Synthesis and Reactivity of Low-Valent Group 14 Element Compounds Brian P. Johnson,^[a] Stefan Almstätter,^[a] Fabian Dielmann,^[a] Michael Bodensteiner,^[a] and Manfred Scheer*^[a]

Dedicated to Professor Gerd Becker on the Occasion of His 70th Birthday

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Abstract. The tetravalent germanium and tin compounds of the general formulae Ph^*EX_3 ($Ph^* = C_6H_3$ Trip-2,6, Trip = $C_6H_2iPr_3$ -2,4,6; E = Sn, X = Cl (1a), Br (1b); E = Ge, X = Cl (2)) are synthesized by reaction of Ph*Li·OEt₂ with EX_4 . The subsequent reaction of 1a,b with LiP(SiMe₃)₂ leads to Ph*EP(SiMe₃)₂ (E = Sn (3), Ge (4)) and the diphosphane (Me₃Si)₂PP(SiMe₃)₂ by a redox reaction. In an alternative approach 3 and 4 are synthesized by using the corresponding divalent compounds Ph*ECl (E = Ge, Sn) in the reaction with LiP(SiMe₃)₂. The reactivity of Ph*SnCl is extensively investigated to give with LiP(H)Trip a tin(II)-phosphane derivative Ph*SnP(H)Trip (6) and with Li₂PTrip a proposed product [Ph*SnPTrip]⁻ (7) with multiple bonding

Introduction

Almost three decades ago Becker et al. succeeded in the synthesis of the first stable phosphaalkyne, tert-butylphosphaalkvne [1], which through an improved synthesis [2] gave a general approach to this class of P=C triply bound compounds on a preparative scale, and many representatives have since appeared [3]. In contrast, arsaalkynes are extremely rare, with the first stable compounds, Mes*C≡As, reported in 1986 [4]. A recent development was reported by the synthesis of the borate derivatives $[(F_3C)_3BC\equiv P]^-$ and $[(F_3C)_3BC\equiv As]^-$ representing phosphaethynyl and arsaethynyl systems [5]. The reaction behavior of phosphaalkynes was intensively investigated both for phosphaorganic [6] and coordination chemistry [7] purposes. Moreover, the discovery of Becker opened up the research field of multiple bonding of the heavier main-group elements [8]. Compounds of the type $R_2E = PR'$ with heavier group 14 elements were isolated having Si=P [9], Ge=P [10], and Sn=P [11] double bonds, which were stabilized kinetically by bulky aryl groups (Mes (C₆H₂Me₃-2,3,6); Trip (C₆H₂iPr₃-2,3,6); Mes* ($C_6H_2tBu_3$ -2,3,6)); or by bulky aliphatic groups $(t-Bu \text{ or } CH(SiMe_3)_2)$ at both phosphorus and the group 14 element atom. Additionally, P-silyl and P-phosphanyl derivatives were successfully prepared in compounds of type R_2 Si=

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between tin and phosphorus. The latter feature is confirmed by DFT calculations on a model compound [PhSnPPh]⁻. The reaction with Li[H₂PW(CO)₅] gives the oxo-bridged tin compound [Ph*Sn{W(CO)₅}(μ -O)₂SnPh*] (8) as the only isolable product. However, the existence of 8 as the bis-hydroxo derivative [Ph*Sn{W(CO)₅}(μ -OH)₂SnPh*] (8a) is also possible. The Sn^{IV} derivatives Ph*Sn(OSiMe₃)₂Cl (9) and [Ph*Sn(μ -O)Cl]₂ (10) are obtained by the oxidation of Ph*SnCl with bis(trimethylsilyl)peroxide and with Me₃NO, respectively. Besides the spectroscopic characterization of the isolated products compounds 1a, 2, 3, 4, 8, and 10 are additionally characterized by X-ray diffraction analysis.

PSi*R*'₃ and *R*₂Si=PP*R*'₂ [12]. A novel chapter of multiple-bond chemistry was opened, when the so-called 'terphenyl' substituent was introduced in main group chemistry. Thus, a novel stannaacetylene, Ph*Sn=CSi*i*Pr₃ (Ph* = C₆H₃Trip₂-2,6), was proposed to exist as a reactive intermediate [13], and the asymmetric dipnictenes Ph**E*=PMes (*E* = As, Sb) were synthesized by *Power* et al. [14]. Moreover, novel arsa-Wittig reagents 2,6-Ph'₂-C₆H₃As=PMe₃ (Ph' = Mes, Trip) were developed by *Protasiewicz* and co-workers, whereby the phosphorus atom is in the +5 oxidation state [15].

Our long-term engagement in phosphaalkyne chemistry [16] presents the question of whether group 14 elements other than carbon can be used for the synthesis of compounds with a triple bond to phosphorus. Compounds featuring an $E \equiv P$ (E =Si, Ge, Sn, Pb) triple bond have not yet been detected or isolated. Only a compound with a Si=P triple bond is tentatively proposed as an unobserved intermediate, the identity of which is suggested based solely on the nature of the isolated product (Scheme 1) [17]. Matrix isolation studies show the access to H₃SiP and its isomers [18]. Moreover, a phosphasilene, RR'Si= PH ($R = Ph^*$, $R' = tBu_3Si$), and its zinc salt were synthesized by Driess et al. [19] and $Cp^*(Cl)_2 EP(SnMe_3)_2$ (E = Si, Ge) was synthesized by Niecke and Pietschnig [20]. All these compounds are on the way to realizing stable derivatives with an $E \equiv P$ triple bond. Interestingly, the stability of triply bonded RSn=P systems has been predicted by quantum chemical calculations only for examples in which R represents a bulky terphenyl group [21].



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Scheme 1. Reaction pathway of thermolysis of Mes*Si(F)₂P{Li(thf)₃}SiMe₃ and proposed generation of intermediate Mes*Si≡P [17].

Thus, the use of bulky terphenyl substituents like, e.g., Ph* (Ph* = C₆H₃Trip₂-2,6; Trip = C₆H₂*i*Pr₃-2,4,6) on tin or germanium (*E*) provides a unique heteroleptic template for preparing element–phosphorus compounds with low-coordination arrangements. With the relatively stable E–C_{aryl} bond anchoring the group 14 atom at one site, reactivity with phosphorus compounds is probed at the remaining coordination sites. As a result, a heteroleptic terphenyl-tin or germanium phosphanide would represent an optimal precursor for the synthesis of $E\equiv P$ triple-bond compounds of the type Ph* $E\equiv P$ (E = Sn, Ge). The experiments reported in the following are partly directed toward this goal. Moreover, the results described give insight into the reaction behavior of low-valent tin compounds.

Results and Discussion

Synthesis of Terphenyl-Trihalogeno-Germanium(IV)- and Tin(IV) Compounds

The most direct preparation of compounds of the formulae Ph^*EX_3 ($Ph^* = C_6H_3Trip-2,6$, $Trip = C_6H_2iPr_3-2,4,6$) is achieved by treating $Ph^*Li \cdot OEt_2$ with EX_4 in a mixture of *n*-hexane and Et_2O [Equation (1)]. Colorless crystals of the products are obtained after work-up and recrystallization from *n*-hexane in moderate yields of 37–45 %. The oxidation of Ph*SnCl (**3**) by PCl₃ gives a higher yield of **1a** (68 %). However, the current transmetalation method saves the step of preparing Ph*SnCl and allows the synthesis of **1a** in a larger scale. *Saito* et al. obtained a yield of 45 % by oxidizing Ph*SnCl with CCl₄ [22].

Ph*Li·OEt₂ +
$$EX_4$$
 $\xrightarrow{Et_2O}$ Ph* EX_3 (1)
- LiX
1a: $E = \text{Sn}, X = \text{Cl}$
1b: $E = \text{Sn}, X = \text{Br}$
2: $E = \text{Ge}, X = \text{Cl}$

Compound **1a** crystallizes in the triclinic space group $P\overline{1}$, and **2** crystallizes in the orthorhombic space group $C222_1$. The molecular structure of **1a** and **2** is shown in Figure 1. The structure of **2** is disordered due to contamination of the product

with Ph*GeCl. The arrangement around the group 14 element atom is a distorted tetrahedron with the chloride ligands pinched toward each other and away from the Ph* ligand, presumably a result of the bulkiness of the Ph* ligand.



Figure 1. Molecular structure of $Ph*ECl_3$ (1a: E = Sn, 2: E = Ge) in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /° for 1a: Sn–Cl 2.155(5), Sn–Cl1 2.322(3), Sn–Cl2 2.321(3), Sn–Cl3 2.328(2); Cl–Sn–Cl1 119.89(13), Cl–Sn–Cl2 122.05(13), Cl–Sn–Cl3 109.26(14), Cl1–Sn–Cl2 98.12(7), Cl1–Sn–Cl3 102.96(8), Cl2–Sn–Cl3 101.67(8) [58].

Formation of Group 14 Element/Phosphorus Compounds

An interesting aspect of the synthesized reagents 1a and 2 is the potential use as starting materials for the synthesis of Sn/ Ge-P compounds in the oxidation state +4 of the group 14 element. Compound 1a was treated with LiP(SiMe₃)₂·1.8THF in Et₂O at low temperature. The ³¹P NMR spectrum of the reaction mixture reveals the formation crude of Ph*SnP(SiMe₃)₂ (**3**) $(\delta(^{31}P) = -123.1)$ and $(Me_3Si)_2PP(SiMe_3)_2$ $(\delta(^{31}P) = -216 [23])$ in an approximate 1:1 ratio as the main phosphorus-containing products [Equation (2)]. As the reduction potential for germanium is generally lower than that for tin, compound 2 reacted with LiP(SiMe₃)₂·1.8THF in Et₂O at low temperature in order to give Ph*GeCl₂P(SiMe₃)₂. However, the same result was achieved and, along with of the forof $(Me_3Si)_2PP(SiMe_3)_2$ as a mation side-product, Ph*GeP(SiMe₃)₂ (4) was isolated [Equation (2)]. Obviously, metal-halogen exchange reactions play a decisive role which is also unavoidable using higher reaction temperatures (up to 0 °C). Similar results are obtained if reaction (2) is carried out under the conditions of the multiple P-P bond formation reactions [24], for which an excess of LiP(SiMe₃)₂ has to be present to assure the autometalation reaction of the silvlphosphorus atom by LiP(SiMe₃)₂ with formation of P(SiMe₃)₃. In order to ascertain whether a heavier alkali-metal phosphanide can induce preferential salt elimination over reduction, the analogous reaction was carried out with 1a and KP(SiMe₃)₂. The ³¹P NMR spectrum of the crude reaction mixture reveals the same phosphorus-containing products as that with LiP(SiMe₃)₂·1.8THF.

 $Ph^{*}ECl_{3} + 3 \operatorname{LiP}(\operatorname{SiMe}_{3})_{2} \xrightarrow{\operatorname{Et}_{2}O} Ph^{*}EP(\operatorname{SiMe}_{3})_{2} + (\operatorname{Me}_{3}\operatorname{Si})_{2}P - P(\operatorname{SiMe}_{3})_{2} \quad (2)$ 3: $E = \operatorname{Sn}_{4}$ 4: $E = \operatorname{Ge}_{4}$

The reduction of **1a** and **2** by $\text{LiP}(\text{SiMe}_3)_2$ and P–P bond formation are unexpected in light of the reports on the reaction of Ph*SiF₃ with LiP(SiMe₃)₂ to give the silane-elimination product shown in Scheme 1 [17]. Clearly, the relative stability of divalent stannylenes and germylenes over silylenes plays a key role in the differing redox behavior of **1a** and **2** in reactions with the lithium phosphanide.

A byproduct-free synthesis of **3** and **4** is achieved, if the corresponding group 14 starting material is already in the oxidation state +2. Thus, Ph**E*Cl (*E* = Sn [25], Ge) was treated with LiP(SiMe₃)₂·1.8THF in *n*-hexane at low temperature. According to the ³¹P NMR spectra of the reaction mixtures only Ph*SnP(SiMe₃)₂ (**3**) (δ (³¹P) = -123.1) and Ph*GeP(SiMe₃)₂ (**4**) (δ (³¹P) = -48.5), respectively, are detected as the main phosphorus-containing products along with traces of HP(SiMe₃)₂ (δ (³¹P) = -236.3), resulting from hydrolysis of LiP(SiMe₃)₂ [Equation (3)]. From these reactions X-ray quality violet crystals of **3** and dark red crystals of **4** are obtained. Interestingly, the isolated yields are similar to the ones obtained by reaction (2).

Ph*ECl + LiP(SiMe₃)₂ $\xrightarrow{n-hexane}$ Ph*EP(SiMe₃)₂ (3) - LiCl 3: E = Sn4: E = Ge

The molecular structure of the compounds 3 and 4 are depicted in Figure 2. Compound 3 crystallizes in the triclinic space group $P\bar{1}$ and **4** in the monoclinic space group $P2_1/c$. In the crystal structure of $Ph^*EP(SiMe_3)_2$ (3: E = Sn, 4: E = Ge) the group 14 atom has a coordination number of two and lies in a bent arrangement (Cipso-Ge-P: 106.88°, Cipso-Sn-P: $105.56(9)^{\circ}$), which is a characteristic feature for structurally characterized stannylene/germylene compounds. The phosphorus atom is located in a distorted trigonal-pyramidal geometry between the group 14 atom and two silicon atoms. Since the phosphorus atom does not approach planarity, it can be concluded that the phosphorus lone pair does not participate significantly in donation to the group 14 element atom. This correlates well with the tin-phosphorus coupling constants of compound **3** (${}^{1}J_{P}117_{Sn} = 1396$, ${}^{1}J_{P}119_{Sn} = 1453$ Hz), which are well below the range for compounds known to exhibit tinphosphorus double bonding (${}^{1}J_{PSn} \approx 2000$ Hz). The bulky nature of the Ph* ligand allows the isolation of the terminal stannylene phosphanide 3 and the terminal germylene phosphanide 4. This is in contrast to the well-established field of phosphastannylenes and -germylenes usually representing phosphanido-bridged dimers [26] or donor-stabilized monomers [27].

Reactivity of Ph*SnP(SiMe₃)₂ (3)

Given the wealth of oxidative reactions of bivalent tin amides with organic halides, transition-metal halides [28], acid



Figure 2. Molecular structures of Ph**E*P(SiMe₃)₂ (**3**: *E* = Sn, **4**: *E* = Ge) in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /° for **3**: C7–Sn 2.229(3), Sn–P 2.527(1), P–Si1 2.244(2), P–Si2 2.243(4); C7–Sn–P 105.61(8), Sn–P–Si1 97.40(5), Sn–P–Si2 110.02(5), Si1–P–Si2 110.58(6). Selected bond lengths /Å and angles /° for **4**: C7–Ge 2.018(5), Ge–P 2.291(4), P–Si1 2.240(5), P–Si2 2.248(1); C7–Ge–P 106.89(5), Ge–P–Si1 119.53(2), Ge–P–Si2 97.49(2), Si1–P–Si2 109.87(3).

chlorides/anhydrides [29], and chalcogens [30], among others, to give well-defined Sn^{IV} addition products, it is expected that chemical oxidation of Ph*SnP(SiMe₃)₂ would be feasible. A variety of reagents bearing halides or pseudohalides were selected such that either spontaneous or thermal silane elimination would be viable upon oxidation and formation of Ph*Sn≡P or similar products would be conceivable. However, low-temperature reactions of Ph*SnP(SiMe₃)₂ with C₂Cl₆, Cp₂Ti(OTf)₂, Hg(OTf)₂, Tl(OOCCF₃)₃, benzoyl chloride, Me₃NO, and tropylium tetrafluoroborate each results in cleavage of the Sn-P bond and generation of an intractable mixture of products, according to ³¹P NMR spectra of the respective crude reaction mixtures. Reaction of Ph*SnP(SiMe₃)₂ with BrCH₂CH₂Br at low temperature results in gradual discoloration of the violet solution to clear beige. The ³¹P NMR spectrum reveals a main phosphorus-containing product (> 65 %) at -167.2 ppm with tin satellites $({}^{1}J_{P}117_{Sn} = 1719, {}^{1}J_{P}119_{Sn} =$ 1799 Hz). Work-up of the solution and crystallization from nhexane afforded only colorless crystals of Ph*Br [31], as identified by X-ray diffraction experiments.

Reactivity of Ph*SnCl (5)

Moreover, the reactivity of the divalent compound Ph*SnCl (5) was of interest and the reactions shown in Scheme 2 were carried out.

The reaction of **5** with LiP(H)Trip was carried out in Et₂O at low temperature and afforded the monomeric arylstannylene phosphanide, Ph*SnP(H)Trip (**6**), with a Trip group and a reactive proton at the phosphorus atom. The ³¹P{¹H} NMR spectrum of the crude reaction mixture reveals a relatively clean reaction with a slightly broadened main signal (ca. 70 %, $\Delta v_{1/2} = 150$ Hz) attributable to **6** ($\delta = -70.9$, ¹J_P117/119_{Sn} = 934 Hz), which is split into a doublet upon proton coupling



Scheme 2. Reactivity of Ph*SnCl (5) with (a) LiP(H)Trip in Et₂O at -78 °C; (b) Li₂PTrip in Et₂O at -78 °C; (c) Li[H₂PW(CO)₅] in *n*-hexane at -78 °C; (d) Me₃SiO–OSiMe₃ in Et₂O at 0 °C; (e) Me₃NO in Et₂O at 0 °C.

 $({}^{1}J_{\rm PH} = 186 \text{ Hz})$, along with traces of Trip(H)P–P(H)Trip (-113.9 ppm) and TripPH₂ (-158.3 ppm) as the only other phosphorus-containing products. The color of the proposed product **6** is intense violet, the same color as for the analogous bis(trimethylsilyl)phosphanide **3**. In the ${}^{31}P{}^{1}H$ } NMR spectrum of **6** a singlet with unresolved ${}^{117/119}$ Sn satellites is observed, which in the proton-coupled ${}^{31}P$ NMR splits into a doublet with two sets of unresolved ${}^{117/119}$ Sn satellites. The observation of unresolved ${}^{117/119}$ Sn satellites is reminiscent of the poorly resolved satellites observed in the ${}^{31}P$ signal for **5**. Owing to the same excellent solubility of the byproducts compound **6** can not be isolated in analytically pure form.

Experiments aimed at deprotonating in situ generated 6 with n-BuLi produced a mixture of unidentified products according to ³¹P NMR spectroscopy. In recognition of the possibility of nucleophilic attack of n-BuLi on the tin atom, a route was chosen to circumvent the direct use of n-BuLi with the stannylene. Thus, TripPH₂ was twice deprotonated by *n*-BuLi, and the resulting doubly lithiated phosphanide Li₂PTrip was added to 5. According to ³¹P NMR, a mixture of products was generated by this protocol, from which Trip(H)P-P(H)Trip could be identified (ca. 20 %). The main product (ca. 40 %) was observed as a broad downfield signal proposed tentatively to be $Li^{+}[Ph*SnPTrip]^{-}$ (7) $(\delta(^{31}P) = 229.7, \Delta v_{1/2} = 280, {}^{1}J_{P}117_{Sn} =$ 1735, ${}^{1}J_{P}119_{Sn} = 2004$ Hz). The broadness of the observed signal is a characteristic indicator for lithium-coordinated anions, where the lithium shifts rapidly between ion-contact and ionseparated forms. No P-H coupling is observed in the protoncoupled spectrum. Attempts to produce 7 by lithiation of 6 with n-BuLi did not result in the observation of the downfield signal observed in the reaction of Ph*SnCl (5) with Li₂PTrip.

The low-field ³¹P NMR shift of the proposed compound 7 (Scheme 2) and the large ${}^{1}J_{P}117/119_{Sn}$ coupling constants signify a situation of multiple bonding between tin and phosphorus. The bonding about tin and phosphorus in the anionic moiety [Ph*SnPTrip]⁻ is isoelectronic to the neutral compound Ph*Sb=PMes with a known double bond [32]. [Ph*SnPTrip]⁻ can also be thought of as isolobal to the doubly reduced acetylene analogue [Ph*Sn=SnPh*]²⁻, which has been suggested as having a Sn=Sn double bond [33], as well as isolobal to the general family of dipnictenes RE=ER (E = P, As, Sb), each with undisputed double-bond character [34]. The bonding between tin and phosphorus is tentatively represented in Scheme 2 with a bond order greater than one, with the possibility that double bonding is the more accurate description for anionic compounds of the form [Ph^RSnPPh^R]⁻.

Theoretical Considerations for Li⁺[Ph*SnPTrip]⁻ (7)

A Sn^{II} compound in which both the tin and phosphorus atoms are two-coordinated is so far unprecedented, as all known doubly bonded Sn=P species are three-coordinated at the tin atom. As noted above, the Sn–P bonding in the anionic compound 7 is expected to be isolobal to dianionic [Ph^RSnSnPh^R]²⁻ or neutral [Ph^RPPPh^R]. Three interesting considerations for 7 are the energetically lowest molecular geometry about tin and phosphorus, the appearance of the frontier molecular orbitals, and the charge distribution within the anionic compound. Calculations were carried out on the model compound [PhSnPPh]⁻ (7') using the Gaussian 03 program [35] at the DFT-B3LYP level with the SDD basis set consisting of an pseudorelativistic effective core potential for the tin atom and Dunning/Huzinaga



full double zeta basis set for all other atoms. In the current study, the lithium counterion is not considered in order to rule out influence of contacts between the lithium cation and anionic portions of [PhSnPPh]⁻.

The calculated structure of [PhSnPPh]⁻ results in a transbent orientation of the phenyl substituents, which are slightly rotated relative to one another. The Carvi-Sn-P and Sn-P-Carvi angles in the optimized structure are 94.3° and 103.2°, respectively. The angle about tin is considerably less obtuse than that in compound 3 $(105.56(9)^{\circ})$, which could be attributed partially to the lower degree of steric bulk of Ph in comparison to Ph*. In Figure 3, the orbital iso-surfaces for the frontier molecular orbitals are represented. The HOMO-1 (lower right) and HOMO (upper right) are of the bonding σ and π types, respectively, while the LUMO (upper left) is of the antibonding π^* type. This situation is in agreement with the view of [PhSnPPh]⁻ having an Sn=P double bond, though a concrete bond order cannot be assigned from these data. Furthermore, the molecular orbital representations reveal participation of the phenyl groups in the Sn–P bonding, particularly in the π -type and π^* -type orbitals, which is an indication of the stabilization which aryl groups offer to such multiply bonded systems. The Mulliken atomic charges in [PhSnPPh] are calculated to be +0.12 for tin and -0.25 for phosphorus, whereas the remainder of the overall negative charge is distributed throughout the phenyl groups (av. charge on C: -0.23; av. charge on H: +0.20). The negative charge is weighted slightly more heavily toward the phosphorus-bound phenyl group (total = -0.45) than the tin-bound phenyl group (total = -0.42). The distribution of charge throughout the phenyl groups also demonstrates an aspect of the stabilization of aryl groups in multiply bonded anionic main-group moieties.



Figure 3. Iso-surfaces of the molecular orbitals for model compound [PhSnPPh]⁻ (7'). Upper left: LUMO; upper right: HOMO; lower left: graphical representation of anion considered; lower right: HOMO–1.

Synthesis of Tin-Oxo Derivatives

In order to probe the possibility of preparing a monomeric aryl stannylene with reactive P–H bonds and without organic substituents at phosphorus, **5** was treated with $\text{Li}[\text{H}_2\text{PW}(\text{CO})_5]$ in *n*-hexane at -78 °C (Scheme 2). The orange solution gradu-

ally became light red, and overnight stirring produced a beigered solution. The ${}^{31}P{}^{1}H{}$ and ${}^{31}P$ NMR spectra for the crude reaction mixture reveal an array of six main phosphorus-containing products in approximately equal proportions. One signal at $\delta = -187$ ppm bears tungsten satellites (${}^{1}J_{PW} = 213$ Hz) and is split into a quartet in the proton-coupled spectrum $({}^{1}J_{PH} = 342 \text{ Hz})$ and is assigned as $[H_{3}PW(CO)_{5}]$. Each of the remaining five signals is split into triplets in the proton-coupled ³¹P NMR spectra, indicating preservation of the intact PH₂ unit. Decanting the mother liquor away from [H₃PW(CO)₅] and storage of the highly concentrated solution at -25 °C for several weeks resulted in deposition of a few orange crystals, alongside co-crystallized [H₃PW(CO)₅], from which one was selected for an X-ray diffraction experiment. $[Ph*Sn{W(CO)_5}(\mu-O)_2SnPh*]$ (8) crystallizes in the orthorhombic space group *Pnma*, in which one of the tin atoms is coordinated to a tungsten pentacarbonyl fragment. The molecular structure and selected bond lengths and angles are shown in Figure 4. The formation of 8 comes apparently as a result of contamination with moisture or oxygen, likely due to the excess handling and long crystallization period. The most notable feature of 8 is the coordination of tin to the $W(CO)_5$ fragment, which had been introduced into the reaction mixture as a phosphorus-coordinated adduct. The bridging oxygen atoms are slightly bowed in the same direction and the Ph* groups lie in trans-bent arrangement.



Figure 4. Molecular structure of $[Ph*Sn\{W(CO)_5\}(\mu-O)_2SnPh^*]$ (8) in the crystal. The hydrogen atoms and *o*-Trip groups are omitted for clarity. Selected bond lengths /Å and angles /°: W1–Sn1 2.743(2), Sn1–C1 2.183(9), Sn2–C20 2.183(9), Sn1–O1 2.140(5), Sn2–O1 2.224(5), W1–C_{trans} 1.978(15), W1–C_{cis} 2.058(14) (mean value is given); O1–Sn1–O1 73.0(3), O1–Sn2–O1 69.9(3), O1–Sn1–W1 111.57(14), Sn1–O1–Sn2 105.6(2), C1–Sn1–W1 137.9(3), C1–Sn1–O1 101.9(3), C20–Sn2–O1 99.2(3).

The large C_{aryl} -Sn1-W1 angle (137.9(3)°) illustrates the steric crowding about Sn1 in **8** as does the pronounced pinching of the oxygen atoms about the tin atoms (O1–Sn1–O1: 73.0(3)°; O1–Sn2–O1: 69.9(3)°). The Sn–W bond length (2.743(2) Å) falls within the range of other known tungstenpentacarbonyl-coordinated stannylene complexes (compare: [(salen)SnW(CO)₅]

ARTICLE

B. P. Johnson, S. Almstätter, F. Dielmann, M. Bodensteiner, M. Scheer

(salen = 2,2'-N,N'-bis(salicylidene)ethylenediamine) (2.712(1) Å) $[(CO)_5WSn(Cl)Fe(CO)_4]_2^2$ [36a]; (2.799(1) Å) [36b]; $[Mes^{*}(R)Sn=W(CO)_{5}] \quad (R = CH_{2}CMe_{2}C_{6}H_{3})$ $tBu_{2}-3,5)$ $(2.751(1) \text{ Å}) [36c]; [(o-C_6H_4CH_2E)_2SnW(CO)_5] (E = NMe_2,$ PPh₂) (2.749(1) and 2.762(1) Å [36d]). A most conspicuous feature of the structure of 8 is the tricoordinate tin atom, Sn2. Whereas the donation to W(CO)₅ designates Sn1 as a divalent atom, the logical description of Sn2 as tetravalent does not agree well with Sn2 being only tricoordinate, unless multiple Sn-O bonding is involved. The Sn-O bond lengths (Sn1-O1: 2.140(5) Å, Sn2-O1: 2.224(5) Å) differ slightly from one another, but are considerably longer than the Sn-O bonds in cyclo-[Trip₂SnO]₃ (1.956(2) Å, 1.970(2) Å), which contains exclusively Sn-O single bonds [37]. The elongated Sn-O bonds in 8 can be attributed to the steric crowding about the tin atoms caused by the bulky terphenyl substituents and the W(CO)₅ unit. Thus, the most logical bonding scheme which fits the existence of the tricoordinate tin atom is one in which the Sn2-O bond is represented by a double bond, and this oxygen ligand further donates to the stannylene center, Sn1. One resonance form for this description is depicted in Scheme 3. The structure proposal of 8 in Scheme 3 is not consistent with the Sn–O bond lengths, since the Sn2-O bond should be a multiple bond by this description but is longer than the Sn1-O bond. An explanation for this discrepancy may be the constrained geometry of the core in 8 caused by steric repulsion from the W(CO)₅ group. However, the existence of a bis-hydroxo derivative 8a (Scheme 3) can not be excluded, since a residue electron density is found close to the O1 atoms (Figure 4). Yet, the experimental distance found of 0.58 Å is too short for an O-H bond. Nevertheless, in view of a recent report on hydroxo-bridged Sn^{II} dimers (Ph'SnOH)₂ (Ph' = $C_6H_3-2.6(C_6H_3-2.6-iPr_2)_2$) by Power et al. [38], for which Sn-O bond lengths of 2.145(2) and 2.149(1) Å were found, the existence of 8a is also an appropriate description.



Scheme 3. Proposed bonding scheme in $Sn_2O_2\{W(CO)_5\}$ core of 8 and its alternative existence as a bis-hydroxy derivative 8a.

Treatment of **5** with trimethylsilylperoxide, Me₃SiOOSiMe₃ [39], at 0 °C in Et₂O resulted in immediate discoloration of the orange solution (Scheme 2). Ph*Sn(OSiMe₃)₂Cl (**9**) was isolated as a sticky oil and is highly soluble in common hydrocarbons. The ¹H NMR spectrum of **9** reveals a sharp signal at 0.13 ppm for the trimethylsiloxy groups along with a few neighboring peaks likely resulting from impurity or unreacted trimethylsilylperoxide. The *i*Pr protons on the tertiary carbon atoms overlap and give a broad multiplet. In the EI mass spectrum a peak corresponding to the molecular ion minus one methyl group is found, along with further peaks signaling successive loss of the silyloxy ligands and fragmentation of the Ph* ligand. No higher peaks, which could indicate a dimeric structure with bridging silyloxy ligands, are found. Thus, the structure is proposed to be monomeric, as shown in Scheme 2.

In an attempt to prepare the kinetically stabilized heavier Group 14 acid halide analogue Ph*Sn(O)Cl, 5 was treated with solid trimethylamine N-oxide, Me₃NO, at 0 °C in Et₂O (Scheme 2). Immediately upon mixing the orange solution underwent rapid discoloration and colorless crystals of [Ph*Sn(µ-O)Cl]₂ (10) were isolated by crystallization from the filtered reaction mixture. 10 formally represents a dimerization of the targeted acid halide analogue, Ph*Sn(O)Cl, a compound class which has yet not been described experimentally for tin. The clean addition of oxygen to Sn^{II} to form 10 stands in contrast to attempts to prepare a ketone analogue for tin by Power et al., in which the reaction of $Ph'_2Sn (Ph' = C_6H_3Mes_2-2,6)$ with Me₃NO resulted in the formal addition of H₂O to the expected product Ph₂Sn=O and led instead to the dihydroxy compound Ph'₂Sn(OH)₂ [40]. Compound 10 crystallizes in the triclinic space group $P\overline{1}$. The molecular structure and selected bond lengths and angles are shown in Figure 5.



Figure 5. Molecular structure of $[Ph*Sn(\mu-O)Cl]_2$ (10) in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: Sn1–O1 1.994(2), Sn1–Cl1 2.343(1), Sn1–C_{ipso} 2.137(3); Sn1–O1–Sn1 95.38(9), O1–Sn1–O1 84.62(9), Cl1–Sn1–O1 108.47(6), Cl1–Sn1–O1 106.36(7), C_{ipso}–Sn1–O1 117.28(10), C_{ipso}–Sn1–O1 119.98(9), Cl1–Sn1–C_{ipso} 115.76(8).

The molecular structure of **10** is located on an inversion center, such that the central Sn_2O_2 unit is a planar thombus and only one unique Sn-O bond length results. The planarity of the Sn_2O_2 core mirrors that of $[R_2Sn(\mu-O)]_2$ ($R = CH(SiMe_3)_2$) [41] and analogues having heavier chalcogenide ligands, as in $[tBu_2Sn(\mu-E)]_2$ (E = S, Se, Te) [42] or $[(Trip_2Sn)_2(\mu-O)(\mu-S)]$ [43]. However, whereas all Sn-O bonds in **10** have the same length, the Sn-O bonds in $[\{(Me_3Si)_2CH\}_2Sn(\mu-O)]_2$ are of varying lengths, such that a non-rhomboidal parallelogram form of the Sn_2O_2 core results. The tin atoms are in distorted tetrahedral arrangement with the C_{ipso} -Sn1-O1 angles (117.28(10)°, 119.98(9)°) significantly larger than the Cl-Sn-O angles (106.36(7)°, 108.47(6)°), which is likely a result of steric repulsion from the Ph* ligands. The O-Sn-O angles



(84.62(9)°) are considerably more acute than the Sn–O–Sn angles $(95.38(9)^{\circ})$ in **10**. The Sn–O bond length (1.994(2) Å) is significantly shorter than those in compound 8 (2.140(5) Å, 2.224(5) Å) and compares well with the Sn-O bond lengths in cyclo-[(Me₃Si)₃CSn(OH)O]₃ (Sn–O_{ring}: 1.965 Å; Sn–O_{OH}: 1.968 Å) [44], but is longer than those of $[\{(Me_3Si)_2CH\}_2Sn(\mu-O)]_2$ (1.94(2) Å, 1.98(1) Å). The Sn- C_{ipso} bond length (2.137(3) Å) is considerably shorter than the Sn– C_{inso} bond length (2.226(4) Å) in 3, reflecting the difference in a tetravalent aryl stannane and a divalent aryl stannylene.

Conclusions

The results showed that the reaction of tetravalent trichlorogermanium and -tin compounds containing a bulky terphenyl substituent Ph**E*Cl₃ with LiP(SiMe₃)₂ did not result in lowvalent products possessing element-phosphorus triple bonds. Instead, redox reactions proceed and the divalent group 14/ phosphanide products Ph**E*P(SiMe₃)₂ (E = Sn, Ge) were isolated and structurally characterized. These products were also obtained by using the divalent compounds Ph**E*Cl. Comprehensive studies of the reaction behavior of Ph*SnCl were carried out resulting in novel low valent tin–phosphorus and tin– oxygen derivatives. Some of them reveal unprecedented bonding features. The reaction pattern shown clearly reveals the high potential of the bulky terphenyl substituent in low-valent group 14 element chemistry.

Experimental Section

General Remarks

All manipulations were performed in an atmosphere of dry argon using standard glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. NMR spectra were recorded with either a Bruker AMX 300 or Bruker Avance 400 spectrometer with δ referenced to external SiMe₄ (¹H, ¹³C), H₃PO₄ (³¹P), or SnMe₄ (¹¹⁹Sn). The substances LiP(SiMe₃)₂·1.8THF [45], Ph*I [46], Ph*Li·OEt₂ [46], Ph*GeCl [47], and Ph*SnCl [48] were prepared according to literature methods. Due to the sensibility of the compounds and, in some cases, the lack of material no elemental analyses of **2–10** could be performed. However, in most cases the MS analyses reported the composition of the products.

Syntheses

Ph*SnCl₃ (1a): *Method A:* SnCl₄ (0.90 mL, 2.0 g, 7.7 mmol) was dissolved in *n*-hexane (5 mL). Et₂O (5 mL) was added, and the resulting white suspension was cooled to -78 °C. A solution of Ph*Li·OEt₂ (4.319 g, 7.7 mmol) in Et₂O (50 mL) was afterwards added dropwise. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo, and the white residue was extracted with *n*-hexane (40 mL). Upon filtration through Kieselgur, the filtrate was concentrated under reduced pressure to about 15 mL and stored at -25 °C, whereby colorless microcrystals of **1a** precipitated overnight. The mother liquor was decanted, and the crystals were dried under vacuum (2.01 g, 37 %).

Method B: PCl₃ (45 μ L, 72 mg, 0.52 mmol) was added by pipette to a solution of Ph*SnCl (5) (333 mg, 0.52 mmol) in *n*-hexane (20 mL) at -78 °C. The solution turned immediately from orange to colorless. The solution was allowed to warm to room temperature and stirred overnight, after which a colorless solution with yellow precipitate (probably (PCl)_n) was observed. The solution was filtered through a plug of Kieselgur, and the filtrate was concentrated to 5 mL under vacuum. Storage at -25 °C for five days afforded colorless crystals of **1a** (249 mg, 68 %).

1a: MS (EI, 70 eV, 160 °C): m/z = 706.2 (M⁺, 13 %), 671.2 (M⁺ – Cl, 4 %), 481.4 (M⁺ – SnCl₃, 99 %), 466.3 (M⁺ – SnCl₃ – CH₃, 34 %), 438.4 (M⁺ – SnCl₃ – C₃H₇, 14 %). **Element. Analysis:** C₃₆H₄₉SnCl₃ (706.2 g·mol⁻¹): C 62.10 (calcd. 61.20); H 6.41 (6.99)%. ¹H NMR (C₆D₆, 25 °C): $\delta = 1.04$ (d, ³J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 1.23 (d, ³J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 7.07 (t, ³J_{HH} = 6.9 Hz, 12 H, *p*-CH(CH₃)₂), 2.82 (m, CH(CH₃)₂), 7.07 (t, ³J_{HH} = 7.7 Hz, 1 H, *p*-C₆H₃), 7.22 (s, 4 H, *m*-Trip), 7.24 (br., 2 H, *m*-C₆H₃). ¹³C NMR (75.47 MHz, C₆D₆): $\delta = 23.01$ (s, CH(CH₃)₂), 24.12 (s, CH(CH₃)₂), 26.04 (s, CH(CH₃)₂), 31.41 (s, CH(CH₃)₂), 34.96 (s, CH(CH₃)₂), 122.07 (s), 131.11 (s), 131.63 (s), 134.77 (s), 141.50 (s), 147.66 (s), 147.97 (s), 151.18 (s). ¹¹⁹Sn{¹H} NMR (149.21 MHz, C₆D₆): $\delta = -113.8$ (s).

Ph*SnBr₃ (1b): Ph*SnBr₃ (1b) was prepared using the same procedure as for **1a** (*Method A*) starting from SnBr₄ (326 mg, 0.74 mmol) and Ph*Li \cdot OEt₂ (418 mg, 0.74 mmol) to give colorless crystals of **1b** in two crops (248 mg, 40 %).

1b: MS (EI, 70 eV): m/z = 837.9 (M⁺, 7%), 796.9 (M⁺ – C₃H₇, 3.5%), 759.0 (M⁺ – Br, 19%), 481.4 (M⁺ – SnBr₃, 100%), 466.3 (M⁺ – SnBr₃ – CH₃, 16%), 43.0 (C₃H₇⁺, 14%). **Element. Analysis:** C₃₆H₄₉SnBr₃ (837.9 g·mol⁻¹): C 53.11 (calcd. 51.49); H 6.11 (5.88)%. ¹H **NMR** (C₆D₆, 25 °C): $\delta = 1.04$ (d, ³J_{HH} = 6.6 Hz, 12 H, *o*-CH(CH₃)₂), 1.23 (d, ³J_{HH} = 6.6 Hz, 12 H, *o*-CH(CH₃)₂), 1.46 (d, ³J_{HH} = 6.8 Hz, 12 H, *p*-CH(CH₃)₂), 2.87 (m, CH(CH₃)₂), 7.03 (t, ³J_{HH} = 7.6 Hz, 1 H, *p*-C₆H₃), 7.21 (s, 4 H, *m*-Trip). ¹³C **NMR** (75.47 MHz, C₆D₆): $\delta = 23.39$ (s, CH(CH₃)₂), 24.16 (s, CH(CH₃)₂), 26.11 (s, CH(CH₃)₂), 31.40 (s, CH(CH₃)₂), 34.97 (s, CH(CH₃)₂), 122.15 (s), 130.65 (s), 132.10 (s), 134.35 (s), 139.37 (s), 147.30 (s), 147.82 (s), 151.02 (s). ¹¹⁹Sn{¹H} **NMR** (149.21 MHz, C₆D₆): $\delta = -332.6$ (s).

Ph*GeCl₃ (2): GeCl₄ (0.67 mL, 1.265 g, 5.9 mmol) was dissolved in Et₂O (10 mL). A solution of Ph*Li·OEt₂ (3.318 g, 5.9 mmol) in Et₂O (50 mL) was afterwards added dropwise at -78 °C. The solution was slowly allowed to warm to room temperature and was stirred overnight. The solvent was removed under reduced pressure, and the white residue extracted with *n*-hexane (40 mL). Upon filtration through Kieselgur, the filtrate was concentrated under vacuum until the onset of crystallization. Storage at -25 °C for five days afforded colorless crystals of **2**. The mother liquor was decanted, and the crystals were dried under vacuum (1.752 g, 45 %).

2: MS (EI, 70 eV): m/z = 660 (M⁺, 26 %), 645 (M⁺ – CH₃, 3 %), 481 (M⁺ – GeCl₃, 71 %), 466 (M⁺ – GeCl₃ – CH₃, 22 %). ¹**H NMR** (300 MHz, C₆D₆, 25 °C): $\delta = 1.24$ (d, ³J_{HH} = 6.9 Hz, 12 H, *p*-CH(CH₃)₂), 1.29 (d, ³J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 1.32 (d, ³J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 1.32 (d, ³J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 3.56 (sept, ³J_{HH} = 6.9 Hz, 4 H, *o*-CH(CH₃)₂), 7.05 (s, 4 H, *m*-Trip), 7.31 (d, ³J_{HH} = 6.9 Hz, 2 H, *m*-Phenyl), 7.39 (t, ³J_{HH} = 6.9 Hz, 1 H, *p*-Phenyl).

Ph*SnP(SiMe₃)₂ (3): *Method A*: A solution of Ph*SnCl₃ (1a) (1.452 g, 2.06 mmol) in Et₂O (40 mL) was cooled to -78 °C.

LiP(SiMe₃)₂·1.8THF (677 mg, 2.06 mmol) was added as a solid, and the solution slowly turned violet. The solution was allowed to stir overnight at room temperature, and then filtered through Kieselgur. A aliquot of the filtrate (5 mL) was taken for ³¹P NMR spectroscopic analysis, while the rest was concentrated to ca. 5 mL under reduced pressure and was stored at –25 °C for one week, after which colorless crystals of **3** deposited (750 mg, 46 %).

Method B: Ph*SnCl (1.356 g, 2.1 mmol) was dissolved in *n*-hexane (20 mL) and cooled to -78 °C. KP(SiMe₃)₂ (465 mg, 2.1 mmol) was added as a solid. Upon warming to room temperature, the color changed from orange to deep violet. The solution was stirred overnight and filtered through Kieselgur. The filtrate was concentrated to about 5 mL under vacuum and stored at -25 °C, whereby violet crystals of **3** deposited after one week (799 mg, 49 %). Compound **3** can also be synthesized from **5** and LiP(SiMe₃)₂·1.8THF by an analogous procedure in approximately the same yield.

3: MS (EI, 70 eV, 120 °C): m/z = 778.2 (M⁺, 2.2 %), 763.2 (M⁺ – CH_3 , 0.3 %), 705.1 (M⁺ – SiMe₃, 0.3 %), 690.2 (M⁺ – SiMe₃ – CH₃, 1.5 %), 675.3 (M^+ – SiMe₃ – 2 CH₃, 1.6 %), 601.1 (M^+ – P(SiMe₃)₂, 70 %), 482.4 (M^+ – SnP(SiMe₃)₂, 100 %), 467.3 (M^+ – SnP(SiMe₃)₂ – CH₃, 47 %), 439.3 (M⁺ - SnP(SiMe₃)₂ - C₃H₇, 14 %), 73 (SiMe₃⁺, 4 %), 43.1 (C₃H₇⁺3 %). ¹**H NMR** (C₆D₆, 25 °C): $\delta = 0.16$ (d, ³*J*_{HP} = 4.0 Hz, 18 H, Si(CH₃)₃), 1.13 (d, ${}^{3}J_{HH} = 6.7$ Hz, 12 H, *o*-CH(CH₃)₂), 1.23 (d, ${}^{3}J_{\text{HH}} = 6.9$ Hz, 12 H, *o*-CH(CH₃)₂), 1.46 (d, ${}^{3}J_{\text{HH}} = 6.7$ Hz, 12 H, p-CH(CH₃)₂), 2.79 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 2 H, p-CH(CH₃)₂), 3.28 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 4 H, o-CH(CH₃)₂), 7.14 (s, 4 H, m-Trip). ${}^{13}C$ **NMR** (62.90 MHz, C₆D₆): $\delta = 6.50$ (d, ${}^{2}J_{CP} = 9.5$ Hz), 24.25 (s, CH(CH₃)₂), 25.09 (s, CH(CH₃)₂), 27.95 (s, CH(CH₃)₂), 32.01 (s, CH(CH₃)₂), 35.54 (s, CH(CH₃)₂), 122.81 (s), 127.73 (s), 131.90 (s), 136.10 (s), 146.28 (s), 147.69 (s), 150.10 (s), 181.31 (s, ipso-C₆H₃). ²⁹Si{¹H} NMR (49.69 MHz, C₆D₆): δ = 4.08 (d, ¹J_{SiP} = 38.5 Hz). ²⁹Si **NMR** (49.69 MHz, C₆D₆): $\delta = 4.08$ (dm, ¹J_{SiP} = 38.5, ²J_{SiH} = 6.6 Hz). ³¹**P** NMR (101.36 MHz, C₆D₆): $\delta = -123.1$ (s, ¹*J*_P117_{Sn} = 1396, ¹*J*_P119_{Sn} = 1453 Hz, total Sn satellite intensity = 12 %). ¹¹⁹Sn NMR (112.02 MHz, C_6D_6): $\delta = 1919$ (d, ${}^1J_{SnP} = 1453$ Hz).

Ph*GeP(SiMe₃)₂ (4): *Method A*: A solution of LiP(SiMe₃)₂ (499 mg, 1.52 mmol) in Et₂O (20 mL) was added dropwise to a solution of Ph*GeCl₃ (2) (1 g, 1.52 mmol) in Et₂O (40 mL) at -78 °C. Upon warming to room temperature, the color changed from orange to deep red. The solution was allowed to warm to room temperature and was stirred for 16 h. After filtration through Kieselgur the filtrate was concentrated under vacuum to about 5 mL and stored at -25 °C, whereby red crystals of 4 deposited after two weeks (70 mg, 7 %).

Method B: Ph*GeCl (897 mg, 1.52 mmol) was dissolved in Et₂O (40 mL) and cooled to -78 °C. A solution of LiP(SiMe₃)₂ (499 mg, 1.52 mmol) in Et₂O (20 mL) was added dropwise. Upon warming to room temperature, the color changed from orange to deep red. The solution was stirred overnight and filtered through Kieselgur. Red crystals of Ph*GeP(SiMe₃)₂ (4) were obtained in similar yield as for method A.

4: MS (EI, 70 eV): m/z = 733 (M⁺, 40 %), 719 (M⁺ – CH₃, 4 %), 677 (M⁺ – *i*Pr, 13 %). ³¹P **NMR** (101.36 MHz, C₆D₆): $\delta = -48.6$ (s).

Ph*SnP(H)Trip (6): TripPH₂ (57 mg, 0.24 mmol) was dissolved in Et₂O (10 mL) and cooled to -78 °C. A solution of *n*BuLi (0.15 mL, 1.6 M in *n*-hexane, 0.24 mmol) was added slowly by pipette. The mixture was allowed to warm to room temperature and stirred for one hour. The resulting LiP(H)Trip solution was added dropwise to a solution of Ph*SnCl (5) (154 mg, 0.24 mmol) in Et₂O (8 mL) and cooled to -

78 °C. The solution was allowed to warm slowly to room temperature, whereby the orange solution slowly became brown. After stirring overnight, the solution was filtered through Kieselgur and the solvent removed. The resulting brown residue was analyzed by ³¹P NMR spectroscopy, which indicated formation of Trip(H)P–P(H)Trip (ca. 20 %) and **6** (ca. 70 %) alongside unreacted TripPH₂ (ca. 10 %).

6: ³¹**P NMR** (162 MHz, C₆D₆): $\delta = -70.9$ (br., $\Delta v_{1/2} = 150$, ${}^{1}J_{PH} = 186$, ${}^{1}J_{P}117/119_{Sn} = 934$ Hz; ${}^{117/119}Sn$ satellites could not be resolved, total Sn satellite intensity = 12 %).

Li⁺[Ph*SnPTrip]⁻ (7, proposed): To a solution of TripPH₂ (64 mg, 0.27 mmol) in Et₂O (10 mL) was added a solution of *n*BuLi (0.34 mL, 1.6 M in *n*-hexane, 0.54 mmol) at -78 °C. The resulting solution was allowed to warm to room temperature and stirred for 3 hours. The yellow solution of Li₂PTrip was added slowly to a solution of Ph*SnCl (5) (171 mg, 0.27 mmol) in Et₂O (10 mL) at -78 °C. The resulting solution was allowed to warm slowly to room temperature, whereby the orange color gradually became brown. After overnight stirring, the solution was filtered through Kieselgur and the solvent removed. The resulting brown residue was analyzed by ³¹P NMR spectroscopy, whereby a mixture of signals indicated formation of Trip(H)P–P(H)Trip (ca. 20 %) and Li⁺[Ph*SnPTrip]⁻ (7, proposed, ca. 40 %).

7: ³¹**P** NMR (162 MHz, C₆D₆): δ = 229.7 (br., $\Delta v_{1/2}$ = 280, ¹ J_P 117_{Sn} = 1735, ¹ J_P 119_{Sn} = 2004 Hz, total Sn satellite intensity = ca. 14 %).

[Ph*Sn{W(CO)₅}(µ-O)₂SnPh*] (8): A solution of Ph*SnCl (5) (198 mg, 0.31 mmol) in n-hexane (10 mL) was added dropwise to a vigorously stirred suspension of Li[H₂PW(CO)₅] (113 mg, 0.31 mmol) in n-hexane (5 mL) at -78 °C. The resulting pale red-brown suspension was allowed to warm to room temperature and stirred overnight. The solution was filtered through Kieselgur, and the volume was reduced under vacuum to 1 mL. Storage at -25 °C for several weeks yielded a mixture of colorless, yellow, and orange crystals, from which an orange crystal was selected for an X-ray diffraction experiment and determined crystallographically to be compound 8. Among the mixture of crystals the presence of [H₃PW(CO)₅] was shown by EI mass spectrometry, but no other compounds could be unambiguously identified. The synthesis of 8 could not be reproduced, thus preventing preparative isolation and further spectroscopic characterization. The mass spectrometric data given below were measured for the actual crystal that was used in the X-ray experiment.

8: MS (EI, 70 eV, 380 °C): m/z = 594.5 ([Sn₂O₂W(CO)₅]⁺, 11 %), 566.5 ([Sn₂O₂W(CO)₄]⁺, 33 %), 538.5 ([Sn₂O₂W(CO)₃]⁺, 38 %), 510.5 ([Sn₂O₂W(CO)₂]⁺, 16 %), 43.1 ([C₃H₇]⁺, 54 %).

Ph*Sn(OSiMe₃)₂Cl (9): Excess trimethylsilylperoxide (0.2 mL, ca. 200 mg, ca. 1.1 mmol) was added by pipette to a solution of Ph*SnCl (5) (560 mg, 0.88 mmol) in Et₂O (10 mL) at 0 °C. The color changed immediately from orange to colorless. The solution was allowed to warm to room temperature and stirred for one hour. After filtration through Kieselgur, the filtrate was concentrated under reduced pressure to 2 mL and stored at -25 °C. Colorless crystals formed after one week, were separated from the mother liquor by decantation, and dried under vacuum (172 mg, 24 %).

9: MS (EI, 70 eV, 120 °C): $m/z = 799.1 (M^+ - CH_3, 1 \%), 741.0 (M^+ - SiMe_3, 1.2 \%), 725.1 (M^+ - OSiMe_3, 1.6 \%), 652.1 (M^+ - OSiMe_3 - SiMe_3, 1.3 \%), 636.1 (M^+ - 2 OSiMe_3, 0.8 \%), 601.1 (M^+ - 2 OSiMe_3 - Cl, 1.2 \%), 482.2 (M^+ - Sn(OSiMe_3)_2Cl, 100 \%), 467.2 (M^+ - Sn(OSiMe_3)_2Cl - CH_3, 100 \%), 439.1 (M^+ - Sn(OSiMe_3)_2Cl - C_3H_7, 46 \%), 424.2 (M^+ - Sn(OSiMe_3)_2Cl - C_3H_7 - CH_3, 20 \%). ¹H$



NMR (C₆D₆, 25 °C): δ = 0.13 (d, 18 H, Si(CH₃)₃), 1.07 (d, ³J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 1.20 (d, ³J_{HH} = 6.8 Hz, 12 H, *o*-CH(CH₃)₂), 1.30 (d, ³J_{HH} = 6.9 Hz, 12 H, *p*-CH(CH₃)₂), 2.91 (m, 6 H, CH(CH₃)₂), 7.06 (t, ³J_{HH} = 7.5 Hz, 1 H, *p*- C₆H₃), 7.18 (s, 4 H, *m*-Trip), 7.21 (br., 2 H, *m*- C₆H₃).

[Ph*Sn(\mu-O)Cl]₂ (10): Trimethylamine *N*-oxide (59 mg, 0.79 mmol) was added as a solid to a solution of Ph*SnCl (500 mg, 0.79 mmol) in Et₂O (15 mL) at 0 °C. The color changed within 30 minutes from orange to colorless. The solution was allowed to warm to room temperature and stirred for two hours, after which the solution had become cloudy. Et₂O was added by Teflon cannula until the solution became clear (ca. 15 mL). After filtration through Kieselgur, the filtrate was concentrated under reduced pressure until the onset of crystallization and stored at -25 °C. Colorless crystals formed after four days, were separated from the mother liquor by decantation, and dried under vacuum (216 mg, 42 %).

10: IR(KBr): $\tilde{v} = 3053$ (m), 2860 (m), 1962 (w), 1760 (m), 1605 (s), 1564 (s), 1385 (s), 1362 (s), 1318 (s), 1251 (s), 1240 (s), 1188 (m), 1164 (vs), 1154 (m), 1100 (vs), 1080 (s), 1071 (s), 1055 (s), 916 (s), 875 (s), 805 (s), 776 (s), 750 (s), 654 (s), 497 (s) cm⁻¹. **MS** (FD,

toluene solution): $m/z = 1304.6 \text{ (M}^+, 100 \%)$. ¹**H NMR** (C₆D₆, 25 °C): $\delta = 1.02 \text{ (d}, {}^{3}J_{\text{HH}} = 6.9 \text{ Hz}, 12 \text{ H}, \text{CH}(CH_3)_2)$, 1.36 (d, ${}^{3}J_{\text{HH}} = 6.8 \text{ Hz},$ 12 H, CH(CH₃)₂), 1.46 (d, ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}, 12 \text{ H}, \text{CH}(CH_3)_2)$, 2.86 (m, 6 H, CH(CH₃)₂), 7.22 (s, 4 H, *m*-Trip). ¹³**C NMR** (75.48 MHz, C₆D₆): $\delta = 23.45$ (s, CH(CH₃)₂), 24.20 (s, CH(CH₃)₂), 26.17 (s, CH(CH₃)₂), 31.34 (s, CH(CH₃)₂), 34.75 (s, CH(CH₃)₂), 121.64 (s), 127.71 (s), 130.17 (s), 131.08 (s), 136.59 (s), 147.22 (s), 147.90 (s), 149.88 (s).

Crystal Structure Analysis

The crystal structure analyses were performed on an Oxford Diffraction Gemini R Ultra CCD (2, 4) using Cu- K_{α} radiation ($\lambda = 1.54184$ Å) and a STOE IPDS diffractometer (1a, 3, 8, 10) using Mo- K_{α} radiation ($\lambda = 0.71073$ Å), respectively. Semi-empirical absorption corrections from equivalents (multi-scan) were applied for 2 and 4 [49]. For 1a, 3, 8 and 10 numerical absorption corrections from crystal faces were carried out [50]. 1a, 3, 8 and 10 were solved by direct methods with the program SIR-97 [51]. Compound 2 could not be solved by direct methods or Patterson methods. Hence it was solved using charge-flipping algorithms from SUPERFLIP [52]. Full matrix least-square refinement on F^2 in SHELXL-97 [53] was performed with anisotropic

Table 1. Crystallographic Data for compounds 1a, 2, 3, 4, 8, and 10.

	1a	2	3	4	8	10
Empirical						
formula Formula	$C_{36}Cl_3H_{49}Sn$	$C_{36}Cl_2H_{49}Ge$	$\mathrm{C}_{42}\mathrm{H}_{67}\mathrm{PSi}_{2}\mathrm{Sn}$	$\mathrm{C}_{42}\mathrm{H}_{67}\mathrm{PSi}_{2}\mathrm{Ge}$	$C_{77}H_{98}O_7Sn_2W$	$C_{72}Cl_{2}H_{98}O_{2}Sn_{2}$
mass /g·mol-	¹ 706.81	625.26	777.82	731.72	1556.81	1303.82
T/K	203(2)	123(1)	200(1)	123(1)	203(1)	173(1)
Crystal						
dimensions						
/mm	$0.12 \times 0.10 \times 0.03$	$0.29\times0.09\times0.08$	$0.20\times0.20\times0.02$	$0.24\times0.11\times0.11$	$0.20\times0.20\times0.06$	$0.22\times0.16\times0.12$
Crystal						
system	Triclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P\overline{1}$	C222 ₁	$P\overline{1}$	$P2_{1}/c$	Pnma	$P\overline{1}$
<i>a</i> /Å	8.479(1)	11.017(9)	9.280(1)	15.279(7)	18.983(4)	9.887(9)
b /Å	13.799(3)	12.212(6)	13.240(3)	16.004(8)	18.340(4)	12.945(9)
c /Å	16.691(3)	25.526(3)	19.576(4)	18.090(5)	23.227(5)	15.833(8)
$\alpha /^{\circ}$	70.59(3)	90	83.19(3)	90	90	66.61(8)
β /°	85.67(3)	90	88.44(3)	103.60(9)	90	87.09(8)
γ /°	72.24(3)	90	70.83(3)	90	90	86.62(5)
$V/Å^3$	1753.4(8)	3434.7(6)	2255.7(9)	4299.8(2)	8086(3)	1856.3(3)
Ζ	2	4	2	4	4	1
$D_{\rm calc} / \rm g \cdot \rm cm^{-3}$	1.339	1.209	1.145	1.130	1.279	1.166
μ / mm^{-1}	0.980	2.788	0.680	2.031	2.077	0.783
F(000)	732	1324	824	1576	3160	680
radiation	$Mo-K_{\alpha}$	$Cu-K_{\alpha}$	$Mo-K_{\alpha}$	$Cu-K_{\alpha}$	$Mo-K_{\alpha}$	$Mo-K_{\alpha}$
θ range	2.40-25.94	3.41-62.21	2.32-26.00	3.41-66.73	2.06-25.90	2.46-25.81
reflections						
collected	12082	12127	16260	20851	34356	13161
unique						
reflections	6320	2639	8232	7497	7703	6646
GOF on F^2	1.034	1.094	1.029	1.062	1.056	0.949
R_{int} $R_1^{(a)}$	0.0617	0.0485	0.0359	0.0272	0.0750	0.0234
$\begin{bmatrix} I > 2s(I) \end{bmatrix}$ wR ₂ ^{b)}	0.0532	0.0927	0.0409	0.0331	0.0554	0.0317
(all data)	0.1263	0.2515	0.1073	0.0883	0.1308	0.0709
Flack para-						
meter	_	0.50(7)	_	_	_	_
Max/min		0.20(7)				
$\Delta \rho / e \cdot Å^{-3}$	0.713/-0.902	1.287/-1.633	0.651/-0.730	0.464/0.243	1.030/-1.515	1.488/-0.310

a) $R_1 = \Sigma |F_0| - |F_c| / \Sigma |F_0|$. b) $wR_2 = [\Sigma \omega (F_0^2 - F_c^2)^2] / [\Sigma (F_0^2)^2]^{\frac{1}{2}}$.

ARTICLE

displacements for non-hydrogen atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. In 8 and 10 *isopropyl* groups are disordered over two positions. Thus, several constraints and restraints were used for refinement. Disordered hexane molecules in 8 and 10 could not be refined properly and were squeezed using the appropriate function in PLATON software [54]. Additionally, 2 is an inversion twin (50:50) and a mixed crystal with 50 percent occupancy each site for Ph*GeCl and Ph*GeCl₃. Further all four chlorine- and *isopropyl* positions are disordered over two positions. For this reasons constraints and restraints are required and *R* values are poor for 2. Further details are given in Table 1.

CCDC-760737 (1a), -760738 (2), -760739 (3), -760740 (4), -760741 (8), and -760736 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk).

DFT Calculations

All calculations were performed using the Gaussian 03 program package [35]. For structure optimisation we employed the functional theory (DFT) method along with the B3LYP exchange-correlation functional [55] and SDD basis set (Stuttgart/Dresden pseudorelativistic effective core potential for tin [56] and D95 full double zeta basis sets for all other atoms [57]).

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