Synthesis and Reactivity of Low-Valent Group 14 Element Compounds

Manfred Scheer, Brian Johnson, Stefan Almstätter, Fabian Dielmann, Michael
Bodensteiner

► To cite this version:

Manfred Scheer, Brian Johnson, Stefan Almstätter, Fabian Dielmann, Michael Bodensteiner. Synthesis and Reactivity of Low-Valent Group 14 Element Compounds. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2010, 636 (7), pp.1275. 10.1002/zaac.201000029 . hal-00552445

HAL Id: hal-00552445

<https://hal.science/hal-00552445>

Submitted on 6 Jan 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Zeitschrift für Anorganische und
Allgemeine Chemie

Synthesis and Reactivity of Low-Valent Group 14 Element Compounds

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000029.R2
Wiley - Manuscript type:	Article
Date Submitted by the Author:	01-Apr-2010
Complete List of Authors:	Scheer, Manfred; Universitaet Regensburg, Institut für Anorganische Chemie Johnson, Brian Almstätter, Stefan Dielmann, Fabian Bodensteiner, Michael
Keywords:	tin, germanium, phosphorus
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.	
scheme1.cdx scheme2.cdx scheme3.cdx equations.cdx

Synthesis and Reactivity of Low-Valent Group 14 Element Compounds

Brian P. Johnson, Stefan Almstätter, Fabian Dielmann, Michael Bodensteiner, and Manfred Scheer*

Regensburg, Institut für Anorganische Chemie der Universität

Received:

Dedicated to Professor Gerd Becker on the occasion of his 70th birthday

Keywords: Germanium / Tin / Phosphorus / Multiple bonding / DFT calculations

Abstract: The tetravalent germanium and tin compounds of the general formulae Ph^*EX_3 ($\text{Ph}^* = 2,6\text{-Trip}_2\text{-C}_6\text{H}_3$, $\text{Trip} = \text{C}_6\text{H}_2\text{iPr}_3\text{-2,4,6}$; $\text{E} = \text{Sn}$, $\text{X} = \text{Cl}$ (**1a**), Br (**1b**); $\text{E} = \text{Ge}$, $\text{X} = \text{Cl}$ (**2**)) are synthesised by reaction of $\text{Ph}^*\text{Li}\cdot\text{OEt}_2$ with EX_4 . The subsequent reaction of **1a,b** with $\text{LiP}(\text{SiMe}_3)_2$ leads to $\text{Ph}^*\text{EP}(\text{SiMe}_3)_2$ ($\text{E} = \text{Sn}$ (**3**), Ge (**4**)) and the diphosphine $(\text{Me}_3\text{Si})_2\text{PP}(\text{SiMe}_3)_2$ via a redox reaction. In an alternative approach **3** and **4** are synthesised by using the corresponding divalent compounds Ph^*ECl ($\text{E} = \text{Ge}$, Sn) in the reaction with $\text{LiP}(\text{SiMe}_3)_2$. The reactivity of Ph^*SnCl is extensively investigated to give with $\text{LiP}(\text{H})\text{Trip}$ a tin(II)-phosphine derivative $\text{Ph}^*\text{SnP}(\text{H})\text{Trip}$ (**6**) and with Li_2PTrip a proposed product $[\text{Ph}^*\text{SnPTrip}]^-$ (**7**) with multiple bonding between tin and phosphorus. The latter feature is confirmed by DFT calculations on a model compound $[\text{PhSnPPh}]^-$. The reaction with $\text{Li}[\text{H}_2\text{PW}(\text{CO})_5]$ gives the oxo-bridged tin compound $[\text{Ph}^*\text{Sn}\{\text{W}(\text{CO})_5\}(\mu\text{-O})_2\text{SnPh}^*]$ (**8**) as the only isolable product. However, the existence of **8** as the bis-hydroxo derivative $[\text{Ph}^*\text{Sn}\{\text{W}(\text{CO})_5\}(\mu\text{-OH})_2\text{SnPh}^*]$ (**8a**) is also possible. The Sn(IV) derivatives $\text{Ph}^*\text{Sn}(\text{OSiMe}_3)_2\text{Cl}$ (**9**) and $[\text{Ph}^*\text{Sn}(\mu\text{-O})\text{Cl}]_2$ (**10**) are obtained by the oxidation of Ph^*SnCl with bis(trimethylsilyl)peroxide and with Me_3NO , respectively. Besides the spectroscopic characterisation of the isolated products compounds **1a**, **2**, **3**, **4**, **8**, and **10** are additionally characterised by X-ray diffraction analysis.

* Prof. Dr. M. Scheer

Institut für Anorganische Chemie der Universität Regensburg,

D-93040 Regensburg (Germany)

Fax: (+49) 941/943-4441

E-mail: manfred.scheer@chemie.uni-regensburg.de

Introduction

Almost 3 decades ago *G. Becker* et al. succeeded in the synthesis of the first stable phosphalkyne, *tert*-butylphosphalkyne,^[1] which through an improved synthesis^[2] gave a general approach to this class of $P\equiv C$ 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, $Mes^*C\equiv As$, 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 phosphaehtynyl and arsaethynyl systems.^[5] The reaction behaviour of phosphalkynes was intensively investigated both for phosphoorganic^[6] and coordination chemistry^[7] purposes. Moreover, the discovery of *G. 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 possessing $Si=P$,^[9] $Ge=P$,^[10] and $Sn=P$ ^[11] double bonds, which were stabilised kinetically by bulky aryl groups (*Mes* ($C_6H_2Me_{3-2,3,6}$); *Trip* ($C_6H_2iPr_{3-2,3,6}$); *Mes** ($C_6H_2tBu_{3-2,3,6}$)); or by bulky aliphatic groups (*tBu* 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 $R_2Si=PSiR'_3$ and $R_2Si=PPR'_2$.^[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, $Ph^*Sn\equiv CSiPr_3$ ($Ph^* = C_6H_3Trip_{2-2,6}$), was proposed to exist as a reactive intermediate,^[13] and the asymmetric dipnictenes $Ph^*E=PMes$ ($E = As, Sb$) were synthesized by the Power group.^[14] Moreover, novel arsa-Wittig reagents $2,6-Ph'_2-C_6H_3As=PMe_3$ ($Ph' = Mes, Trip$) were developed by Protasiewicz and co-workers, whereby the phosphorus atom is in the +5 oxidation state.^[15]

Our long-term engagement in phosphalkyne 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 a $E\equiv P$ ($E = Si, Ge, Sn, Pb$) triple bond have not yet been detected or isolated. Only a compound with a $Si\equiv P$ 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 H_3SiP and its isomers.^[18] Moreover, a phosphasilene, $RR'Si=PH$ ($R = Ph^*, R' = tBu_3Si$), and its Zinc salt were synthesised in the Driess group^[19] and $Cp^*(Cl)_2EP(SnMe_3)_2$ ($E = Si, Ge$) was synthesised by Niecke and Pietschnig.^[20] All these compounds are on the way to realising stable derivatives with an $E\equiv P$ triple bond. Interestingly, the stability of triply bonded $RSn\equiv P$

systems has been predicted by quantum chemical calculations only for examples in which R represents a bulky terphenyl group.^[21]

Scheme 1. Reaction pathway of thermolysis of $\text{Mes}^*\text{Si}(\text{F})_2\text{P}\{\text{Li}(\text{thf})_3\}\text{SiMe}_3$ and proposed generation of intermediate $\text{Mes}^*\text{Si}\equiv\text{P}$.^[17]

Thus, the use of bulky terphenyl substituents like, e.g., Ph^* ($\text{Ph}^* = \text{C}_6\text{H}_3\text{Trip}_{2-2,6}$; $\text{Trip} = \text{C}_6\text{H}_2\text{iPr}_{3-2,4,6}$) on tin or germanium (E) provides a unique heteroleptic template for preparing element-phosphorus compounds with low-coordination geometries. With the relatively stable $\text{E}-\text{C}_{\text{aryl}}$ 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 $\text{E}\equiv\text{P}$ triple-bond compounds of the type $\text{Ph}^*\text{E}\equiv\text{P}$ ($\text{E} = \text{Sn}, \text{Ge}$). The experiments reported in the following are partly directed toward this goal. Moreover, the results described give insight into the reaction behaviour 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 ($\text{Ph}^* = 2,6\text{-Trip}_2\text{-C}_6\text{H}_3$, $\text{Trip} = \text{C}_6\text{H}_2\text{iPr}_{3-2,4,6}$) is achieved by treating $\text{Ph}^*\text{Li}\cdot\text{OEt}_2$ with EX_4 in a mixture of *n*-hexane and Et_2O (Eq. 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 PCl_3 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 CCl_4 .^[22]

1a crystallizes in the triclinic space group $P\bar{1}$, 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 geometry about 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. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **1a**: Sn–C1 2.155(5), Sn–Cl1 2.322(3), Sn–Cl2 2.321(3), Sn–Cl3 2.328(2); C1–Sn–Cl1 119.89(13), C1–Sn–Cl2 122.05(13), C1–Sn–Cl3 109.26(14), Cl1–Sn–Cl2 98.12(7), Cl1–Sn–Cl3 102.96(8), Cl2–Sn–Cl3 101.67(8).^[23]

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 $\text{LiP}(\text{SiMe}_3)_2 \cdot 1.8\text{THF}$ in Et_2O at low temperature. The ^{31}P NMR spectrum of the crude reaction mixture reveals the formation of $\text{Ph}^*\text{SnP}(\text{SiMe}_3)_2$ (**3**) ($\delta(^{31}\text{P}) = -123.1$ ppm) and $(\text{Me}_3\text{Si})_2\text{PP}(\text{SiMe}_3)_2$ ($\delta(^{31}\text{P}) = -216$ ppm^[24]) in an approximate 1:1 ratio as the main phosphorus-containing products (Eq. 2). As the reduction potential for Ge is generally lower

than that for Sn, **2** was reacted with $\text{LiP}(\text{SiMe}_3)_2 \cdot 1.8\text{THF}$ in Et_2O at low temperature in order to give $\text{Ph}^*\text{GeCl}_2\text{P}(\text{SiMe}_3)_2$. However, the same result was achieved and, along with of the formation of $(\text{Me}_3\text{Si})_2\text{PP}(\text{SiMe}_3)_2$ as a side-product, $\text{Ph}^*\text{GeP}(\text{SiMe}_3)_2$ (**4**) was isolated (Eq. 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,^[25] for which an excess of $\text{LiP}(\text{SiMe}_3)_2$ has to be present to assure the autometalation reaction of the silylphosphorus atom by $\text{LiP}(\text{SiMe}_3)_2$ under formation of $\text{P}(\text{SiMe}_3)_3$. 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 $\text{KP}(\text{SiMe}_3)_2$. The ^{31}P NMR spectrum of the crude reaction mixture reveals the same phosphorus-containing products as that with $\text{LiP}(\text{SiMe}_3)_2 \cdot 1.8\text{THF}$.

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^*SiF_3 with $\text{LiP}(\text{SiMe}_3)_2$ to give the silane-elimination product shown in scheme 1.^[17] Clearly, the relative stability of divalent stannylenes and germlylenes 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^*ECl (E = Sn,^[26] Ge) were treated with $\text{LiP}(\text{SiMe}_3)_2 \cdot 1.8\text{THF}$ in *n*-hexane at low temperature. According to the ^{31}P NMR spectra of the reaction mixtures only $\text{Ph}^*\text{SnP}(\text{SiMe}_3)_2$ (**3**) ($\delta(^{31}\text{P}) = -123.1$ ppm) and $\text{Ph}^*\text{GeP}(\text{SiMe}_3)_2$ (**4**) ($\delta(^{31}\text{P}) = -48.5$ ppm), respectively, are detected as the main phosphorus-containing products along with traces of $\text{HP}(\text{SiMe}_3)_2$ ($\delta(^{31}\text{P}) = -236.3$ ppm), resulting from hydrolysis of $\text{LiP}(\text{SiMe}_3)_2$ (Eq. 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).

The molecular structure of the compounds **3** and **4** are depicted in Figure 2. **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 $\text{Ph}^*\text{EP}(\text{SiMe}_3)_2$ (**3**: E = Sn, **4**: E = Ge) the group 14 atom possesses a coordination number of two and lies in a bent geometry ($\text{C}_{\text{ipso}}\text{-Ge-P}$: 106.88° , $\text{C}_{\text{ipso}}\text{-Sn-P}$: $105.56(9)^\circ$), 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 P 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 center. This correlates well with the tin-phosphorus coupling constants of compound **3** ($^1J_{\text{P}117\text{Sn}} = 1396 \text{ Hz}$, $^1J_{\text{P}119\text{Sn}} = 1453 \text{ Hz}$), which are well below the range for compounds known to exhibit tin-phosphorus double bonding ($^1J_{\text{PSn}} \approx 2000 \text{ Hz}$). The bulky nature of the Ph^* ligand allows the isolation of the terminal stannylene phosphanide **3** and the terminal germanylene phosphanide **4**. This is in contrast to the well-established field of phosphastannylenes and -germylenes usually representing phosphanido-bridged dimers^[27] or donor-stabilised monomers.^[28]

Figure 2. Molecular structures of $\text{Ph}^*\text{EP}(\text{SiMe}_3)_2$ (**3**: E = Sn, **4**: E = Ge) in the crystal. H atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] 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 [$\text{\AA}$] and angles [$^\circ$] 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).

Reactivity of $\text{Ph}^*\text{SnP}(\text{SiMe}_3)_2$ (3**):** Given the wealth of oxidative reactions of bivalent tin amides with organic halides, transition-metal halides,^[29] acid chlorides/anhydrides,^[30] and chalcogens,^[31] among others, to give well-defined Sn(IV) addition products, it is expected that chemical oxidation of $\text{Ph}^*\text{SnP}(\text{SiMe}_3)_2$ 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 $\text{Ph}^*\text{Sn}\equiv\text{P}$ or similar products would be conceivable. However, low-temperature reactions of $\text{Ph}^*\text{SnP}(\text{SiMe}_3)_2$ with C_2Cl_6 , $\text{Cp}_2\text{Ti}(\text{OTf})_2$, $\text{Hg}(\text{OTf})_2$, $\text{Ti}(\text{OOCF}_3)_3$, benzoyl chloride, Me_3NO , and tropylium tetrafluoroborate each results in cleavage of the Sn–P bond and generation of an intractable mixture of products, according to ^{31}P NMR spectra of the respective crude reaction mixtures. Reaction of $\text{Ph}^*\text{SnP}(\text{SiMe}_3)_2$ with $\text{BrCH}_2\text{CH}_2\text{Br}$ at low temperature results in gradual discoloration of the violet solution to clear beige. The ^{31}P NMR spectrum reveals a main phosphorus-containing product ($> 65\%$) at $\delta -167.2$ ppm with tin satellites ($^1J_{\text{P117Sn}} = 1719$ Hz, $^1J_{\text{P119Sn}} = 1799$ Hz). Work-up of the solution and crystallization from *n*-hexane afforded only colourless crystals of Ph^*Br ,^[32] as identified by a X-ray diffraction experiment.

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.

Scheme 2. Reactivity of Ph^*SnCl (5) with (a) $\text{LiP}(\text{H})\text{Trip}$ in Et_2O at -78 °C; (b) Li_2PTrip in Et_2O at -78 °C; (c) $\text{Li}[\text{H}_2\text{PW}(\text{CO})_5]$ in *n*-hexane at -78 °C; (d) $\text{Me}_3\text{SiO}-\text{OSiMe}_3$ in Et_2O at 0 °C; (e) Me_3NO Et_2O at 0 °C.

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%, Δν_{1/2} = 150 Hz) attributable to **6** (δ = -70.9 ppm, ¹J_{P117/119Sn} = 934 Hz), which is split into a doublet upon proton coupling (¹J_{PH} = 186 Hz), along with traces of Trip(H)P–P(H)Trip (δ = -113.9 ppm) and TripPH₂ (δ = -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 ³¹P{¹H} NMR spectrum of **6** a singlet with unresolved ^{117/119}Sn satellites is observed, which in the proton-coupled ³¹P 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 ³¹P 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. In recognition of the possibility of nucleophilic attack of *n*BuLi on the tin center, 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**) (δ(³¹P) = 229.7 ppm, Δν_{1/2} = 280 Hz, ¹J_{P117Sn} = 1735 Hz, ¹J_{P119Sn} = 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 ion-separated forms. No P–H coupling is observed in the proton-coupled 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 ¹J_{P117/119Sn} 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.^[33] [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,^[34] as well as isolobal to the general family of dipnictenes

RE=ER (E = P, As, Sb), each with undisputed double-bond character.^[35] The bonding between Sn and P 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 $[\text{Ph}^R\text{SnPPh}^R]^-$.

Theoretical Considerations for $\text{Li}^+[\text{Ph}^*\text{SnPTrip}]^-$ (7): A Sn(II) compound in which both the tin and phosphorus atoms are two-coordinate is so far unprecedented, as all known doubly bonded Sn=P species are three-coordinate at the tin atom. As noted above, the Sn–P bonding in the anionic compound **7** is expected to be isolobal to dianionic $[\text{Ph}^R\text{SnSnPh}^R]^{2-}$ or neutral $[\text{Ph}^R\text{PPPh}^R]$. 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 $[\text{PhSnPPh}]^-$ (**7'**) using the Gaussian 03 program^[36] at the DFT-B3LYP level with the SDD basis set consisting of an pseudorelativistic effective core potential for the Sn 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 $[\text{PhSnPPh}]^-$.

Figure 3. Iso-surfaces of the molecular orbitals for model compound $[\text{PhSnPPh}]^-$ (**7'**). Upper left: LUMO; upper right: HOMO; lower left: graphical representation of anion considered; lower right: HOMO-1.

The calculated structure of $[\text{PhSnPPh}]^-$ results in a *trans*-bent orientation of the phenyl substituents, which are slightly rotated relative to one another. The $\text{C}_{\text{aryl}}\text{--Sn--P}$ and $\text{Sn--P--C}_{\text{aryl}}$ 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 isosurfaces 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 $[\text{PhSnPPh}]^-$ having an $\text{Sn}=\text{P}$ 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 $[\text{PhSnPPh}]^-$ are calculated to be +0.12 for Sn and –0.25 for P, while 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.

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 gradually became light red, and overnight stirring produced a beige-red solution. The $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra for the crude reaction mixture reveal an array of 6 main phosphorus-containing products in approximately equal proportions. One signal at –187 ppm bears tungsten satellites ($^1J_{\text{PW}} = 213$ Hz) and is split into a quartet in the proton-coupled spectrum ($^1J_{\text{PH}} = 342$ Hz) and is assigned as $[\text{H}_3\text{PW}(\text{CO})_5]$. Each of the remaining five signals is split into triplets in the proton-coupled ^{31}P NMR spectra, indicating preservation of the intact PH_2 unit. Decanting the mother liquor away from $[\text{H}_3\text{PW}(\text{CO})_5]$ and storage of the highly concentrated solution at -25°C for several weeks resulted in deposition of a few orange crystals, alongside co-crystallized $[\text{H}_3\text{PW}(\text{CO})_5]$, from which one was selected for an X-ray diffraction experiment. $[\text{Ph}^*\text{Sn}\{\text{W}(\text{CO})_5\}(\mu\text{-O})_2\text{SnPh}^*]$ (**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 H 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] (salen = 2,2'-*N,N'*-bis(salicylidene)ethylenediamine) (2.712(1) Å);^[37a] [(CO)₅WSn(Cl)Fe(CO)₄]₂²⁻ (2.799(1) Å);^[37b] [Mes*(R)Sn=W(CO)₅] (R = CH₂CMe₂C₆H₃*t*Bu₂-3,5) (2.751(1) Å)^[37c]; [(*o*-C₆H₄CH₂E)₂SnW(CO)₅] (E = NMe₂, PPh₂) (2.749(1) and 2.762(1) Å)^[37d]). A most conspicuous feature of the structure of **8** is the 3-coordinate tin atom, Sn2. While the donation to $W(CO)_5$ designates Sn1 as a divalent center, the logical description of Sn2 as tetravalent does not agree well with Sn2 being only 3-coordinate, 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.^[38] The elongated Sn–O bonds in **8** can be attributed to the steric crowding about the tin centers caused by the bulky terphenyl substituents and the W(CO)₅ unit. Thus, the most logical bonding scheme which fits the existence of the 3-coordinate tin centre is one in which the Sn2–O bond is represented by a double bond, and this oxygen ligand further donates to the stannylene centre, 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' = C₆H₃-2,6(C₆H₃-2,6-*i*Pr₂)₂) by Power et al.,^[39] 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 Sn₂O₂{W(CO)₅} core of **8** and its alternative existence as a bis-hydroxy derivative **8a**.

Treatment of **5** with trimethylsilylperoxide, Me₃SiOOSiMe₃,^[40] 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 signalling successive loss of the silyloxy ligands and fragmentation of the

Ph* ligand. No higher peaks indicating 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 colourless 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' = C₆H₃MeS_{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.^[41] **10** crystallizes in the triclinic space group *P* $\bar{1}$. The molecular structure and selected bond lengths and angles are shown in Figure 5.

Figure 5. Molecular structure of [Ph*Sn(μ-O)Cl]₂ (**10**) in the crystal. H 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 Sn₂O₂ unit is a planar rhombus and only one unique Sn–O bond length results. The planarity of the

Sn₂O₂ core mirrors that of [R₂Sn(μ-O)]₂ (R = CH(SiMe₃)₂)^[42] and analogues possessing heavier chalcogenide ligands, as in [tBu₂Sn(μ-E)]₂ (E = S, Se, Te)^[43] or [(Trip₂Sn)₂(μ-O) (μ-S)]^[44]. However, while all Sn–O bonds in **10** have the same length, the Sn–O bonds in [{(Me₃Si)₂CH}₂Sn(μ-O)]₂ are of varying lengths, such that a non-rhomboidal parallelogram form of the Sn₂O₂ core results. The Sn atoms are in distorted tetrahedral geometry 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)°), 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)°) in **10**. The Sn–O bond distance (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)₃C Sn(OH)O]₃ (Sn–O_{ring}: 1.965 Å; Sn–O_{OH}: 1.968 Å),^[45] but is longer than those of [{(Me₃Si)₂CH}₂Sn(μ-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_{ipso} bond length (2.226(4) Å) in **3**, reflecting the difference in a tetravalent aryl stannane and a divalent aryl stannylene.

Conclusions

The results have shown that the reaction of tetravalent trichloro-germanium and -tin compounds containing a bulky terphenyl substituent Ph*ECl₃ with LiP(SiMe₃)₂ do not result in low-valent products possessing element-phosphorus triple bonds. Instead, redox reactions proceed and the divalent group 14/phosphanide products Ph*EP(SiMe₃)₂ (E = Sn, Ge) have been isolated and structurally characterised. These products were also obtained by using the divalent compounds Ph*ECl. Comprehensive studies of the reaction behaviour 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.

Table 1. Crystallographic Data for compound **1a**, **2** and **3**.

	1a	2	3	4	8	10
Empirical formula	C ₃₆ Cl ₃ H ₄₉ Sn	C ₃₆ Cl ₂ H ₄₉ Ge	C ₄₂ H ₆₇ PSi ₂ Sn	C ₄₂ H ₆₇ PSi ₂ Ge	C ₇₇ H ₉₈ O ₇ Sn ₂ W	C ₇₂ Cl ₂ H ₉₈ O ₂ Sn ₂
Formula 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 × 0.10 × 0.03	0.29 × 0.09 × 0.08	0.20 × 0.20 × 0.02	0.24 × 0.11 × 0.11	0.20 × 0.20 × 0.06	0.22 × 0.16 × 0.12
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 222 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.479(1)	11.017(9)	9.280(1)	15.279(7)	18.983(4)	9.887(9)
<i>b</i> (Å)	13.799(3)	12.212(6)	13.240(3)	16.004(8)	18.340(4)	12.945(9)
<i>c</i> (Å)	16.691(3)	25.526(3)	19.576(4)	18.090(5)	23.227(5)	15.833(8)
α (°)	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)
<i>V</i> (Å ³)	1753.4(8)	3434.7(6)	2255.7(9)	4299.8(2)	8086(3)	1856.3(3)
<i>Z</i>	2	4	2	4	4	1
<i>D</i> _{calc} /g·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
<i>F</i> (000)	732	1324	824	1576	3160	680
radiation	MoK α	CuK α	MoK α	CuK α	MoK α	MoK α
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 <i>F</i> ²	1.034	1.094	1.029	1.062	1.056	0.949
<i>R</i> _{int}	0.0617	0.0485	0.0359	0.0272	0.0750	0.0234
<i>R</i> ₁ ^[a] [<i>I</i> > 2 <i>s</i> (<i>I</i>)]	0.0532	0.0927	0.0409	0.0331	0.0554	0.0317
w <i>R</i> ₂ ^[b] (all data)	0.1263	0.2515	0.1073	0.0883	0.1308	0.0709
Flack parameter	-	0.50(7)	-	-	-	-
Max/min $\Delta\rho$ /e·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] $R_I = \sum |F_0| - |F_c| / \sum |F_0|$. ^[b] $wR_2 = [\sum \omega(F_0^2 - F_c^2)^2] / [\sum (\omega F_0^2)^2]^{1/2}$.

Experimental Section

General remarks: All manipulations are performed under an atmosphere of dry argon using standard glovebox and Schlenck techniques. Solvents are purified and degassed by standard procedures. NMR spectra are recorded on 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,^[46] Ph*I,^[47] Ph*Li·OEt₂,^[47] Ph*GeCl,^[48] and Ph*SnCl^[49] are 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 report the composition of the products.

Synthesis of Ph*SnCl₃ (1a): *Method A:* SnCl₄ (0.90 mL, 2.0 g, 7.7 mmol) was dissolved in 5 mL *n*-hexane. 5 mL Et₂O 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 50 mL Et₂O was then 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 40 mL *n*-hexane. 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** precipitate 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 ($M^+ - SnCl_3$, 99%), 466.3 ($M^+ - SnCl_3 - CH_3$, 34%), 438.4 ($M^+ - SnCl_3 - C_3H_7$, 14%). **Element. Analysis:** C₃₆H₄₉SnCl₃ (706.2 g/mol): C 62.10 (calc. 61.20); H 6.41 (6.99)%. **¹H NMR** (C₆D₆, 25°C): δ = 1.04 (d, ³ J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 1.23 (d, ³ J_{HH} = 6.9 Hz, 12 H, *o*-CH(CH₃)₂), 1.44 (d, ³ J_{HH} = 6.9 Hz, 12 H, *p*-CH(CH₃)₂), 2.82 (m, CH(CH₃)₂), 7.07 (t, ³ J_{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): δ = 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): δ = −113.8 (s).

Synthesis of Ph*SnBr₃ (1b): Ph*SnBr₃ (**1b**) was prepared in the same manner as for **1a** (*Method A*) starting from SnBr₄ (326 mg, 0.74 mmol) and Ph*Li·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): C 53.11 (calc. 51.49); H 6.11 (5.88)%. ¹H NMR (C₆D₆, 25°C): δ = 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): δ = 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): δ = −332.6 (s).

Synthesis of Ph*GeCl₃ (2): GeCl₄ (0.67 mL, 1.265 g, 5.9 mmol) was dissolved 10 mL Et₂O. A solution of Ph*Li·OEt₂ (3.318 g, 5.9 mmol) in 50 mL Et₂O was then 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 40 mL *n*-hexane. 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%). ¹H NMR (300 MHz, C₆D₆, 25°C): δ = 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), 2.89 (sept, ³J_{HH} = 6.9 Hz, 2 H, *p*-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).

Synthesis of Ph*SnP(SiMe₃)₂ (3): *Method A:* A solution of Ph*SnCl₃ (**1a**) (1.452 g, 2.06 mmol) in 40 mL Et₂O 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 5-mL aliquot of the filtrate was taken for ^{31}P NMR 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 20 mL *n*-hexane and cooled to -78°C . $\text{KP}(\text{SiMe}_3)_2$ (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%). **3** can also be synthesized from **5** and $\text{LiP}(\text{SiMe}_3)_2 \cdot 1.8\text{THF}$ 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 ($\text{M}^+ - \text{CH}_3$, 0.3%), 705.1 ($\text{M}^+ - \text{SiMe}_3$, 0.3%), 690.2 ($\text{M}^+ - \text{SiMe}_3 - \text{CH}_3$, 1.5%), 675.3 ($\text{M}^+ - \text{SiMe}_3 - 2 \text{CH}_3$, 1.6%), 601.1 ($\text{M}^+ - \text{P}(\text{SiMe}_3)_2$, 70%), 482.4 ($\text{M}^+ - \text{SnP}(\text{SiMe}_3)_2$, 100%), 467.3 ($\text{M}^+ - \text{SnP}(\text{SiMe}_3)_2 - \text{CH}_3$, 47%), 439.3 ($\text{M}^+ - \text{SnP}(\text{SiMe}_3)_2 - \text{C}_3\text{H}_7$, 14%), 73 (SiMe_3^+ , 4%), 43.1 (C_3H_7^+ , 3%). **^1H NMR** (C_6D_6 , 25°C): $\delta = 0.16$ (d, $^3J_{\text{HP}} = 4.0$ Hz, 18 H, $\text{Si}(\text{CH}_3)_3$), 1.13 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12 H, *o*- $\text{CH}(\text{CH}_3)_2$), 1.23 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12 H, *o*- $\text{CH}(\text{CH}_3)_2$), 1.46 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12 H, *p*- $\text{CH}(\text{CH}_3)_2$), 2.79 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2 H, *p*- $\text{CH}(\text{CH}_3)_2$), 3.28 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4 H, *o*- $\text{CH}(\text{CH}_3)_2$), 7.14 (s, 4 H, *m*-Trip). **^{13}C NMR** (62.90 MHz, C_6D_6): $\delta = 6.50$ (d, $^2J_{\text{CP}} = 9.5$ Hz), 24.25 (s, $\text{CH}(\text{CH}_3)_2$), 25.09 (s, $\text{CH}(\text{CH}_3)_2$), 27.95 (s, $\text{CH}(\text{CH}_3)_2$), 32.01 (s, $\text{CH}(\text{CH}_3)_2$), 35.54 (s, $\text{CH}(\text{CH}_3)_2$), 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*- C_6H_3). **$^{29}\text{Si}\{^1\text{H}\}$ NMR** (49.69 MHz, C_6D_6): $\delta = 4.08$ (d, $^1J_{\text{SiP}} = 38.5$ Hz). **^{29}Si NMR** (49.69 MHz, C_6D_6): $\delta = 4.08$ (dm, $^1J_{\text{SiP}} = 38.5$ Hz, $^2J_{\text{SiH}} = 6.6$ Hz). **^{31}P NMR** (101.36 MHz, C_6D_6): $\delta = -123.1$ (s, $^1J_{\text{P}^{117}\text{Sn}} = 1396$ Hz, $^1J_{\text{P}^{119}\text{Sn}} = 1453$ Hz, total Sn satellite intensity = 12%). **^{119}Sn NMR** (112.02 MHz, C_6D_6): $\delta = 1919$ (d, $^1J_{\text{SnP}} = 1453$ Hz).

Synthesis of $\text{Ph}^*\text{GeP}(\text{SiMe}_3)_2$ (4**):** **Method A:** A solution of $\text{LiP}(\text{SiMe}_3)_2$ (499 mg, 1.52 mmol) in 20 mL Et_2O was added dropwise to a solution of Ph^*GeCl_3 (**2**) (1 g, 1.52 mmol) in 40 mL Et_2O 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 40 mL Et₂O and cooled to –78°C. A solution of LiP(SiMe₃)₂ (499 mg, 1.52 mmol) in 20 mL Et₂O 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⁺ – ⁱPr, 13%). ³¹P NMR (101.36 MHz, C₆D₆): δ = –48.6 (s).

Synthesis of Ph*SnP(H)Trip (6**):** TripPH₂ (57 mg, 0.24 mmol) was dissolved in 10 mL Et₂O 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 8 mL Et₂O 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, which indicated formation of Trip(H)P–P(H)Trip (ca. 20%) and **6** (ca. 70%) alongside unreacted TripPH₂ (ca. 10%).

6: ³¹P NMR (162 MHz, C₆D₆): δ = –70.9 (br, Δ_{v1/2} = 150 Hz, ¹J_{PH} = 186 Hz, ¹J_{P117/119Sn} = 934 Hz; ^{117/119}Sn satellites could not be resolved, total Sn satellite intensity = 12%).

Synthesis of Li⁺[Ph*SnPTrip][–] (7**, proposed):** To a solution of TripPH₂ (64 mg, 0.27 mmol) in 10 mL Et₂O 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 10 mL Et₂O 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, 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: ³¹P NMR (162 MHz, C₆D₆): δ = 229.7 (br, Δ_{v1/2} = 280 Hz, ¹J_{P117Sn} = 1735 Hz, ¹J_{P119Sn} = 2004 Hz, total Sn satellite intensity = ca. 14%).

Synthesis of [Ph*Sn{W(CO)₅}(μ-O)₂SnPh*] (8**):** A solution of Ph*SnCl (**5**) (198 mg, 0.31 mmol) in 10 mL *n*-hexane was added dropwise to a vigorously stirred suspension of

Li[H₂PW(CO)₅] (113 mg, 0.31 mmol) in 5 mL *n*-hexane 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%).

Synthesis of 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 10 mL Et₂O 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⁺ – CH₃, 1%), 741.0 (M⁺ – SiMe₃, 1.2%), 725.1 (M⁺ – OSiMe₃, 1.6%), 652.1 (M⁺ – OSiMe₃ – SiMe₃, 1.3%), 636.1 (M⁺ – 2 OSiMe₃, 0.8%), 601.1 (M⁺ – 2 OSiMe₃ – Cl, 1.2%), 482.2 (M⁺ – Sn(OSiMe₃)₂Cl, 100%), 467.2 (M⁺ – Sn(OSiMe₃)₂Cl – CH₃, 100%), 439.1 (M⁺ – Sn(OSiMe₃)₂Cl – C₃H₇, 46%), 424.2 (M⁺ – Sn(OSiMe₃)₂Cl – C₃H₇ – CH₃, 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).

Synthesis of [Ph*Sn(μ-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 15 mL Et₂O 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): $\tilde{\nu}$ = 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 (M^+ , 100%). ^1H NMR (C_6D_6 , 25°C): δ = 1.02 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.36 (d, $^3J_{\text{HH}}$ = 6.8 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.46 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 2.86 (m, 6 H, $\text{CH}(\text{CH}_3)_2$), 7.22 (s, 4 H, *m*-Trip). ^{13}C NMR (75.48 MHz, C_6D_6): δ = 23.45 (s, $\text{CH}(\text{CH}_3)_2$), 24.20 (s, $\text{CH}(\text{CH}_3)_2$), 26.17 (s, $\text{CH}(\text{CH}_3)_2$), 31.34 (s, $\text{CH}(\text{CH}_3)_2$), 34.75 (s, $\text{CH}(\text{CH}_3)_2$), 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 $\text{Cu}_{\text{K}\alpha}$ radiation (λ = 1.54184 Å) and a STOE IPDS diffractometer (**1a**, **3**, **8**, **10**) using $\text{Mo}_{\text{K}\alpha}$ radiation (λ = 0.71073 Å), respectively. Semi-empirical absorption corrections from equivalents (multi-scan) were applied for **2** and **4**.^[50] For **1a**, **3**, **8** and **10** numerical absorption corrections from crystal faces were carried out.^[51] **1a**, **3**, **8** and **10** were solved by direct methods with the program SIR-97.^[52] **2** could not be solved using direct methods or Patterson methods. Hence it was solved using charge-flipping algorithms from SUPERFLIP.^[53] Full matrix least-square refinement on F^2 in SHELXL-97^[54] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. In **8** and **10** *iso*-propyl groups are disordered over two positions. Thus several constraints and restraints have been 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.^[55] Additionally, **2** is an inversion twin (50:50) and a mixed crystal with 50 percent occupancy each site for Ph^*GeCl and Ph^*GeCl_3 . Further all four chlorine- and *iso*-propyl 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.^[36] For structure optimisation we employed the functional theory (DFT) method along with the B3LYP exchange-correlation functional^[56] and SDD basis set (Stuttgart/Dresden pseudorelativistic effective core potential for Sn^[57] and D95 full double zeta basis sets for all other atoms^[58]).

Acknowledgments

This work is comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. F. Dielmann thanks the Studienstiftung des Deutschen Volkes for a PhD fellowship.

References

- [1] G. Becker, G. Gesser, W. Uhl, *Z. Naturforsch. Teil B* **1981**, *36*, 16.
- [2] a) T. Allspach, M. Regitz, G. Becker, W. Becker, *Synthesis* **1986**, 31; b) M. Regitz, P. Binger, *Angew. Chem.* **1988**, *100*, 1541; *Angew. Chem. Int. Ed.* **1988**, *27*, 1484; c) M. Regitz, *Chem. Rev.* **1990**, *90*, 191.
- [3] Some examples: a) A. M. Arif, A. Barron, A. H. Cowley, S. W. Hall, *J. Chem. Soc., Chem. Commun.* **1988**, 171; b) G. Becker, M. Bohringer, R. Gleiter, K.-H. Pfeifer, J. Grobe, D. LeVan, M. Hegemann, *Chem. Ber.* **1994**, *127*, 1041; c) G. Becker, K. Hubler, *Z. Anorg. Allg. Chem.* **1994**, *620*, 405; d) G. Becker, W. Schwarz, N. Seidler, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1992**, *612*, 72.
- [4] G. Märkl, H. Sejpka, *Angew. Chem.* **1986**, *98*, 286; *Angew. Chem. Int. Ed.* **1986**, *25*, 264.
- [5] M. Finze, E. Bernhardt, H. Willner, C. W. Lehmann, *Angew. Chem.* **2004**, *116*, 4254; *Angew. Chem. Int. Ed.* **2004**, *43*, 4160.
- [6] a) M. Regitz, P. Binger, *Angew. Chem.* **1988**, *100*, 1541; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1484; b) M. Regitz, P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Hrsg.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 58; c) M. Regitz, *Chem. Rev.* **1990**, *90*, 191; d) A. Mack, M. Regitz, *Chem. Ber.* **1997**, *130*, 823; e) T. W. Mackewitz, M. Regitz, *Synthesis* **1998**, 125; for synthesis of different phosphalkynes cf.: J.-C. Guillemin, T. Janati, J.-M. Denis, *J. Org. Chem.* **2001**, *66*, 7864; for short living phosphalkynes: A. C. Gaumont, J.-M. Denis, *Chem. Rev.* **1994**, *94*, 1413.
- [7] a) J. F. Nixon, *Chem. Rev.* **1988**, *88*, 1327; b) P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Hrsg.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 90; c) J. F. Nixon, *Chem. Ind.* **1993**, 404; d) J. F. Nixon, *Coord. Chem. Rev.* **1995**, *145*, 201; e) J. F. Nixon, *Chem. Soc. Rev.* **1995**, 319; f) K. B. Dillon, F. Mathey, J. F. Nixon in *Phosphorus, The Carbon Copy*, Wiley, Chichester, **1998**, pp 40; g) F. Mathey, *Angew. Chem.* **2003**, *115*, 1616; *Angew. Chem. Int. Ed.* **2003**, *42*, 1578.

- [8] a) P. P. Power, *J. Chem. Soc., Dalton Trans.* **1998**, 18, 2939; b) P. P. Power, *Chem. Rev.* **1999**, 99, 3463.
- [9] a) C. N. Smit, F. M. Lock, F. Bickelhaupt, *Tetrahedron Lett.* **1984**, 25, 3011; b) C. N. Smit, F. Bickelhaupt, *Organometallics* **1987**, 6, 1156; c) E. Niecke, E. Klein, M. Nieger, *Angew. Chem.* **1989**, 101, 792, *Angew. Chem. Int. Ed.* **1989**, 28, 751.
- [10] a) J. Escudié, C. Couret, J. Satgé, M. Andrianarison, J. D. Andriamizaka, *J. Am. Chem. Soc.* **1985**, 107, 3378; b) H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé, M. Dräger, *New. J. Chem.* **1989**, 13, 389; c) H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé, *J. Organomet. Chem.* **1991**, 415, 327.
- [11] a) C. Couret, J. Escudié, J. Satgé, A. Raharinirina, J. D. Andriamizaka, *J. Am. Chem. Soc.* **1985**, 107, 8280; b) H. Ranaivonjatovo, J. Escudié, C. Couret, J. Satgé, *J. Chem. Soc., Chem. Commun.* **1992**, 1047.
- [12] a) M. Driess, *Angew. Chem.* **1991**, 103, 979, *Angew. Chem. Int. Ed.* **1991**, 30, 1022; b) M. Driess, U. Winkler, W. Imhof, L. Zsolnai, G. Huttner, *Chem. Ber.* **1994**, 127, 1031.
- [13] W. Setaka, K. Hirai, H. Tomioka, K. Sakamoto, M. Kira, *J. Am. Chem. Soc.* **2004**, 126, 2696.
- [14] B. Twamley, P. P. Power, *J. Chem. Soc., Chem. Commun.* **1998**, 1979.
- [15] R. C. Smith, P. Gantzel, A. L. Rheingold, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2003**, 125, 40.
- [16] a) M. Scheer, K. Schuster, T. A. Budzichowski, M. H. Chisholm, W. E. Streib, *J. Chem. Soc., Chem. Commun.* **1995**, 1671. b) P. Kramkowski, M. Scheer, G. Baum, *J. Organomet. Chem.* **1998**, 553, 511; c) M. Scheer, J. Krug, *Z. Anorg. Allg. Chem.* **1998**, 624, 399; d) T. Gröer, G. Baum, M. Scheer, *Organometallics* **1998**, 17, 5916; e) M. Scheer, E. Leiner, P. Kramkowski, M. Schiffer, G. Baum, *Chem. Eur. J.*, **1998**, 4, 1917; f) P. Kramkowski, M. Scheer, *Angew. Chem.* **1999**, 111, 3384; *Angew. Chem. Int. Ed.* **1999**, 38, 3183; g) M. Scheer, P. Kramkowski, K. Schuster, *Organometallics* **1999**, 18, 2874; h) P. Kramkowski, G. Baum, U. Radius, M. Kaupp, M. Scheer, *Chem. Eur. J.* **1999**, 5, 2890; i) P. Kramkowski, M. Scheer, *Angew. Chem.* **2000**, 112, 959; *Angew. Chem. Int. Ed.* **2000**, 39, 928; j) M. Scheer, D. Himmel, B. P. Johnson, C. Kuntz, M. Schiffer, *Angew. Chem.* **2007**, 119, 4045; *Angew. Chem. Int. Ed.* **2007**, 46, 3971.
- [17] A. S. Ionkin, W. J. Marshall, *Organometallics* **2003**, 22, 4136.
- [18] J. Glatthaar, G. Maier, *Angew. Chem.* **2004**, 116, 1314–1317; *Chem. Int. Ed.* **2004**, 43, 1294.
- [19] M. Driess, S. Block, M. Brym, M. T. Gamer, *Angew. Chem.* **2006**, 118, 2351.; *Angew. Chem. Int. Ed.* **2006**, 45, 2293.
- [20] a) M. Bender, E. Niecke, M. Nieger, R. Pietschnig, *Eur. J. Inorg. Chem.* **2006**, 380; b) R. Pietschnig, J. J. Tirré, in *Organosilicon Chemistry - From Molecules to Materials VI*, Vol. 1 (Eds.: N. Auner, J. Weis), Wiley-VCH, 2005, pp. 222.
- [21] Y.-H. Hu, M.-D. Su, *Chem. Phys. Lett.* **2003**, 378, 289.
- [22] M. Saito, H. Hashimoto, T. Tajima, M. Ikeda, *J. Organomet. Chem.* **2007**, 692, 2729.
- [23] Bond lengths and angles for **2** are not listed, because the molecular structure of **2** is disordered due to contamination of the product with the starting material Ph*GeCl.
- [24] H. Schumann, R. Fischer, *J. Organomet. Chem.* **1975**, 88, C13.
- [25] a) M. Scheer, F. Uhlig, T. T. Nam, M. Dargatz, H.-D. Schädler, E. Herrmann, *Z. Anorg. Allg. Chem.* **1990**, 585, 177; b) M. Scheer, St. Gremler, E. Herrmann, U. Grünhagen, M. Dargatz, E. Kleinpeter, *Z. Anorg. Allg. Chem.* **1991**, 600, 203; c) M. Scheer, St. Gremler, E. Herrmann, P. G. Jones, *J. Organomet. Chem.* **1991**, 414, 337; d) S. Gremler, M. Scheer, *Z. Anorg. Allg. Chem.* **1993**, 619, 466; e) M. Scheer, S.

- Gremler, Z. *Anorg. Allg. Chem.* **1993**, 619, 471. M. Scheer, St. Gremler, E. Herrmann, M. Dargatz, H.-D. Schädler, Z. *Anorg. Allg. Chem.* **1993**, 619, 1047.
- [26] B. E. Eichler, L. Pu, M. Stender, P. P. Power, *Polyhedron* **2001**, 20, 551.
- [27] a) W.-W. du Mont, H. Schumann, *Angew. Chem.* **1975**, 87, 354; *Angew. Chem. Int. Ed. Engl.* **1975**, 14, 368; b) W.-W. du Mont, M. Grenz, *Chem. Ber.*, **1985**, 118, 1045.
- [28] K. Izod, J. Stewart, W. Clegg, R. W. Harrington, *Organometallics*, **2010**, 29, 108.
- [29] M. F. Lappert, P. P. Power, *J. Chem. Soc. Dalton Trans.* **1985**, 51.
- [30] M. F. Lappert, M. C. Misra, M. Onyszchuk, R. S. Rowe, P. P. Power, M. J. Slade, *J. Organomet. Chem.* **1987**, 330, 31.
- [31] P. B. Hitchcock, H. A. Jasim, M. F. Lappert, W.-P. Leung, A. K. Rai, R. E. Taylor, *Polyhedron* **1991**, 10, 1203.
- [32] B. Twamley, N. J. Hardman, P. P. Power, *Acta Cryst.* **2000**, C56, E514.
- [33] B. Twamley, P. P. Power, *J. Chem. Soc., Chem. Commun.* **1998**, 1979.
- [34] L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, 125, 11626.
- [35] a) M. Driess, *Chemie in unserer Zeit* **1993**, 27, 141; b) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, 103, 4587; c) A. H. Cowley, *Polyhedron* **1984**, 3, 389; d) L. Weber, *Coord. Chem. Rev.* **1992**, 92, 1839; e) N. C. Norman, *Polyhedron* **1993**, 12, 2431; f) A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski, *J. Am. Chem. Soc.* **1983**, 105, 5506; g) C. Couret, J. Escudie, Y. Madaule, H. Ranaivonjatovo, J.-G. Wolf, *Tetrahedron Lett.* **1983**, 24, 2769; h) N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.* **1998**, 120, 443; i) N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, *Science* **1997**, 277, 78.
- [36] Gaussian 03, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2003**. For a current listing of basis sets and ECPs, see <http://www.gaussian.com>.
- [37] a) D. Agustin, G. Rima, H. Gornitzka, J. Barrau, *Eur. J. Inorg. Chem.* **2000**, 693; b) A. L. Balch, M. M. Olmstead, D. P. Oram, *Inorg. Chem.* **1988**, 27, 4309; c) M. Weidenbruch, A. Stilter, J. Schläpke, K. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1995**, 501, 67; d) H.-P. Abicht, K. Jurkschat, A. Tzschach, K. Peters, E.-M. Peters, H. G. von Schnering, *J. Organometal. Chem.* **1987**, 326, 357.
- [38] J. Beckmann, K. Jurkschat, S. Rabe, M. Schürmann, *Z. Anorg. Allg. Chem.* **2001**, 627, 2413.
- [39] G. H. Spikes, Y. Peng, J. C. Fetting, J. Steiner, P. P. Power, *Chem. Commun.* **2005**, 6041.

- [40] For usage of $\text{Me}_3\text{SiOOSiMe}_3$ as a mild, non-radical oxidation agent, see: a) D. Brandes, A. Blaschette, *J. Organomet. Chem.* **1974**, 73, 217; b) D. Brandes, A. Blaschette, *J. Organomet. Chem.* **1973**, 49, C6; for similar oxidation of Sn(II) with benzoyl peroxide, see: c) A. Tzschach, M. Scheer, K. Jurkschat, *Z. Anorg. Allg. Chem.* **1984**, 508, 73.
- [41] L. Pu, N. J. Hardman, P. P. Power, *Organometallics* **2001**, 20, 5105.
- [42] M. A. Edelman, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1990**, 1116.
- [43] H. Puff, R. Gattermayer, R. Hundt, R. Zimmer, *Angew. Chem.* **1977**, 89, 556; *Angew. Chem. Int. Ed.* **1977**, 16, 547.
- [44] P. Brown, M. F. Mahon, K. C. Molloy, *J. Chem. Soc., Chem. Commun.* **1989**, 1621.
- [45] J. Janssen, J. Magull, H. W. Roesky, *Angew. Chem.* **2002**, 114, 1425; *Angew. Chem. Int. Ed.* **2002**, 41, 1365.
- [46] a) F. Uhlig, St. Gremler, M. Dargatz, M. Scheer, E. Herrmann, *Z. Anorg. Allg. Chem.* **1991**, 606, 105; b) H. H. Karsch, F. Bienlein, T. Rupprich, F. Uhlig, E. Herrmann, M. Scheer, *Synth. Methods Organomet. Inorg. Chem.* **1996**, 3, 58; c) G. Fritz, W. Hölderlin, *Z. Anorg. Allg. Chem.* **1976**, 422, 104.
- [47] B. Schiemenz, P. P. Power, *Organometallics* **1996**, 15, 958.
- [48] L. Pu, M. M. Olmstead, P. P. Power, B. Schiemenz, *Organometallics* **1998**, 17, 5602.
- [49] B. E. Eichler, L. Pu, M. Stender, P. P. Power, *Polyhedron* **2001**, 20, 551.
- [50] *CrysAlis RED*, Oxford Diffraction Ltd. Version 1.171.33.52, **2009**.
- [51] STOE (1998) IPDS-software, version 2.89, program FaceIt, STOE & CIE GmbH, Darmstadt, Germany.
- [52] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, 32, 115.
- [53] L. Palatinus, G. Chapuis, *J. Appl. Cryst.* **2007**, 40, 786.
- [54] a) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**; b) G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112.
- [55] A. L. Spek, *J. Appl. Cryst.* **2003**, 36, 7.
- [56] a) A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785; c) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648.
- [57] A. Bergner, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, 80, 1431,
- [58] T. H. Dunning Jr., P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1976) 1.

Figure 1. Molecular structure of Ph*ECl₃ (1a: E = Sn, 2: E = Ge) in the crystal. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for 1a: Sn–C1 2.155(5), Sn–Cl1 2.322(3), Sn–Cl2 2.321(3), Sn–Cl3 2.328(2); C1–Sn–Cl1 119.89(13), C1–Sn–Cl2 122.05(13), C1–Sn–Cl3 109.26(14), Cl1–Sn–Cl2 98.12(7), Cl1–Sn–Cl3 102.96(8), Cl2–Sn–Cl3 101.67(8).

Figure 2. Molecular structures of $\text{Ph}^*\text{EP}(\text{SiMe}_3)_2$ (3: $\text{E} = \text{Sn}$, 4: $\text{E} = \text{Ge}$) in the crystal. H atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] 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 [$\text{\AA}$] and angles [$^\circ$] 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).

LUMO

HOMO

HOMO-1

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.

638x422mm (96 x 96 DPI)

Figure 4. Molecular structure of $[\text{Ph}^*\text{Sn}\{\text{W}(\text{CO})_5\}(\mu\text{-O})_2\text{SnPh}^*]$ (8) in the crystal. The H 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–Ctrans 1.978(15), W1–Ccis 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).

Figure 5. Molecular structure of $[\text{Ph}^*\text{Sn}(\mu\text{-O})\text{Cl}]_2$ (10) in the crystal. H atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Sn1–O1 1.994(2), Sn1–Cl1 2.343(1), Sn1–Cipso 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), Cipso–Sn1–O1 117.28(10), Cipso–Sn1–O1 119.98(9), Cl1–Sn1–Cipso 115.76(8).