant examples are phosphine-,^[7] carbene-^[8] and

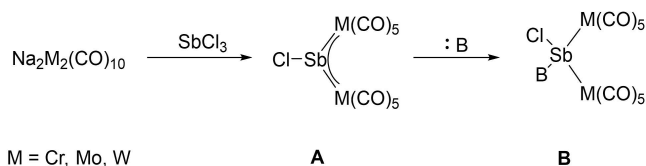
N,C,N pincer-stabilized^[9] pnictinidenes. Especial the later ones got some attention as ligands in transition metal complexes,^[10] in reactions with alkynes^[11] or as catalysts.^[12] For example Cornella et al. could successfully activated N_2O under very mild conditions by using a bismuthinidene complex as catalyst,^[13] emphasizing the potential of pnictinidene complexes in the catalytic activation of small molecules. The first trigonal planar stibinidene complex, $\text{PhSb}[\text{Mn}(\text{CO})_2\text{Cp}]_2$, was synthesized by Huttner *et al.* in 1978 from a diiodostibane. Even back then, the authors proposed the presence of $\text{Sb}-\text{Mn}$ π -bonding in this complex due to its unusual bond lengths and angles as well as the trigonal planar environment at the Sb atom.^[14] In 1984, they reported the first synthesis of the chlorosubstituted stibinidene complex $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2]$ which has a 3-center 4- π electron bond across both $\text{Sb}-\text{Cr}$ bonds as have related phosphinidene and arsinidene complexes with similar spectroscopical features. In thf solutions, the chlorostibinidene complex forms the adduct $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2(\text{thf})]$ (**1**), which can be crystallized and isolated.^[15,16] The trigonal planar stibinidene complexes $[\text{ClSb}\{\text{M}(\text{CO})_5\}_2]$ (**A**; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; Scheme 1) are typically synthesized via a salt elimination reaction between $\text{Na}_2[\text{M}_2(\text{CO})_{10}]$ and SbCl_3 . Since the stibinidene complex **A** is quite unstable and cannot easily be isolated (in the case of $\text{M} = \text{Mo}, \text{W}$), it can be trapped using Lewis bases **B** to form stable adducts with the general formula $[\text{ClSb}\{\text{M}(\text{CO})_5\}_2\text{B}]$ (**B**)^[16] Huttner and co-workers also observed the occurrence of distibene complexes of the type $[\text{RSb}=\text{SbR}][\text{W}(\text{CO})_5]_3$ as side products during the synthesis of stibinidene complexes, especially when using non-donor solvents and Lewis-acidic complex fragments in the reaction. The group also proposed a valence tautomerism for trigonal planar stibinidene complexes (Scheme 2). In the type **A** complex, the

[a] Dr. L. Rummel, Dr. M. Seidl, Prof. Dr. M. Scheer
Department of Inorganic Chemistry
University of Regensburg
Universitaetsstrasse 31, 93053 Regensburg, Germany
E-mail: manfred.scheer@ur.de

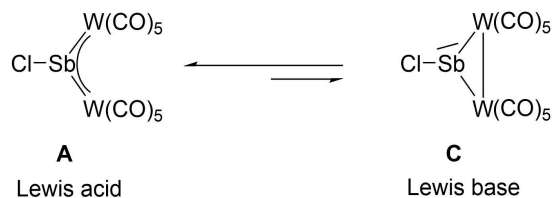
[b] Prof. Dr. A. Y. Timoshkin
Institute of Chemistry
St. Petersburg State University
Universitetskaya emb. 7/9, 199034 St. Petersburg, Russia

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/zaac.202200014>

© 2022 The Authors. *Zeitschrift für anorganische und allgemeine Chemie* published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.



Scheme 1. Synthesis of the chlorostibinidene complexes **A** and subsequent addition of a base.



Scheme 2. Valence tautomerism in trigonal planar stibinidene complexes.

empty *p* orbital at the Sb atom is saturated by the backbonding of the filled metal *d* orbitals, making these compounds stable at standard conditions under inert gas and thus revealing a Lewis-acidic behavior. Adding a base to stibinidene complexes typically results in the formation of adducts, even in cases where **A** is not isolable (*M* = Mo, W). Most importantly, the geometry at the Sb atom changes from trigonally planar in the starting material to tetrahedral in its adducts. The Huttner group further emphasizes their claim with the synthesis and characterization of a type **C** adduct (Scheme 2), [(*t*-Bu)Sb{W(CO)₅}]₂, in the reaction of Na₂[W₂(CO)₁₀] with ^tBuSbCl₂. These adducts are characterized by the formation of a W–W bond, resulting in the growth of two electrons as a lone pair at the Sb atom. Thus, the resulting type **C** stibinidene complexes are Lewis bases in contrast to type **A** complexes (Scheme 2)^[17] Overall, to date, research on stibinidene complexes has focused on their synthesis and characterization, as has recently been shown for [Sb{Cr(CO)₅}][−].^[18]

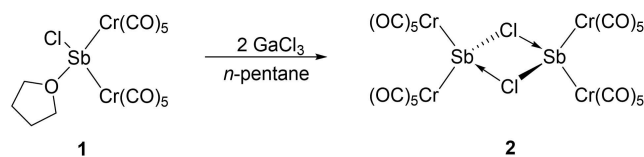
Herein we report on the use of [ClSb{Cr(CO)₅}]₂(thf) (**1**) as a starting material in the reactions with various nucleophiles. By this way diverse products were isolated and characterized.

Results and Discussion

Compound [ClSb{Cr(CO)₅}]₂(thf) (**1**) offers a variety of interesting properties, including thermochromism as well as solvatochromism, as already reported for this type of compounds.^[15] In *n*-pentane, the compound is orange at low temperatures (−90 °C to −30 °C) and barely soluble, while at room temperature, **1** dissolves to give a turquoise solution. This phenomenon had previously been described as the result of the reversible formation of adducts of stibinidene complexes in solution. While the trigonal planar complexes of the type [ClSb{M(CO)₅}]₂ are known to give intensively green colored solutions, their adducts, on the other hand, are known to form less intensively colored products, mostly between yellow and orange.^[15] We also found that, in ether or dme at room temperature, **1** exhibits a red color and, in toluene, forms an orange suspension at −90 °C and a green solution at room temperature, respectively. All these color changes are reversible upon cooling down or warming the respective solutions.

As reported for [ClSb{Mn(CO)₂Cp*}]₂, its reaction with GaCl₃ leads to the formation of the linear heterocumulene cation [Cp*(CO)₂Mn=Sb=Mn(CO)₂Cp*]⁺ (Cp* = C₅Me₅).^[19] We therefore

wanted to ascertain if that was also possible for **1**. To this end, the reaction was conducted accordingly with 2 equivalents of GaCl₃ in *n*-pentane (Scheme 3). However, the formation of a heterocumulene was not observed, instead it turned out to be possible to crystallize the dimer [ClSb{Cr(CO)₅}]₂ (**2**) from the reaction solution. Apparently, GaCl₃ is not strong enough to abstract Cl[−] from **1**. In exchange, in a non-polar solvent as for instance pentane, the starting material is partly dissociated into thf and [ClSb{Cr(CO)₅}]₂, to which one of the lone pairs of a Cl atom of **1** can add itself to result in the dimer **2**. Notably, this is the first time that crystals of this type of a stibinidene could be obtained without thf as an additional Lewis base. The molecular structure of **2** is shown in Figure 1. The two Sb{Cr(CO)₅} fragments are connected via two bridging Cl atoms, forming an Sb₂Cl₂ four-membered ring. The Sb–Cl distances are 2.5093(9) Å and 2.8997(10) Å, respectively, both of them being significantly longer than the sum of the single-bond covalent radii of 2.39 Å for Sb and Cl according to *Pyykkö and Atsumi*, revealing the dative nature of the Sb–Cl bonds (*χ*_{Cl-Sb} = 1.11).^[20] The Sb–Cr distances in **2** are also worth mentioning, since they are shorter compared to **1**, indicating a partially double bond character because of the backbonding from a *d* orbital of Cr into the vacant *p* orbital at the Sb atom. The Sb atoms possess a distorted tetrahedral coordination geometry, with a



Scheme 3. Reaction of **1** with 2 eq. GaCl₃.

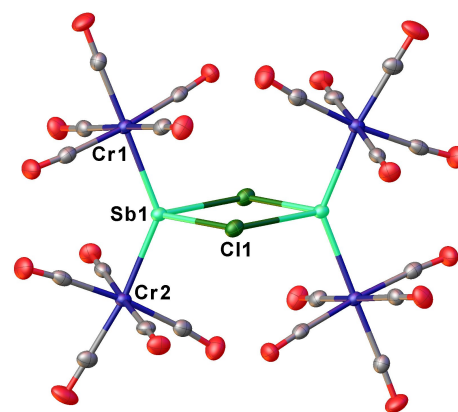


Figure 1. Molecular structure of **2**. Anisotropic displacement parameters set to 50% probability level. Selected bond lengths [Å] and angles [°]: Sb1–Cr1 2.5126(6), Sb1–Cr2 2.5167(6), Sb1–Cl1 2.5091(9), Sb1–Cl1 (1−*x*, 1−*y*, 1−*z*) 2.8999(9); Cr1–Sb1–Cr2 137.28(2), Cr1–Sb1–Cl1 (1−*x*, 1−*y*, 1−*z*) 104.78(2), Cr2–Sb1–Cl1 (1−*x*, 1−*y*, 1−*z*) 105.62(2), Cl1–Sb1–Cr1 107.20(3), Cl1–Sb1–Cr2 108.60(3), Cl1–Sb1–Cl1 (1−*x*, 1−*y*, 1−*z*) 76.39(3), Sb1–Cl–Sb1 (1−*x*, 1−*y*, 1−*z*) 103.61(3).

Cr1–Sb1–Cr2 angle of 137.28(2)° and a Cl1–Sb1–Cl1 (1–x, 1–y, 1–z) angle of 76.39(3)°. This can be explained by the steric bulk of the Cr(CO)₅ groups, which are arranged in the largest possible distance. A similar Bi compound, [(Cp(CO)₂Mn)₂BiCl]₂, is known with Cp(CO)₂Mn as a metal fragment, obtained by the reaction of Cp(CO)₂Mn(thf) with BiCl₃. The authors point out its asymmetric Bi–Cl distances, which are explained by the tendency of halogens to form adducts.^[21]

Optimized at the M06-2X/def2-TZVP level of theory, the gas phase structure of **2** is D₂ symmetric and different from the asymmetric structure as observed in the solid state. The optimized gas phase Sb–Cl distance of 2.651 Å is in between the experimental values of 2.5093(9) and 2.8997(10) Å for the asymmetric structure. This is also reflected by the Wiberg bond index (WBI) values for the Sb–Cl bonds in optimized (0.379) and experimental (0.503 and 0.232) geometries. Bonding in **2** can be described using the donor-acceptor bonding model, similar to the one used for the description of the CAAC stabilized Sb⁺,^[22] only in the present case the stabilization is caused by the interaction with two Lewis acids Cr(CO)₅ and one of the bridging Cl atoms as a Lewis base. The interaction of the LUMO of the SbCl{Cr(CO)₅}₂ monomer (Figure 2a) with lone pairs of the Cl atom of the second molecule results in **2** (respective MOs are given on Figure 2b,c). The LUMO of SbCl{Cr(CO)₅}₂ can also interact with Lewis bases, forming **1**, **4–7** (vide infra).

DFT computations show that the reaction (1) is exothermic and exergonic, validating the experimental observations.

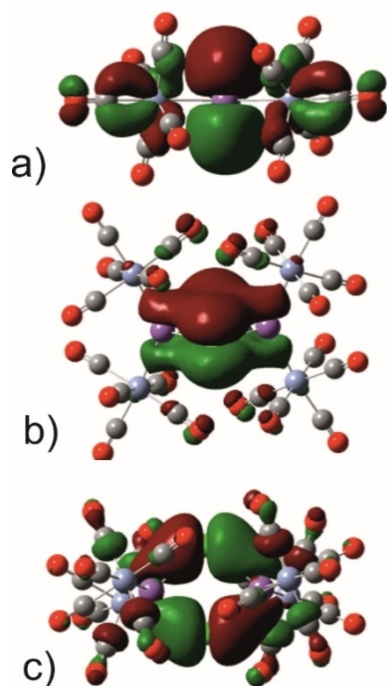


Figure 2. a) LUMO of ClSb{Cr(CO)₅}₂ (side view); b) HOMO-16 (perspective view) and c) HOMO-19 (top view) of **2** (both compounds at gas phase optimized geometries).

The dissociation of **2** into two SbCl{Cr(CO)₅}₂ monomers in the gas phase is endothermic by 75 kJ mol⁻¹. Additional stabilization of **2** may be provided by intermolecular interactions in the solid state, as indicated by Sb...OC contacts of 3.448 and 3.872 Å. In order to estimate the energetics of the additional interactions, a fragment of the solid-state structure, containing three molecules of **2**, was computed. It is by 156 kJ mol⁻¹ lower in energy than three isolated molecules of **2**, confirming the importance of intermolecular interactions. The LUMO of the monomeric ClSb{Cr(CO)₅}₂ can be interpreted as vacant p orbital of the antimony atom (87% of p character, 10% of d character). The antibonding Sb–Cl sigma orbital (LUMO + 2) lies only 8 kJ mol⁻¹ higher in energy than the LUMO. However, its interaction with Lewis bases is sterically hindered by carbonyl groups of two Cr(CO)₅ moieties.

Next, **1** was reacted with different ionic nucleophiles to test its reactivity. Huttner investigated the adduct formation of the pnictinidene complexes mostly on the basis of [ClE{M(CO)₅}₂] (E = As, Sb) with only a few examples of stibinidene and only a few products with non-ionic nucleophiles could be isolated: [ClSb{M(CO)₅}₂B] (B = PPh₃, SC(NHCH₃)₂).^[12,16,23] The reactivity of the trigonal planar pnictinidene complexes [Cp*E{W(CO)₅}₂] (E = P, As) towards ionic nucleophiles was investigated in our group showing adducts of the type [Cp*E{W(CO)₅}₂Nu]⁻ (Nu = CN, ⁿBu, N₃, NH₂, OH, F, Cl, Br, I) to be formed.^[24]

Surprisingly, in the case of the reactions of **1** with charged nucleophiles Nu⁻ (Nu = NH₂, AsH₂, PH₂, CN), no formation of adducts of the type [ClSb{Cr(CO)₅}₂Nu]⁻ could be observed. Instead, in all cases, the anionic chloride adduct [Cl₂Sb{Cr(CO)₅}₂]⁻ (**3**) was the only product that could be isolated. Initial assumptions that the chlorination of **1** occurs because of the use of CH₂Cl₂ as solvent could not be confirmed, since, even after exclusion of CH₂Cl₂ and using Et₂O or thf instead, the only product that could be isolated in all these reactions was the anionic complex [Cl₂Sb{Cr(CO)₅}₂]⁻ (**3**). Using NH₂⁻ as a nucleophile, **3** could be isolated in 30% yield. An explanation for the formation of **3** might be the additional formation of neutral stibinidene complexes of the type [NuSb{Cr(CO)₅}₂] alongside, as was described in the similar reaction of [ClSb{Cp*Mn(CO)₂}₂] with 2,2'-bipyridine.^[25] However, we never succeeded in isolating such complexes.

In the crude ³¹P{¹H} NMR spectrum of the reaction of **1** with LiPH₂·dme, a signal at –172 ppm was found, which could be hinting to the formation of the stibinidene complex [(PH₂)Sb{Cr(CO)₅}₂]. A similar chemical shift of –244.3 ppm was reported for tBu₂SbPH₂,^[26] but unfortunately, due to its instability in solution, no NMR data with better resolution could be recorded for [(PH₂)Sb{Cr(CO)₅}₂]. Moreover, due to the crystallization of the more stable **3**, no such compound could be isolated. The ¹H and ¹³C{¹H} NMR spectra of **3** with different counteranions show the typical chemical shifts for the crown ether used in the respective reaction (cf. Supporting information). In the IR spectrum typical CO resonances could be detected.

The molecular structure of [Na@{(18-crown-6)-dioxane}]⁺[Cl₂Sb{Cr(CO)₅}₂]⁻ is shown in Figure 3. The Cr2–Sb1–Cr1 angle is 129.830(11)° and the Cl2–Sb1–Cl1 angle 90.434(18)°, revealing a distorted tetrahedral geometry at the Sb atom. One of the CO

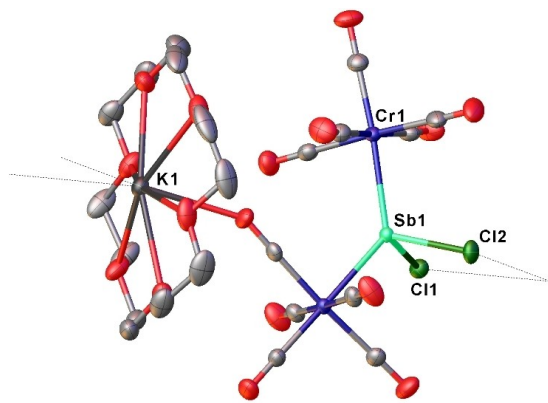
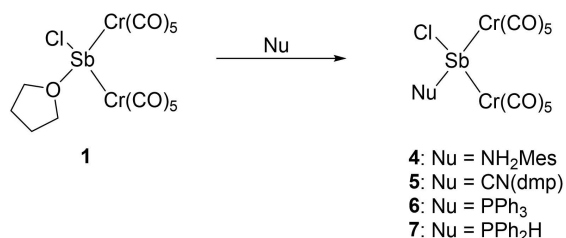


Figure 3. Molecular structure of $[\text{Na}@\text{(18-crown-6)-dioxane}]^+[\text{Cl}_2\text{Sb}\{\text{Cr}(\text{CO})_5\}_2]^-$. Anisotropic displacement parameters are set to 50% probability level. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sb1–Cr2 2.5683(3), Sb1–Cr1 2.5807(3), Sb1–Cl1 2.4218(5), Sb1–Cl2 2.4129(5); Cr2–Sb1–Cr1 129.830(11), Cl1–Sb1–Cr2 104.959(15), Cl1–Sb1–Cr1 108.716(15), Cl2–Sb1–Cr2 106.161(16), Cl2–Sb1–Cr1 109.598(16), Cl2–Sb1–Cl1 90.434(18).

groups as well as both Cl atoms also act as a bridge between the anionic $[\text{Cl}_2\text{Sb}\{\text{Cr}(\text{CO})_5\}_2]^-$ moiety and its counterion, K(18-c-6). Thus, a one-dimensional polymeric structure of the type $[\text{K}(\text{18-c-6})]_n[\text{Cl}_2\text{Sb}\{\text{Cr}(\text{CO})_5\}_2]_n$ (K=counter-ion) is formed (cf. Supporting Information). In comparison, the Cl1–Sb–Cl2 angle of the previously reported $[\text{Na}(\text{thf})][\text{Cl}_2\text{Sb}\{\text{W}(\text{CO})_5\}_2]$ is slightly larger ($94.1(4)^\circ$) than that of **3**, which can be explained by the coordination of both Cl atoms to the K atom in contrast to only one coordinated chlorine atom in $[\text{Na}(\text{thf})][\text{Cl}_2\text{Sb}\{\text{W}(\text{CO})_5\}_2]$.^[27]

Since the reactions of **1** with ionic nucleophiles did not lead to the expected products, non-ionic nucleophiles were used instead and adducts of the type $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2\text{Nu}]$ (**4**: Nu = NH_2Mes , **5**: Nu = $\text{CN}(\text{dmp})$, **6**: Nu = PPh_3 , **7**: Nu = PPh_2H ; Mes = 2,4,6-triisopropylphenyl, dmp = 2,6-dimethylphenyl) could be isolated (Scheme 4). The reactions were conducted in toluene, except for the reaction of **1** with $\text{dmp}(\text{NC})$ where CH_2Cl_2 was used. With the exception of **4**, which crystallizes at room temperature, single crystals of the products were obtained at low temperatures.

$[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2\text{NH}_2\text{Mes}]$ (**4**) was isolated in 53% crystalline yield. Its ^1H NMR spectrum shows signals at chemical shifts of 1.86 and 1.95 ppm for the methyl groups of the mesityl substituent and a signal at 6.43 ppm for its CH groups. The



Scheme 4. Reaction of **1** with different nucleophiles.

chemical shift of the NH_2 protons reveals at 4.64 ppm. The IR spectrum of **4** shows typical CO bands between 1904 cm^{-1} and 2073 cm^{-1} as well as bands for the N–H stretching vibrations at 3260 cm^{-1} and 3316 cm^{-1} . In the reaction of **1** with $(\text{dmp})\text{NC}$, $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2\text{CN}(\text{dmp})]$ (**5**) was obtained in 10% yield. Signals at chemical shifts of 7.14 and 7.45 ppm were detected by ^1H NMR spectroscopy as well as a signal at $\delta = 2.43$ ppm. The IR spectrum shows CO bands between 1904 cm^{-1} and 2076 cm^{-1} . Compound **6** could be obtained in 60% yield and shows a singlet at $\delta = -24.1$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which is in good agreement with the chemical shift of -24.7 ppm that Huttner and co-workers reported in 1985 for the same compound, considering that they recorded the spectrum in a different solvent and at 0°C . However, they obtained this product by the reaction between $\text{Na}_2\text{Cr}_2(\text{CO})_{10}$, SbCl_3 and PPh_3 . Typical CO bands for **6** are found between 1915 cm^{-1} and 2065 cm^{-1} for the $\text{Cr}(\text{CO})_5$ moieties in its IR spectrum.^[16] Compound **7** was isolated in 40% yield. Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at -50 ppm which splits into a doublet in the ^{31}P NMR spectrum with a P,H coupling constant of 411 Hz (Figure 4). In the IR spectrum, multiple CO bands could be detected between 1890 cm^{-1} and 2067 cm^{-1} . In order to generate a phosphinostibinidene complex by an HCl elimination, attempts were made to deprotonate **7** with DBU (DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene). The color change of the reaction solution indicates that a reaction did take place, but unfortunately no phosphinostibinidene complex could be isolated. In the ^{31}P NMR spectrum of the reaction solution, a variety of new signals could be detected which cannot be assigned. Due to the extreme instability of this solution towards moisture and air, the products could not be separated and isolated, which still might be a starting point of further investigations of the reactivity of phosphine-substituted stibinidene complexes.

The molecular structures of the complexes **4–7** are depicted in Figure 5. All of them consist of a $[\text{ClSb}\{\text{Cr}(\text{CO})_5\}_2]$ unit that

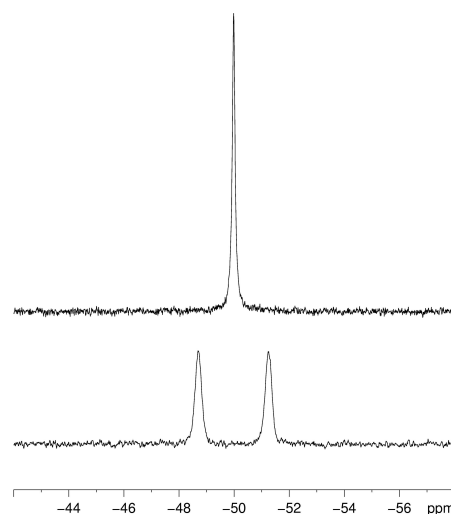


Figure 4. Section of the $^{31}\text{P}\{^1\text{H}\}$ (top) and ^{31}P NMR (bottom) spectra of **7** in C_6D_6 .

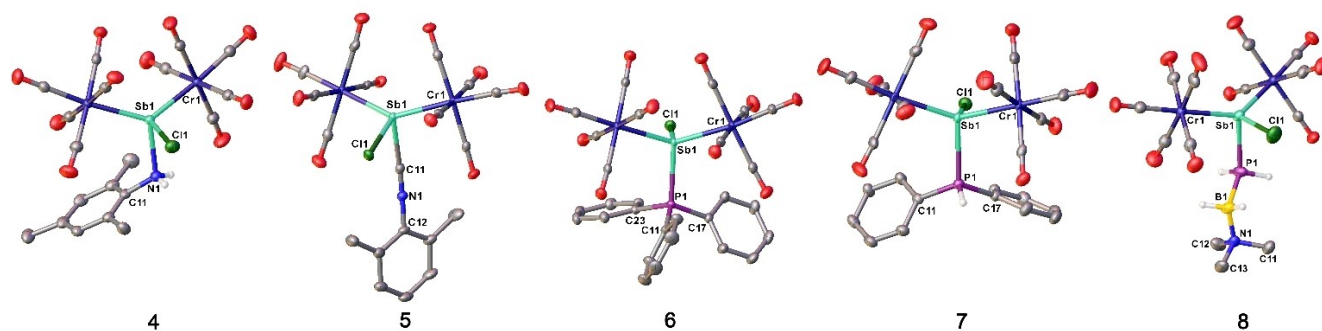


Figure 5. Molecular structures of compounds 4–7. Anisotropic displacement parameters are set to 50% probability level. H atoms at C atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **4**: Sb1–N1 2.3745(16), Sb1–Cl1 2.4018(5); Cr2–Sb1–Cr1 128.217(10), N1–Sb1–Cl1 82.52(5). **5**: Sb1–C11 2.286(3), Sb1–Cl1 2.4439(8); Cr1–Sb1–Cr2 141.578(17), C11–Sb1–Cl1 79.68(8). **6**: Sb1–P1 2.6143(3), Sb1–Cl1 2.4071(3); Cr2–Sb1–Cr1 127.447(7), Cl1–Sb1–P1 88.546(11). **7**: Sb1–P1 2.6091(4), Sb1–Cl1 2.4143(5); Cr1–Sb1–Cr2 131.787(10), Cl1–Sb1–P1 85.571(15).

forms an adduct with the respective nucleophile at the Sb atom, resulting in a tetrahedrally configured Sb atom. The tetrahedral geometries are distorted, with Cr–Sb–Cr angles between 127.447(7)° (**6**) and 141.578(17)° (**5**) and Cl–Sb–Nu angles between 79.68(8)° (**5**) and 88.546(11)° (**6**). This is most likely due to the different steric bulk of the used nucleophiles. All of the Sb–E (E=C, N, P) bonds are slightly elongated single bonds, agreeing with the proposed coordinative nature of the bonds, while the Sb–Cl distances are all within the range of a single bond.^[14] Compound **6** has been reported before, but no X-ray crystal structure was described. However, a similar compound, [MeSb{W(CO)₅}₂PPh₃], was characterized by X-ray crystallography with a similar Sb–P distance.^[16]

After reacting **1** with these various C, N and P nucleophiles, the intention was to use an Sb-based nucleophile in order to generate novel Sb–Sb bonds. For this purpose, (Me₃Si)₂CHSbH₂ was used as a nucleophile, since it is stable enough to be handled for synthesis and the formation of an Sb=Sb double bond compound through HCl- or H₂-elimination was suggested. In the reaction of **1** with (Me₃Si)₂CHSbH₂, only a few crystals of the isomers *d,l*-[(Me₃Si)₂CHSb(H){Cr(CO)₅}]₂ (**8a**) and *meso*-[(Me₃Si)₂CHSb(H){Cr(CO)₅}]₂ (**8b**) suitable for X-ray crystallography could be obtained. **8a** crystallizes as yellow blocks from a mixture of diethyl ether and *n*-pentane, while **8b** crystallizes from a concentrated hexane solution as greenish yellow blocks. Due to their low stability in solution and low quantity because of the low yield of this reaction, no further spectroscopic characterization was possible. The molecular structures of **8a** and **8b** are shown in Figure 6. Both compounds can be described as distibanes with three different moieties (H, CH-(SiMe₃)₂ and Cr(CO)₅) attached in different ways. **8a** is the *R,R'*/*S,S'*-enantiomer of *d,l*-[(Me₃Si)₂CHSb(H){Cr(CO)₅}]₂ and **8b** is its *meso*-isomer. The X-ray crystallographic data reveal disorders in both structures (cf. Supporting Information). The formation pathway of **8a** and **8b** is not clear, however, there has to be a formal migration of Cr(CO)₅ fragments during the reaction. Similar compounds were synthesized by Breunig *et al.* in 2003 via the reaction of R(H)Sb–Sb(H)R (R=(Me₃Si)₂CH) with two

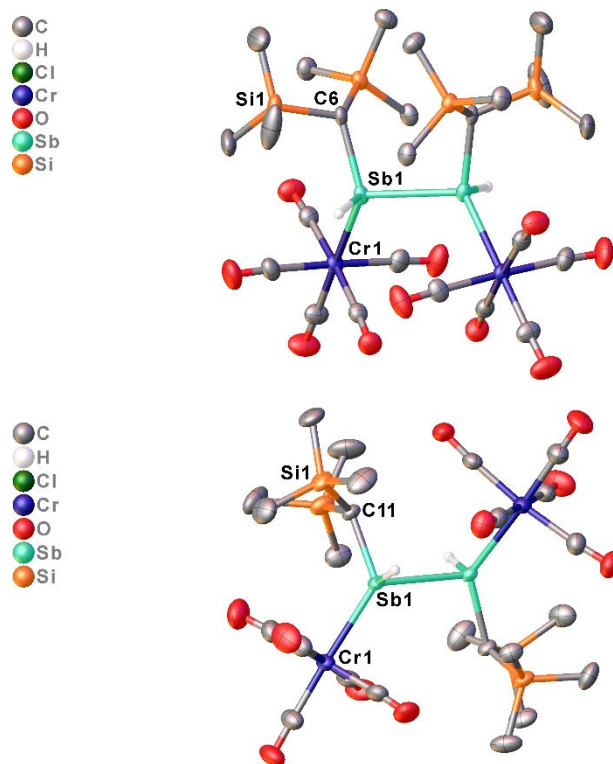


Figure 6. Molecular structures of **8a** (top) and **8b** (bottom). Anisotropic displacement parameters are set to 50% probability level. H atoms bound to C atoms and disordered parts omitted for clarity. Selected bond lengths [Å] and angles [°]: **8a**: Sb1–Sb1 (1–*x*, +*y*, 3/2–*z*) 2.8533(3), Sb1–Cr1 2.6342(4), Sb1–C6 2.161(2); Cr1–Sb1–Sb1 (1–*x*, +*y*, 3/2–*z*) 117.732(9) C6–Sb1–Sb1 (1–*x*, +*y*, 3/2–*z*) 102.29(5). **8b**: Sb1–Sb2 2.8395(3), Sb1–Cr1 2.6325(6), Sb1–C11 2.151(3), Sb2–Cr2 2.6471(6), Sb2–C18 2.164(3); Cr1–Sb1–Sb2 124.229(15), C11–Sb1–Sb2 97.77(9), Cr2–Sb2–Sb1 115.460(16), C18–Sb2–Sb1 102.38(9).

equivalents of W(CO)₅thf. *D,l*- and *meso*-[(Me₃Si)₂CHSb(H){W(CO)₅}]₂ show Sb–Sb single bond lengths of 2.8417(13) and 2.8325(1) Å which are similar to the Sb–Sb bond lengths of **8a**

and **8b**. Additionally, the tetrahedral environment of the Sb atoms is significantly distorted from the ideal geometry because of the steric repulsion between the bulky Cr(CO)₅ moieties and CH(SiMe₃)₂ groups. The same applies to [(Me₃Si)₂CHSb(H){W(CO)₅}]₂.^[28]

With the exception of **2**, all of the abovementioned compounds are fairly stable as solids, even under air. However, in solution, the compounds readily decompose, which can be seen in the color change of these solutions from yellow to green.

Conclusions

In summary, the synthesis, isolation and characterization of various antimony-containing compounds via the reaction of the stibinidene complex **1** with a variety of nucleophiles were reported. Compounds **2**, **4**, **5** and **7** are the first of their kind of nucleophilic substituted stibinidenes which could be isolated and characterized. **6** had already been reported before, but only now could its X-ray structure be obtained. The X-ray structures of the chloro-bridged dimer **3** and the distibanes **8a,b** reveal similarities to other reported complexes. The synthesis of these products paves the way to a deeper understanding of the reaction behavior of stibinidene complexes.

Experimental Section

The following reactions were carried out under an atmosphere of dry nitrogen or argon using standard Schlenk techniques. Traces of O₂ and water were eliminated by leading the inert gas (N₂ or Ar) through a copper catalyst heated to 145 °C, subsequently washing it with concentrated sulphuric acid and drying it with orange gel and phosphorus pentoxide. Solvents were either collected from a solvent purification system (MBraun SPS 800) or dried, degassed and distilled according to standard techniques. Before use, the diatomaceous earth required for filtration was stored at 110 °C. The silica gel 60 (particle size 0.063–0.2 mm) was dried at 150 °C in vacuo for 3 d prior to use.

Synthesis of 1: A clear colorless solution of 912 mg (4 mmol) SbCl₃ in 20 mL thf is added dropwise to a yellow suspension of 2.15 g (5 mmol) Na₂[Cr₂(CO)₁₀] in 150 mL thf. The solution slowly turns orange and then brownish red before it is filtered over diatomaceous earth. Silica gel is then added to the deep red filtrate solution and the solvent removed in vacuo. The brownish residue is then transferred into a Soxhlet apparatus and extracted with 700 mL pentane at 44 °C for 4 h until the solution is dark turquoise. The solvent is largely removed in vacuo and the remaining solution stored at –80 °C. After 3 days, an orange powder of [ClSb{Cr(CO)₅}₂(thf)] (**1**) has formed which is filtered off quickly from the clear solution (which turns turquoise again upon warming to room temperature) and dried in vacuo. Yield: 817 mg (1.3 mmol, 33%); ¹H NMR (CD₂Cl₂, 400 MHz): δ [ppm] = 2.07 (s, 2H, CH₂), 4.13 (s, 2H, CH₂); ¹³C NMR (CD₂Cl₂, 100 MHz): δ [ppm] = 25.3 (s, CH₂), 78.5 (s, CH₂), 213.7 (s, CO), 220.4 (s, CO); IR (ATR, Diamond) ν_{max}/cm⁻¹ = 1917 (m, CO), 2042 (w, CO).

Reaction of 1 with GaCl₃: 62 mg (0.1 mmol) **1** and 35 mg (0.2 mmol) GaCl₃ are dissolved in 10 mL n-pentane. The solution immediately turns first turquoise and then brown. After 1 h of stirring at room temperature, the solution turns green while a black

insoluble residue has formed which is filtered off. [ClSb{Cr(CO)₅}₂]₂ (**2**) crystallizes as dark blocks from the concentrated pentane solution at –28 °C. Yield: 35 mg (0.03 mmol, 30%); ¹³C{¹H} NMR (C₆D₆, 100 MHz): δ [ppm] = 211.2 (s, CO), 211.4 (s, CO); MS (FD): m/z (%): 889.4 [M⁺-Cr(CO)₅] (54), 804.9 [M⁺-Cr(CO)₅-3CO] (54), 746.2 [M⁺-12CO] (51), 711.0 [M⁺-ClCr(CO)₁₀] (57), 576.6 [M⁺-SbCr₂(CO)₁₀] (55), 550.1 [M⁺-19 CO] (100), 522.2 [M⁺-20 CO] (51), 473.8 [M⁺-Cr₂(CO)₁₈] (64); IR (ATR, Ge) ν_{max}/cm⁻¹ = 1930 (s, CO), 1944 (s, CO), 1991 (m, CO), 2042 (m, CO).

Reaction of 1 with various ionic nucleophiles: A solution of 0.1 mmol of the nucleophile (and 0.1 mmol of a suitable crown ether) in the respective solvent was added dropwise to 62 mg (0.1 mmol) **1** in the same solvent at –80 °C. The solution was warmed to room temperature and stirred until a color change occurred. The reaction solution was then filtered and either concentrated and layered with another solvent or recrystallized from another solvent. In either case, [Cl₂Sb{Cr(CO)₅}₂]⁻ (**3**) crystallizes as yellow blocks (Table 1).

Yield of [Na@(18-crown-6)-dioxane]⁺[Cl₂Sb{Cr(CO)₅}₂]⁻ (Nu = NaNH₂): 30 mg (0.03 mmol, 30%); ¹H NMR (CD₂Cl₂, 400 MHz): δ [ppm] = 3.68 (s, CH₂); ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz): δ [ppm] = 69.2 (s, CH₂), 216.7 (s, CO), 217.5 (s, CO); IR (ATR, Diamond) ν_{max}/cm⁻¹ = 1872 (s, CO), 2032 (m, CO).

Synthesis of 4: A solution of 246 mg (0.4 mmol) **1** in 20 mL toluene is added dropwise to a solution of 0.11 mL (108 mg, 0.8 mmol) of MesNH₂ in 30 mL toluene at –20 °C. To the resulting orange suspension, a few mL CH₂Cl₂ are added and the reaction mixture is warmed to room temperature and stirred for 16 h. The solvent is then removed in vacuo and n-hexane is added to the residue. The resulting orange suspension is then filtered, the solvent of the filtrate once more removed in vacuo and the residue dissolved in warm hexane (50–60 °C), concentrated and stored at room temperature. [ClSb{Cr(CO)₅}₂NH₂Mes] (**4**) crystallizes as orange rods and yellowish orange blocks. Yield: 140 mg (0.21 mmol, 53%). ¹H NMR (C₆D₆, 400 MHz): δ [ppm] = 1.86 (s, 6H, CH₃), 1.95 (s, 3H, CH₃), 4.64 (s, 2H, NH₂), 6.43 (s, 2H, CH); IR (ATR, Diamond) ν_{max}/cm⁻¹ = 1904 (s, CO), 2009 (s, CO), 2043 (s, CO), 2073 (m, CO), 3260 (w, NH), 3316 (w, NH). elemental analysis calcd (%) for **4**: C 33.73, H 1.94, N 2.07; found: C 33.77, H 1.77, N 2.14.

Synthesis of 5: A solution of 13 mg (0.1 mmol) (dmp)NC in 10 mL CH₂Cl₂ is added dropwise to a solution of 62 mg (0.1 mmol) **1** in 10 mL CH₂Cl₂ at –78 °C. The resulting yellow solution is stirred and warmed to room temperature. After removing the solvent in vacuo, n-hexane is added to the residue and the resulting suspension is filtered. The solvent is once again removed from the filtrate, the residue is dissolved in Et₂O. [ClSb{Cr(CO)₅}₂CN(dmp)] (**5**) is obtained as greenish yellow plates from the concentrated Et₂O solution at 4 °C. Yield: 9 mg (0.01 mmol, 10%); ¹H NMR (CD₂Cl₂, 400 MHz): δ [ppm] = 2.43 (s, 6H), 7.14 (m, 2H), 7.45 (m, 1H); ¹³C{¹H} NMR (CD₂Cl₂,

Table 1. Details of the reactions.

nucleophile	solvent	color change	crystallization method	counterion
NaNH ₂	Et ₂ O	yellow	layering: Et ₂ O/pentane 1:2	[Na@(18-crown-6)-dioxane] ⁺
KAsH ₂	thf	brown	layering: Et ₂ O/pentane 1:2	[K@18-crown-6] ⁺
LiPH ₂	thf	red	layering: thf/pentane 1:2	[Li@(12-crown-4) ₂] ⁺
KCN	thf	orange	layering: Et ₂ O/pentane 1:2	[K@18-crown-6] ⁺

100 MHz): δ [ppm] = 18.2 (s), 127.9 (s), 128.4 (s), 137.5 (s), 214.6 (s, CO), 214.8 (s, CO), 217.2 (s, CO), 221.0 (s, CO); MS (FD): m/z (%): 626.8 [M^+ -CO-CH₃] (8), 541.7 [M^+ -3CO-C₃H₉] (37), 426.1 [M^+ -5CO-C₆H₃(CH₃)₂] (100), 372.9 [M^+ -Cr(CO)₅-C₆H₃(CH₃)₂] (9), 323.0 [M^+ -Cr(CO)₅-CO-Cl-C₆H₃(CH₃)₂] (54); IR (ATR, Diamond) $\nu_{\max}/\text{cm}^{-1}$ = 1904 (s, CO), 1987 (s, CO), 2047 (m, CO), 2076 (m, CO).

Synthesis of 6: A solution of 26 mg (0.1 mmol) PPh₃ in 10 mL toluene is added dropwise to a dark green solution of 62 mg (0.1 mmol) **1** in 15 mL toluene. The reaction mixture turns brown and then to a bright orange. After filtration of the solution, it is stored at -28 °C and [ClSb{Cr(CO)₅}₂PPH₃] (**6**) crystallizes as yellow plates. Yield: 20 mg (0.06 mmol, 60%); ¹H NMR (C₆D₆, 400 MHz): δ [ppm] = 6.99 (m, 12H, arom.), 7.50 (m, 6H, arom.); ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ [ppm] = -24.1 (s); ³¹P NMR (C₆D₆, 162 MHz): δ [ppm] = -24.8 (br); ¹³C{¹H} NMR (C₆D₆, 100 MHz): δ [ppm] = 129.9 (d, arom. C), 133.6 (d, arom. C), 134.1 (d, arom. C), 216.1 (s, CO); IR (ATR, Ge) $\nu_{\max}/\text{cm}^{-1}$ = 1915 (s, CO), 1957 (s, CO), 1998 (m, CO), 2043 (s, CO), 2065 (m, CO); MS (FD): m/z (%): 803.7 [M^+] (100), 759.9 [M^+ -C₃H₆] (4), 485.9 [M^+ -PPH₃-2CO] (13), 454.0 [M^+ -PPH₃-3CO] (7); elemental analysis calcd (%) for 6 · 0.17 C₇H₈: C 42.77, H 2.01; found: C 42.81, H 1.91.

Synthesis of 7: A solution of 0.08 mL (0.4 mmol) Ph₂PH in 3 mL toluene is added dropwise to a dark green solution of 246 mg (0.4 mmol) **1** in 20 mL toluene. The reaction mixture turns first red, then brown and then orange. After filtration of the solution, it is stored at -28 °C and [ClSb{Cr(CO)₅}₂PPH₂H] (**7**) crystallizes as yellow blocks. Yield: 119 mg (0.16 mmol, 40%). ¹H NMR (C₆D₆, 400 MHz): δ [ppm] = 6.11 (s, 1H, PH), 6.93 (m, 8H, arom. CH), 7.33 (s, 4H, arom. CH); ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ [ppm] = -50.0 (s); ³¹P NMR (C₆D₆, 162 MHz): δ [ppm] = -50.0 (d, ¹J_{PH} = 411 Hz); ¹³C{¹H} NMR (C₆D₆, 100 MHz): δ [ppm] = 130.0 (d, arom. C), 133.8 (d, arom. C), 215.9 (s, CO), 221.6 (s, CO); IR (ATR, Ge) $\nu_{\max}/\text{cm}^{-1}$ = 1890 (m, CO), 1923 (s, CO), 1953 (s, CO), 1999 (m, CO), 2043 (m, CO), 2067 (m, CO); MS (FD): m/z (%): 727.8 [M^+] (100), 562.1 [M^+ -4CO-C₄H₄] (40), 478.9 [M^+ -6CO-Ph-H] (38), 291.0 [M^+ -Cr(CO)₅-2CO-PPH₂H] (38); elemental analysis calcd (%) for 7: C 36.32, H 1.52; found: C 37.08, H 1.51.

Synthesis of 8: A solution of 0.02 mL (0.1 mmol) of (Me₃Si)₂CHSbH₂ in 3 mL toluene is added dropwise to a dark green solution of 62 mg (0.1 mmol) **1** in 20 mL toluene. Upon stirring, the reaction mixture turns red. The solvent is removed and the residue dissolved in a few mL of a 1:3 mixture of Et₂O and n-pentane. *d,l*-[(Me₃Si)₂CHSb(X){Cr(CO)₅}₂] (**8a**, X=H, Cl) crystallizes as yellow blocks at -28 °C. From the decanted solution, the solvent is removed in vacuo and the residue extracted with n-hexane. From the concentrated green n-hexane solution, *meso*-[(Me₃Si)₂CHSb(X)-{Cr(CO)₅}₂] (**8b**) crystallizes as greenish yellow blocks. Yield: few crystals.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft (DFG) for financial support. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords: antimony · stibinidenes · main group chemistry · reactivity · complexes

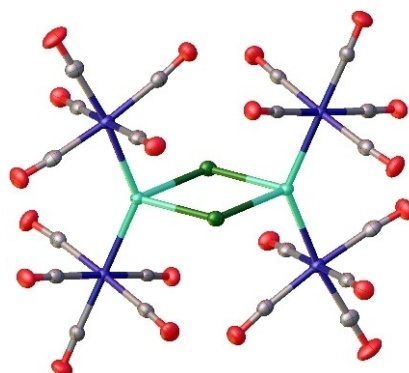
- [1] A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463.
- [2] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
- [3] F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* **2012**, *337*, 1526.
- [4] K. Lammertsma in *Topics in Current Chemistry*, Vol. 229 (Eds.: J.-P. Majoral, T. Chivers), Springer, Berlin, **2003**, pp. 95–119.
- [5] M. E. García, D. García-Vivó, A. Ramos, M. A. Ruiz, *Coord. Chem. Rev.* **2017**, *330*, 1.
- [6] G. Huttner, K. Evertz, *Acc. Chem. Res.* **1986**, *19*, 406.
- [7] D. Raiser, K. Eichele, H. Schubert, L. Wesemann, *Chem. Eur. J.* **2021**, *27*, 14073.
- [8] a) C. L. Dorsey, R. M. Mushinski, T. W. Hudnall, *Chem. Eur. J.* **2014**, *20*, 8914; b) R. Kretschmer, D. A. Ruiz, C. E. Moore, A. L. Rheingold, G. Bertrand, *Angew. Chem. Int. Ed.* **2014**, *53*, 8176; c) J. Krüger, C. Wölper, L. John, L. Song, P. R. Schreiner, S. Schulz, *Eur. J. Inorg. Chem.* **2019**, 1669.
- [9] a) P. Šimon, F. De Proft, R. Jambor, A. Růžička, L. Dostál, *Angew. Chem. Int. Ed.* **2010**, *49*, 5468; b) J. Abbenseth, J. M. Goicoechea, *Chem. Sci.* **2020**, *11*, 9728.
- [10] a) I. Vránová, M. Alonso, R. Jambor, A. Růžička, M. Erben, L. Dostál, *Chem. Eur. J.* **2016**, *22*, 7376; b) I. Vránová, V. Kremláček, M. Erben, J. Turek, R. Jambor, A. Růžička, M. Alonso, L. Dostál, *Dalton Trans.* **2017**, *46*, 3556; c) M. Kořenková, V. Kremláček, M. Erben, R. Jambor, Z. Růžičkova, L. Dostál, *Organomet. Chem.* **2017**, *845*, 49; d) M. Kořenková, M. Hejda, P. Štěpnička, F. Uhlík, R. Jambor, A. Růžička, L. Dostál, *Dalton Trans.* **2018**, *47*, 5812; e) M. Kořenková, M. Hejda, R. Jirásko, T. Block, F. Uhlík, R. Jambor, A. Růžička, R. Pöttgen, L. Dostál, *Dalton Trans.* **2019**, *48*, 11912.
- [11] M. Kořenková, V. Kremláček, M. Hejda, J. Turek, R. Khuda-verdyan, M. Erben, R. Jambor, A. Růžička, L. Dostál, *Chem. Eur. J.* **2020**, *26*, 1144.
- [12] a) F. Wang, O. Planas, J. Cornella, *J. Am. Chem. Soc.* **2019**, *141*, 4235; b) Y. Pang, M. Leutzsch, N. Nöthling, F. Katzenburg, J. Cornella, *J. Am. Chem. Soc.* **2021**, *143*, 12487.
- [13] Y. Pang, M. Leutzsch, N. Nöthling, J. Cornella, *J. Am. Chem. Soc.* **2020**, *142*, 19473.
- [14] a) J. von Seyerl, G. Huttner, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 843; b) J. von Seyerl, G. Huttner, *Angew. Chem.* **1978**, *90*, 911.
- [15] U. Weber, L. Zsolnai, G. Huttner, *J. Organomet. Chem.* **1984**, *260*, 281.
- [16] B. Sigwarth, U. Weber, L. Zsolnai, G. Huttner, *Chem. Ber.* **1985**, *118*, 3114.
- [17] U. Weber, G. Huttner, O. Scheidsteger, L. Zsolnai, *J. Organomet. Chem.* **1985**, *289*, 357.
- [18] M. Shieh, Y.-H. Li, C.-H. Lin, T.-Y. Sun, *Inorg. Chem.* **2020**, *59*, 16073.
- [19] A. Strube, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* **1990**, *399*, 267.
- [20] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186.
- [21] J. von Seyerl, G. Huttner, *J. Organomet. Chem.* **1980**, *195*, 207.

- [22] M. M. Siddiqui, S. K. Sarkar, M. Nazish, M. Morganti, C. Köhler, J. Cai, L. Zhao, R. Herbst-Irmer, D. Stalke, G. Frenking, *J. Am. Chem. Soc.* **2021**, *143*, 1301.
- [23] a) J. von Seyerl, B. Sigwarth, H.-G. Schmid, G. Mohr, A. Frank, M. Marsili, G. Huttner, *Chem. Ber.* **1981**, *114*, 1392; b) J. von Seyerl, B. Sigwarth, G. Huttner, *Chem. Ber.* **1981**, *114*, 1407.
- [24] M. Stubenhofer, *Dissertation*, University of Regensburg, Regensburg, **2012**.
- [25] A. Strube, G. Huttner, L. Zsolani, *J. Organomet. Chem.* **1990**, *399*, 255.
- [26] C. von Hänisch, K. Volz, W. Stolz, E. Sterzer, A. Beyer, D. Keiper, B. Ringler, WO 2016/046394 A1, **2015**.
- [27] M. Schiffer, B. P. Johnson, M. Scheer, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2498.
- [28] G. Balázs, H. J. Breunig, E. Lork, S. Mason, *Organometallics* **2003**, *22*, 576.

Manuscript received: January 14, 2022

Revised manuscript received: February 7, 2022

Accepted manuscript online: February 11, 2022



*Dr. L. Rummel, Dr. M. Seidl,
Prof. Dr. A. Y. Timoshkin, Prof. Dr. M.
Scheer**

1 – 9

**Reactivity of the stibinidene
complex [ClSb{Cr(CO)₅}₂(thf)]**

