

**Synthesis and some coordination chemistry of the PSnP pincer-type stannylene  $\text{Sn}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$ , attempts to prepare the PSiP analogue, and effect of the E atom on the molecular structures of  $\text{E}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  (E = C, Si, Ge, Sn)†**

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**Abstract:** The non-donor-stabilized P<sub>2</sub>SnP pincer-type stannylene Sn(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**) has been prepared by treating SnCl<sub>2</sub> with Li<sub>2</sub>(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>. All attempts to synthesize the analogous P<sub>2</sub>SiP silylene by reduction of the (previously unknown) silanes SiCl<sub>2</sub>(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**2**), SiHCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**3**) and SiH(HMDS)(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**4**; HMDS = N(SiMe<sub>3</sub>)<sub>2</sub>) have been unsuccessful. The almost planar (excluding the tert-butyl groups) molecular structure of stannylene **1** (determined by X-ray crystallography) has been rationalized with the help of DFT calculations, which have shown that, in the series of diphosphanetetrylenes E(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (E = C, Si, Ge, Sn), the most stable conformation of the compounds with E = Ge and Sn has the P atoms very close to the EN<sub>2</sub>C<sub>6</sub>H<sub>4</sub> plane, near (interacting with) the E atom, whereas for the compounds with E = C and Si, both phosphane groups are located at one side of the EN<sub>2</sub>C<sub>6</sub>H<sub>4</sub> plane and far away from the E atom. The size of the E atom and the strength of stabilizing donor–acceptor P···E interactions (both increase on going down in group 14) are key factors in determining the molecular structures of these diphosphanetetrylenes. The syntheses of the chloridostannyl complexes [Rh{κ<sup>2</sup>Sn,*P*-SnCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(η<sup>4</sup>-cod)] (**5**), [RuCl{κ<sup>2</sup>Sn,*P*-SnCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(η<sup>6</sup>-cym)] (**6**) and [IrCl{κ<sup>2</sup>Sn,*P*-SnCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)] (**7**) have demonstrated the tendency of stannylene **1** to insert its Sn atom into M–Cl bonds of transition metal complexes and the preference of the resulting P<sub>2</sub>SnP chloridostannyl group to act as a κ<sup>2</sup>Sn,*P*-chelating ligand, maintaining an uncoordinated phosphane fragment. X-ray diffraction data (of **6**), <sup>31</sup>P{<sup>1</sup>H} NMR data (of **5–7**) and DFT calculations (on **6**) are consistent with the existence of a weak P···Sn interaction involving the non-coordinated P atom of complexes **5–7**, similar to that found in compound **1**.

## Introduction

In the last years, the field of ligand design has dedicated many efforts to the synthesis of pincer ligands comprising strong electron-donating groups.<sup>1</sup> This intense research activity has been stimulated by the high degree of success that transition metal complexes containing such ligands have presented in stoichiometric and catalytic reactions involving bond activation processes.<sup>1,2</sup> In fact, the coordination of strong electron-donating ligands to transition metals increases the nucleophilicity of the metal atoms, facilitating their involvement in oxidative addition reactions.<sup>3</sup>

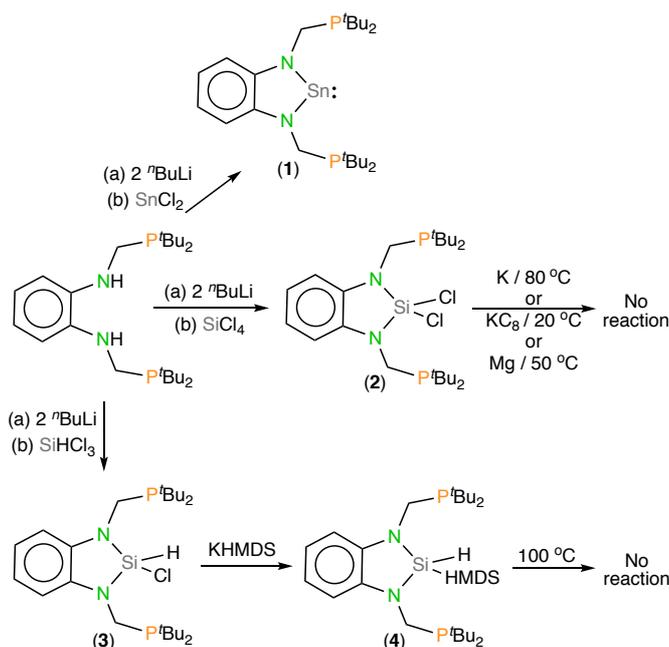
Heavier carbene analogues, also known as heavier tetrylenes, are ambiphilic ligands (they can behave as both Lewis acids and bases<sup>4</sup>) that have been recently recognized as strong electron-donating groups (donor-stabilized silylenes and germylenes are even stronger electron-donors than most N-heterocyclic carbenes and phosphanes).<sup>5</sup> However, prior to our recent contributions to the field of pincer ligands, in which we have described the synthesis<sup>6</sup> and some reactivity<sup>6,7</sup> of the PGeP pincer-type germylene Ge(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, very few tridentate ligands with a pincer topology (free or coordinated to transition metals) were reported to comprise at least one heavier tetrylene as a donor group. They are the P<sub>2</sub>SiP pincers Si(C<sub>6</sub>H<sub>4</sub>P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub><sup>8</sup> and

Si(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>,<sup>9</sup> the NSn pincers Sn{N(CH<sub>2</sub>)<sub>n</sub>NMe<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (n = 1, 2),<sup>10</sup> some ECE<sup>11</sup> and ENE<sup>12</sup> pincers having benzamidinato-silylenes or -germylenes as E-donor groups<sup>13</sup> and GeNGe and GeCGe pincers in which a pyridine-2,6-diyl or a benzene-1,3-diyl group, respectively, are linked to two 2-germabenzimidazol-2-ylidene fragments.<sup>14</sup> Remarkably, some of their transition metal complexes are efficient catalyst precursors for important homogeneous catalytic transformations.<sup>11a,c,12</sup>

We describe herein (a) the isolation and characterization of the first metal-free non-donor-stabilized PSnP pincer-type stannylene,<sup>15</sup> namely, Sn(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**), which contains two very basic phosphane fragments accompanying the stannylene group, (b) our attempts to prepare the analogous PSiP silylene, (c) DFT calculations that demonstrate the existence of a relationship between the structures of the PEP pincer-type compounds E(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and the nature (size) of their E atom (E = C, Si, Ge, Sn), and (d) some reactions of stannylene **1** with transition metal complexes that, leading to chloridostannyl derivatives, have revealed a tendency of **1** to insert the Sn atom into M–Cl bonds of transition metal complexes and the preference of the resulting chloridostannyl PSnP group to act as a chelating κ<sup>2</sup>Sn,*P*-ligand.

## Results and discussion

Following our recently-described synthesis of the PGeP germylene Ge(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>,<sup>6</sup> which was inspired by previously-reported preparations of bis(phosphane)boranes<sup>16</sup> and -silanes,<sup>17</sup> we set out the synthesis of the analogous PSnP stannylene Sn(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**1**) by treating anhydrous tin dichloride with the dilithium salt of the known<sup>16</sup> diamine *o*-(N(H)CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (Scheme 1). The desired product was isolated as an orange air-sensitive solid in 88 % yield.



**Scheme 1** Synthesis of the PSnP stannylene **1** and attempts to prepare its analogous silylene by reduction of the silane precursors **2–4**.

The lack of a commercial silicon(II) precursor and the fact that some silylenes have been prepared by reduction of appropriate dichloridosilane precursors,<sup>18–20</sup> led us to attempt the synthesis of the analogous PSiP pincer silylene  $\text{Si}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  by reduction of  $\text{SiCl}_2(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  (**2**). Dichloridosilane **2** was easily prepared by treating the dilithium salt of  $o\text{-}\{\text{N}(\text{H})\text{CH}_2\text{P}^t\text{Bu}_2\}_2\text{C}_6\text{H}_4$  with  $\text{SiCl}_4$  (Scheme 1). However, unreacted **2** was recovered after strong reducing treatments that have been previously used to transform dihalogenidosilanes into silylenes, such as (a) potassium, THF (or toluene), 2 h, 80 °C;<sup>18</sup> (b) potassium/graphite, THF, 20 °C;<sup>19</sup> and (c) magnesium powder, THF, 50 °C.<sup>20</sup> The lack of success of these reactions has to be associated with two facts that seem to hamper the interaction of the reducing reagent with the silicon atom of **2**, (a) the presence of the very bulky  $\text{CH}_2\text{P}^t\text{Bu}_2$  side arms at both sides of the silicon atom and (b) the heterogeneity of the reaction medium, since the reducing reagent, in solid or liquid phase, is insoluble in the solvent that contains the silicon reagent.

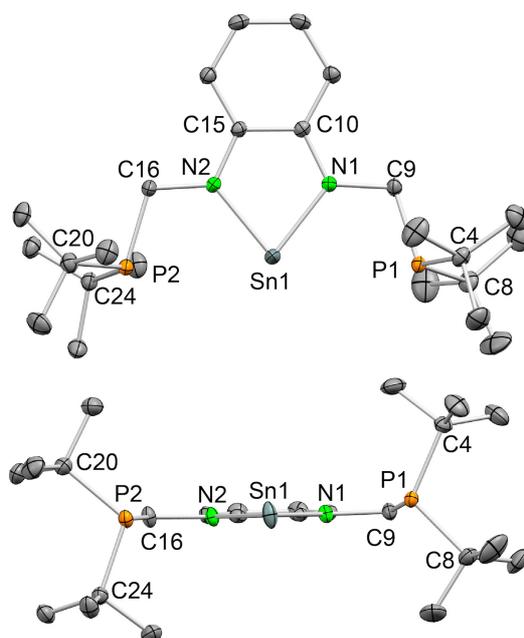
We also attempted the dehydrochlorination of  $\text{SiHCl}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  (**3**),<sup>21</sup> prepared from  $o\text{-}\{\text{N}(\text{H})\text{CH}_2\text{P}^t\text{Bu}_2\}_2\text{C}_6\text{H}_4$ ,  $n\text{BuLi}$  and  $\text{SiHCl}_3$  (Scheme 1), with KHMDS (toluene, 20 °C) or LiHMDS (toluene, 100 °C) (HMDSH = hexamethyldisilazane,  $\text{HN}(\text{SiMe}_3)_2$ ), but these reactions led to the HMDS derivative  $\text{SiH}(\text{HMDS})(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  (**4**), which did not eliminate HMDSH when it was stirred in refluxing toluene for 2 h.<sup>22</sup> An attempt to dehydrochlorinate silane **3** with the N-heterocyclic carbene 1,3-bis(2,5-di-isopropylphenyl)imidazol-2-ylidene was also unsuccessful (no reaction was observed in toluene, 20 °C).<sup>23</sup>

When we were writing up this manuscript, Whited's group communicated a ruthenium(II) complex containing the PSiP pincer silylene  $\text{Si}(\text{C}_6\text{H}_4\text{PPh}_2)_2$ .<sup>24</sup> Previously, Ozerov's<sup>8</sup> and Zybill's<sup>9</sup> groups reported platinum(II) and chromium(0) derivatives of the PSiP silylenes  $\text{Si}(\text{C}_6\text{H}_4\text{P}^i\text{Pr}_2)_2$  and  $\text{Si}(\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2)_2$ , respectively. While the ruthenium<sup>24</sup> and platinum<sup>8</sup> complexes were prepared by hydride abstraction (with trityl salts) from the corresponding hydridosilyl complex precursor, the chromium complex was made by photochemical decarbonylation of a product that resulted from the reaction of  $\text{SiCl}_2(\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2)_2$  with  $\text{Na}_2[\text{Cr}(\text{CO})_5]$ .<sup>9</sup>

The NMR spectra of **1–4** indicated that their  $(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  fragment consists of two equivalent halves (two-fold and/or mirror symmetry). Remarkably, (a) the  $^{31}\text{P}$  resonance of stannylene **1** (34.0 ppm) and also that of germylene  $\text{Ge}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  (25.5 ppm)<sup>6</sup> appear at higher  $\delta$  than those of the silane derivatives **2–4** (14.4, 18.0 and 12.7 ppm, respectively; all in  $d_6$ -benzene) and (b) the  $^{31}\text{P}\{^1\text{H}\}$  and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra of **1** show a  $J_{^{119}\text{Sn}-^{31}\text{P}}$  coupling of 647 Hz. Previously reported  $J_{^{119}\text{Sn}-^{31}\text{P}}$  coupling constants<sup>25</sup> vary from 1756–754 Hz for  $^1J$  (direct P–Sn bond)<sup>25a,c</sup> to 280–40 Hz for  $^2J_{\text{cis}}$ ,<sup>25b,c</sup> and 55–18 Hz for  $^3J$ .<sup>25a,c</sup> Therefore, as 647 Hz is an

unexpectedly large value for a  ${}^3J_{119\text{Sn}-31\text{P}}$  coupling, there should be some kind of Sn $\cdots$ P interaction in **1**.

The molecular structure of stannylene **1** was determined by X-ray diffraction (XRD) crystallography (Fig. 1). Interestingly, the two P atoms of the molecule are almost in the SnN $_2$ C $_6$ H $_4$  plane, near the Sn atom. The small difference between the two Sn $\cdots$ P distances, 3.277(1) Å and 3.313(1) Å, should be due to packing effects in the solid state, because both distances are equivalent in the gas phase (DFT-optimized structure, Fig. S19 of the ESI file) and both phosphane fragments are equivalent in solution (see above).



**Fig. 1** Molecular structure (two views) of stannylene **1** (30% displacement ellipsoids, H atoms have been omitted for clarity). Selected interatomic distances (Å) and angles (°): Sn1 $\cdots$ P1 3.277(1), Sn1 $\cdots$ P2 3.313(1), Sn1–N1 2.089(2), Sn1–N2 2.095(2), P1–C4 1.878(2), P1–C8 1.882(2), P1–C9 1.860(2), P2–C16 1.863(2), P2–C20 1.884(2), P2–C24 1.885(2), N1–C9 1.464(3), N1–C10 1.380(3), N2–C15 1.379(3), N2–C16 1.459(3), C10–C15 1.429(3), N1–Sn1–N2 77.08(7).

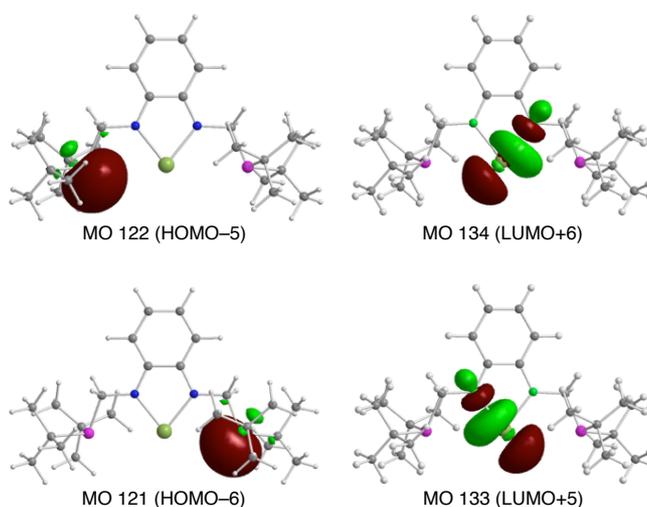
It seems that the short length of the CH $_2$ P $^t$ Bu $_2$  side arms of **1** prevents an intramolecular donor-acceptor interaction between the lone pair of one or both P atoms and the empty p $_x$  orbital of the Sn atom (perpendicular to the SnN $_2$ C $_6$ H $_4$  plane), because an interaction of this type has been observed between one NMe $_2$  group and the Sn atom of Sn{N(CH $_2$ ) $_3$ NMe $_2$ } $_2$ C $_6$ H $_4$ , which has longer (CH $_2$ ) $_3$ NMe $_2$  side arms.<sup>10b</sup>

It is also interesting to note that the reported XRD structures of the related tetrylenes E(NCH $_2^t$ Bu) $_2$ C $_6$ H $_4$  (E = Ge,<sup>26</sup> Sn<sup>27</sup>), which contain bulky but non-coordinable CH $_2^t$ Bu side arms, differ from the “planar” structure of **1** in that the CH $_2^t$ Bu side arms of the former are both located at one side of the EN $_2$ C $_6$ H $_4$  plane and far away from the E atom. This observation led us to calculate by DFT methods the “planar” (**E**<sub>tBu-pli</sub>; analogous to the XRD structure of **1**) and “non planar” (**E**<sub>tBu-npi</sub>; analogous to the XRD structures of E(NCH $_2^t$ Bu) $_2$ C $_6$ H $_4$ , E = Ge,<sup>26</sup> Sn<sup>27</sup>) conformations of

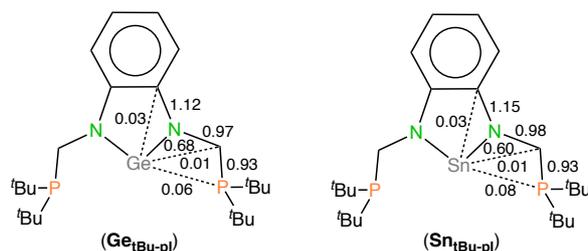
$E(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  ( $E = \text{C, Si, Ge, Sn}$ ) in order to establish the effect of the E atom on the molecular structures.<sup>28,29</sup> We also computed the “planar” ( $\mathbf{E}_{\text{Me-pl}}$ ) and “non-planar” ( $\mathbf{E}_{\text{Me-npl}}$ ) conformations of  $E(\text{NCH}_2\text{PMe}_2)_2\text{C}_6\text{H}_4$  ( $E = \text{C, Si, Ge, Sn}$ ), which have smaller methyl groups on the P atoms,<sup>28</sup> aiming at shedding light on how the volume of the phosphane fragment influences the conformational stability of this type of molecules. The results given in Table 1 indicate that the “non-planar” methyl conformers  $\mathbf{E}_{\text{Me-npl}}$ , which contain small  $\text{CH}_2\text{PMe}_2$  groups, are in all cases ( $E = \text{C, Si, Ge, Sn}$ ) more stable than the corresponding “planar” conformers  $\mathbf{E}_{\text{Me-pl}}$ . The same situation is observed for the tert-butyl conformers  $\mathbf{C}_{\text{tBu-npl}}$  and  $\mathbf{Si}_{\text{tBu-npl}}$ , which are more stable than the “planar”  $\mathbf{C}_{\text{tBu-pl}}$  and  $\mathbf{Si}_{\text{tBu-pl}}$ , respectively. However, for the larger E atoms Ge and Sn, the “planar” conformers  $\mathbf{Ge}_{\text{tBu-pl}}$  and  $\mathbf{Sn}_{\text{tBu-pl}}$  are more stable than the corresponding “non planar” ones and the difference is greater for  $E = \text{Sn}$  ( $5.00 \text{ kcal mol}^{-1}$ ) than for  $E = \text{Ge}$  (only  $0.48 \text{ kcal mol}^{-1}$ ). Space-filling models (ESI file) show that the steric interaction between the E atom and the tert-butyl groups in the “non planar”  $\mathbf{E}_{\text{tBu-npl}}$  conformers increases on going from C to Sn. Therefore, for the larger E atoms (Ge and Sn) such an increased steric hindrance should be responsible for the fact that the most stable conformers are the “planar” ones ( $\mathbf{Ge}_{\text{tBu-pl}}$  and  $\mathbf{Sn}_{\text{tBu-pl}}$ ).

The short  $E\cdots\text{P}$  distances DFT-calculated for  $\mathbf{Ge}_{\text{tBu-pl}}$  ( $3.370 \text{ \AA}$ ) and  $\mathbf{Sn}_{\text{tBu-pl}}$  ( $3.420 \text{ \AA}$ ), which are shorter than the sum of the corresponding Van der Waals radii,<sup>30</sup> and the large  $J_{119\text{Sn}-31\text{P}}$  coupling constant ( $647 \text{ Hz}$ ) measured in the  $^{31}\text{P}\{^1\text{H}\}$  and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra of **1** suggested the existence of some bonding interaction between the E and P atoms in  $E(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  ( $E = \text{Ge, Sn}$ ). The positive NBO atomic charges of the E and P atoms of  $\mathbf{Ge}_{\text{tBu-pl}}$  ( $+1.01$  and  $+0.81$ , respectively) and  $\mathbf{Sn}_{\text{tBu-pl}}$  ( $+1.01$  and  $+0.80$ , respectively) discard an attractive electrostatic interaction between these atoms. An analysis of the second order perturbation donor–acceptor interactions under the NBO basis provided the orbital interactions between the E and P atoms of the “planar” conformers  $\mathbf{E}_{\text{tBu-pl}}$  for  $E = \text{C, Si, Ge, Sn}$  (Table 2). For  $E = \text{C}$ , the lone pair of each P atom interacts only with an empty  $\sigma^*(\text{C}-\text{N})$  orbital. For  $E = \text{Si, Ge}$  and  $\text{Sn}$ , the lone pair of each P atom interacts with the two empty  $\sigma^*(\text{E}-\text{N})$  orbitals associated with the two E–N bonds of the molecule. These orbitals, for  $E = \text{Sn}$  ( $\mathbf{Sn}_{\text{tBu-pl}}$ ), are shown in Fig. 2; those for  $E = \text{C, Si}$  and  $\text{Ge}$  have analogous shapes. The data given in Table 2 show that the contribution of the above-described donor-acceptor interactions to the stability of the corresponding molecule, being small in all cases, increases with the size of the E atom. In fact, although such a stabilization energy is very small for  $\mathbf{C}_{\text{tBu-pl}}$  ( $1.88 \text{ kcal mol}^{-1}$ ), it increases to  $10.84 \text{ kcal mol}^{-1}$  for  $\mathbf{Si}_{\text{tBu-pl}}$ , to  $13.60 \text{ kcal mol}^{-1}$  for  $\mathbf{Ge}_{\text{tBu-pl}}$  and up to  $21.34 \text{ kcal mol}^{-1}$  in the case of  $\mathbf{Sn}_{\text{tBu-pl}}$ . Consequently, the computed  $E\cdots\text{P}$  Wiberg bond indices (WBI) for  $\mathbf{Ge}_{\text{tBu-pl}}$  and  $\mathbf{Sn}_{\text{tBu-pl}}$  (Fig. 3) are small but not negligible and, as expected from the data given in Table 2, the WBI of the  $\text{Ge}\cdots\text{P}$  interaction in  $\mathbf{Ge}_{\text{tBu-pl}}$  ( $0.06$ ) is smaller than that of the  $\text{Sn}\cdots\text{P}$  interaction in  $\mathbf{Sn}_{\text{tBu-pl}}$  ( $0.08$ ). Additionally, the relatively small WBIs of the E–N bonds,  $0.68$  for  $\mathbf{Ge}_{\text{tBu-pl}}$  and  $0.60$  for  $\mathbf{Sn}_{\text{tBu-pl}}$  (in comparison with those of common single bonds, which are close to  $1.00$ ), are in agreement with the fact that the donor–acceptor  $\text{P}\cdots\text{E}$  interaction weakens

the E–N bond (the lone pairs of the P atoms interact with empty  $\sigma^*(E-N)$  orbitals) and, as the Sn $\cdots$ P interaction in **Sn**<sub>tBu-pl</sub> is stronger than the Ge $\cdots$ P interaction in **Ge**<sub>tBu-pl</sub>, the WBI of the Sn–N bond of **Sn**<sub>tBu-pl</sub> (0.60) is smaller than that of the Ge–N bond of **Ge**<sub>tBu-pl</sub> (0.68).



**Fig. 2** P lone pairs (left) and empty  $\sigma^*(Sn-N)$  orbitals (right) involved in the weak donor–acceptor P $\cdots$ Sn interactions found in the “planar” conformer (**Sn**<sub>tBu-pl</sub>) of stannylene **1** (NBO second order perturbation analysis). Each P lone pair overlaps with both MO133 and MO134 (see Table 2).



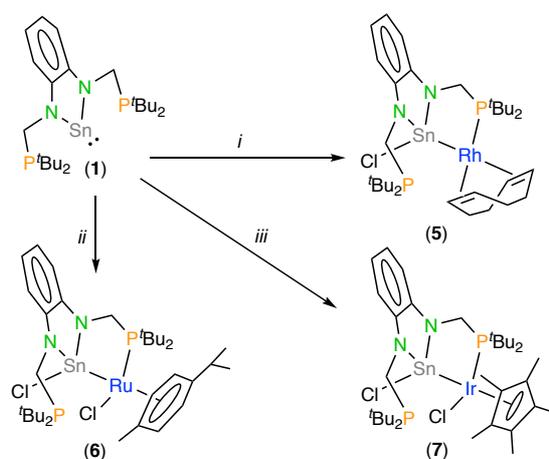
**Fig. 3** Selected Wiberg bond indices between atoms of **Ge**<sub>tBu-pl</sub> and **Sn**<sub>tBu-pl</sub> (the molecules have two-fold symmetry).

Therefore, our theoretical study on the tetrylenes  $E(NCH_2P^tBu_2)_2C_6H_4$  has demonstrated that a larger E atom implies a greater steric hindrance between it and the phosphane tert-butyl groups in the “non-planar” conformation **E**<sub>tBu-npl</sub> and a stronger donor–acceptor P $\cdots$ E interaction in the “planar” **E**<sub>tBu-pl</sub> conformation. As a result of an optimized combination of these two factors (minimum steric hindrance and maximum P $\cdots$ E interaction), the “non-planar” conformation is more stable for the molecules with E = C and Si, whereas the “planar” one is more stable for the molecules with E = Ge and Sn.

Aiming at shedding some light on the coordination chemistry of stannylene **1**, its reactivity toward some common transition metal complexes was examined. We also wanted to compare this reactivity with that previously reported for the related PGeP germylene  $Ge(NCH_2P^tBu_2)_2C_6H_4$  in

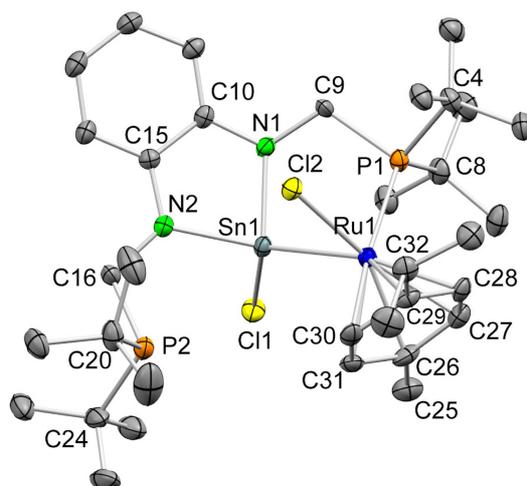
analogous reactions<sup>6,7</sup> in order to establish the effect of the E atom (Sn vs. Ge) on the reaction outcome.

Single reaction products, subsequently identified as  $[\text{Rh}\{\kappa^2\text{Sn},P\text{-SnCl}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4\}(\eta^4\text{-cod})]$  (**5**; cod = 1,5-cyclooctadiene),  $[\text{RuCl}\{\kappa^2\text{Sn},P\text{-SnCl}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4\}(\eta^6\text{-cym})]$  (**6**; cym = *p*-cymene) and  $[\text{IrCl}\{\kappa^2\text{Sn},P\text{-SnCl}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4\}(\eta^5\text{-Cp}^*)]$  (**7**; Cp\* = pentamethylcyclopentadienyl), were obtained when stannylene **1** was treated with toluene solutions of the chlorido-bridged dimeric complexes  $[\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$ ,  $[\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^6\text{-cym})_2]$  and  $[\text{Ir}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^5\text{-Cp}^*)_2]$ , respectively, in 1:0.5 mol ratio (Scheme 2).



**Scheme 2** Synthesis of complexes **5–7**. *i* =  $\frac{1}{2} [\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$ ; *ii* =  $\frac{1}{2} [\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^6\text{-cym})_2]$ ; *iii* =  $\frac{1}{2} [\text{Ir}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^5\text{-Cp}^*)_2]$ .

The structure of compound **6** was determined by XRD. Fig. 4 confirms the insertion of the original stannylene fragment into a Cl–Ru bond and the  $\kappa^2\text{Sn},P$ -bidentate coordination of the resulting chloridostannyl ligand. The insertion of stannylenes into Cl–M bonds has been previously observed for M = Rh,<sup>25b</sup> Ir,<sup>25b</sup> Ge,<sup>25c</sup> Sn,<sup>25c</sup> Au.<sup>25b,31</sup> Overall, the molecule presents the typical pseudo-octahedral three-legged piano stool structure previously found in hundreds of  $\eta^6$ -arene-ruthenium(II) complexes.<sup>32</sup> The Ru–Sn bond distance, 2.5716(6) Å, is comparable to those found in other ruthenium(II) complexes containing stannyl ligands.<sup>33</sup> The most intriguing feature of the structure of **6** is the short separation between the Sn atom and the non-coordinated P atom, Sn1–P2 3.360(3) Å, which is only 0.047 Å longer than the Sn1–P2 distance found in the uncoordinated stannylene **1** (Fig. 1), for which the existence of a weak Sn···P interaction has been theoretically demonstrated (see above). In the previously reported germyl complex  $[\text{RhCl}\{\kappa^2\text{Ge},P\text{-GeCl}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4\}(\eta^4\text{-cod})]$ , which contains the related  $\kappa^2\text{Ge},P$ -(chloridogermyl)diphosphane ligand, the uncoordinated P atom is also unexpectedly close to the Rh atom, 3.364(3) Å,<sup>6</sup> but no DFT studies were performed on this molecule.

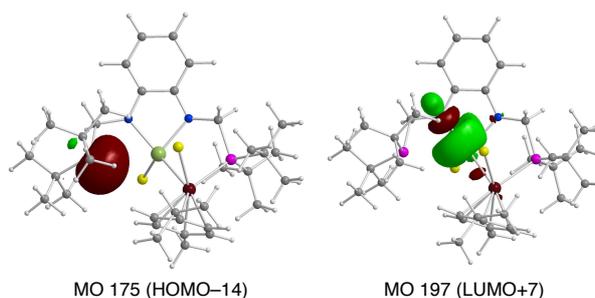


**Fig. 4** Molecular structure of compound **6** (30% displacement ellipsoids, H atoms have been omitted for clarity). Selected interatomic distances (Å) and angles (°): Ru1–C(arene)<sub>av</sub> 2.24(6), Ru1–Cl2 2.410(2), Ru1–P1 2.398(2), Ru1–Sn1 2.5716(6), Sn1–P2 3.360(3), Sn1–N1 2.067(5), Sn1–N2 2.043(5), Sn1–Cl1 2.463(2), P1–C4 1.907(7), P1–C8 1.904(7), P1–C9 1.871(6), P2–C16 1.854(6), P2–C20 1.887(8), P2–C24 1.877(8), N1–C9 1.444(8), N1–C10 1.390(8), N2–C15 1.391(8), N2–C16 1.459(8), C10–C15 1.424(9), C–C(arene)<sub>av</sub> 1.41(2), C25–C26 1.50(1), C29–C32 1.52(1), P1–Ru1–Sn1 81.91(4), N1–Sn1–N2 80.8(2), N1–Sn1–Cl1 109.7(2), N2–Sn1–Cl1 95.2(2), N1–Sn1–Ru1 100.3(1), N2–Sn1–Ru1 141.1(2), Cl1–Sn1–Ru1 119.98(4).

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **5–7** contain the resonances of two inequivalent P atoms, uncoupled to each other, both showing tin satellites with smaller  $J_{\text{P-Sn}}$  coupling constants (in the range 259–523 Hz) than that observed in the spectrum of **1** (647 Hz), but, interestingly, the  $J_{\text{P-Sn}}$  coupling of the uncoordinated P atom (lower chemical shift;  $J_{\text{P-Sn}} = 523$  (**5**), 494 (**6**), 350 (**7**) Hz) is for the three complexes greater than that of the coordinated P atom (higher chemical shift;  $J_{\text{P-Sn}} = 222$  (**5**), 443 (**6**), 259 (**7**) Hz). As a  $^3J_{\text{P-Sn}}$  is expected to be smaller than a *cis*  $^2J_{\text{P-Sn}}$ ,<sup>25</sup> these data clearly indicate the existence in the three complexes of a Sn $\cdots$ P interaction involving the non-coordinated P atom, similar to that described/discussed above for the uncoordinated stannylene **1**. In the case of the rhodium complex **5**, the higher chemical shift resonance is a doublet due to coupling to  $^{103}\text{Rh}$  ( $J_{\text{P-Rh}} = 141$  Hz). Additional analytical data of **5–7**, including  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, are consistent with the structures depicted in Scheme 2 for these complexes. In particular, the NMR spectra of the rhodium complex **5** are similar to those of the XRD-characterized chloridogermyl derivative  $[\text{RhCl}\{\kappa^2\text{Ge}, P\text{-GeCl}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4\}(\eta^4\text{-cod})]^\delta$  (the reactions of  $[\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^6\text{-cym})_2]$  and  $[\text{Ir}_2\text{Cl}_2(\mu\text{-Cl})_2(\eta^5\text{-Cp}^*)_2]$  with the germylene  $\text{Ge}(\text{NCH}_2\text{P}^t\text{Bu}_2)_2\text{C}_6\text{H}_4$  have not been reported).

A DFT study on complex **6** and, in particular, an analysis of the second order perturbation donor–acceptor interactions under the NBO basis, revealed that the greatest donor–acceptor interaction involving the lone pair of the “uncoordinated” P atom corresponds to its overlap with an empty  $\sigma^*(\text{Sn-N})$  orbital (Fig. 5) and that the stabilization energy provided by this interaction is

12.20 kcal mol<sup>-1</sup>. Therefore, this interaction is similar to the Sn⋯P interactions found in stannylene **1** (Fig. 2) and provides a rationale for the close proximity of the P2 and Sn1 atoms found in the XRD structure of complex **6** (3.360(3) Å; Fig. 4) and also for the large  $J_{P-Sn}$  coupling constant (494 Hz) measured in the <sup>31</sup>P{<sup>1</sup>H} NMR signal of the uncoordinated P atom of this complex. These data suggest that the large  $J_{P-Sn}$  coupling constants measured in the <sup>31</sup>P{<sup>1</sup>H} NMR signals of the uncoordinated P atoms of complexes **5** and **7** (see above) may also be caused by weak P⋯Sn interactions.



**Fig. 5** P lone pair (left) and empty  $\sigma^*(Sn-N)$  orbital (right) involved in the weak donor–acceptor P⋯Sn interaction found between the “uncoordinated” P atom and the Sn atom of complex **6** (NBO second order perturbation analysis).

On the other hand, stannylene **1** reacted quickly with [Co<sub>2</sub>(CO)<sub>8</sub>] (1:1 mol ratio) in toluene at room temperature to give a mixture of products (<sup>31</sup>P NMR) that we could not separate and characterize. In a similar reaction, the analogous germylene Ge(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> led to [Co<sub>2</sub>{ $\mu$ - $\kappa^3P, Ge, P$ -Ge(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(CO)<sub>6</sub>], which contains the Ge atom spanning the two Co atoms and each phosphane fragment attached to a Co(CO)<sub>3</sub> unit.<sup>6</sup> Complex mixtures of products (<sup>31</sup>P NMR) were also formed when complex **5** was exposed to a CO atmosphere and when stannylene **1** was treated with [PtCl<sub>2</sub>(cod)], but similar reactions of the chloridogermyl complex [Rh{ $\kappa^2Ge, P$ -GeCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}( $\eta^4$ -cod)] with CO and of Ge(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> with [PtCl<sub>2</sub>(cod)] led to [Rh{ $\kappa^3P, Ge, P$ -GeCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(CO)]<sup>6</sup> and [PtCl{ $\kappa^3P, Ge, P$ -GeCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}]<sup>7</sup>, respectively, both containing a  $\kappa^3P, Ge, P$ -chloridogermyl pincer ligand with the corresponding metal atom in a very strained and distorted square-planar ligand environment due to the short length of the CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub> side arms. The larger size of the tin atom, in comparison with that of germanium, has to be claimed as responsible (at least in part) for the failure of the above-described reactions to give stable reaction products having a  $\kappa^3P, Sn, P$ -chloridostannyl ligand similar to that obtained when germanium was used instead of tin,<sup>6,7</sup> because the larger tin atom should push the metal atom sufficiently far away from the P atoms as to hamper an efficient coordination of both phosphane fragments (the CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub> side-arms of the stannyl P<sub>2</sub>SnP ligand seem to be not long enough to allow the coordination of the Sn and both P atoms to the metal atom). We are currently working on the synthesis of PEP pincer-type heavier tetrylenes

related to **1** but having longer linkers between the N and the P atoms,  $E\{N(CH_2)_nP^tBu_2\}_2C_6H_4$  with  $n > 1$ .

## Conclusions

The reaction of anhydrous  $SnCl_2$  with the dilithium salt of the diamine  $o\text{-}\{N(H)CH_2P^tBu_2\}_2C_6H_4$ , which contains two bulky and very basic phosphane groups hanging from the N atoms, led to the PEP pincer-type stannylene  $Sn(NCH_2P^tBu_2)_2C_6H_4$  (**1**), which is analogous to the known germylene  $Ge(NCH_2P^tBu_2)_2C_6H_4$ .<sup>6</sup> Aiming at the synthesis of the analogous PSiP silylene, the silicon(IV) precursors  $SiCl_2(NCH_2P^tBu_2)_2C_6H_4$  (**2**),  $SiHCl(NCH_2P^tBu_2)_2C_6H_4$  (**3**) and  $SiH(HMDS)(NCH_2P^tBu_2)_2C_6H_4$  (**4**) were also prepared; however, all attempts to reduce them to the silicon(II) derivative were unsuccessful, probably because the bulky  $CH_2P^tBu_2$  side arms prevent the approach of the reducing reagents to the silicon atom.

A theoretical study on PEP tetrylenes of the type  $E(NCH_2P^tBu_2)_2C_6H_4$  ( $E = C, Si, Ge, Sn$ ) has shown that, when  $E = Ge$  and  $Sn$ , the most stable structure (conformation) has the P atoms very close to (almost in) the  $EN_2C_6H_4$  plane, near (interacting with) the E atom, whereas this is not the case for the molecules with  $E = C$  and  $Si$ , in which both phosphane groups are located at one side of the  $EN_2C_6H_4$  plane and far away from the E atom. The size of the E atom and the strength of stabilizing (NBO-characterized) donor–acceptor interactions between the lone pairs of the P atoms and empty antibonding  $\sigma^*(E-N)$  orbitals (both increase on going down in group 14) are key factors that determine the molecular structures.

Comparing the results obtained from reactions of stannylene **1** with a variety of transition metal complexes (complexes **5–7** are the result of some of these reactions) with the outcomes of similar (previously reported) reactions using the analogous germylene  $Ge(NCH_2P^tBu_2)_2C_6H_4$ , it can be concluded that (similarly to the germylene) stannylene **1** has a great tendency to get inserted into M–Cl bonds, to give a chloridostannyl ligand that (in contrast with the corresponding chloridogermyl group, which frequently displays a  $PGeP$  pincer-type  $\kappa^3P,Ge,P$ -coordination to the metal atoms) prefers a chelating  $\kappa^2Sn,P$ -coordination mode, maintaining an uncoordinated phosphane fragment. The short length of the  $CH_2P^tBu_2$  side arms and the fact that tin is larger than germanium are claimed as responsible for the different reactivity observed for the germanium and tin tetrylenes.

XRD data (of **6**),  $^{31}P\{^1H\}$  NMR data (of **5–7**) and DFT calculations (on **6**) are consistent with the existence of a weak  $P\cdots Sn$  interaction involving the non-coordinated P atom of complexes **5–7**, similar to that found in compound **1**.

## Experimental section

**General data.** Solvents were dried by refluxing them over sodium diphenyl ketyl in an argon atmosphere and were distilled under argon immediately before use. The reactions were carried out under argon in an MBraun glovebox or using Schlenk-vacuum line techniques. A published procedure was followed to prepare *o*-{N(H)CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.<sup>16</sup> All remaining reagents were purchased from commercial suppliers. All reaction products were vacuum-dried for several hours prior to being weighted and analyzed. NMR spectra were run in benzene-*d*<sub>6</sub> on Bruker AC-300 and AV-400 instruments and were referenced using the residual protic solvent signal for <sup>1</sup>H (7.16 ppm for *d*<sub>6</sub>-benzene; 5.32 ppm for *d*<sub>2</sub>-dichloromethane), the solvent signal for <sup>13</sup>C (128.1 ppm for *d*<sub>6</sub>-benzene; 53.8 ppm for *d*<sub>2</sub>-dichloromethane), external 85% aqueous H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P (0 ppm), external SnMe<sub>4</sub> in CDCl<sub>3</sub> for <sup>119</sup>Sn (0 ppm) and external SiMe<sub>4</sub> in CDCl<sub>3</sub> for <sup>29</sup>Si (0 ppm). Other analytical instrumentation was as previously reported.<sup>34</sup> The given electrospray ionization (ESI) low resolution mass spectra (LRMS) data refer to the most abundant isotopomer of the species with the greatest mass.

**Sn(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (1).** <sup>n</sup>BuLi (3.8 mL, 6.1 mmol, 1.6 M in hexanes) was added to a solution of *o*-{N(H)CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (1.27 g, 3.0 mmol) in diethylether (20 mL) at -78 °C. The resulting grey suspension was allowed to reach the room temperature. After stirring for 2 h, anhydrous SnCl<sub>2</sub> was added (568 mg, 3.0 mmol). The resulting dark brown suspension was stirred for 18 h. The solvent was evaporated under reduced pressure, the residue was washed with hexanes (20 mL) and the insoluble solid was extracted into toluene (2 x 15 mL). A white solid (LiCl) was separated by decantation and the clear solution was evaporated to dryness to give **1** as an orange solid (1.44 g, 88 %). Anal. (%) calcd. for C<sub>24</sub>H<sub>44</sub>N<sub>2</sub>P<sub>2</sub>Sn (*M* = 541.28): C, 53.26; H, 8.19; N, 5.18; found: C, 53.32; H, 8.29; N, 5.11. (+)-ESI LRMS: No spectrum was obtained. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.1 MHz, 293 K): δ 7.30–7.23 (m, 4 H, 4 CH of C<sub>6</sub>H<sub>4</sub>), 4.30 (s, 4 H, 4 CH of 2 PCH<sub>2</sub>), 1.09 (d, *J*<sub>H-P</sub> = 12.0 Hz, 36 H, 12 CH<sub>3</sub> of 4 <sup>t</sup>Bu) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 293 K): δ 150.0 (s, 2 C of C<sub>6</sub>H<sub>4</sub>), 117.7 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 109.2 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 44.3 (s, 2 CH<sub>2</sub> of 2 PCH<sub>2</sub>), 33.0–32.7 (m, 4 C of 4 <sup>t</sup>Bu), 29.8 (m, 12 CH<sub>3</sub> of 4 <sup>t</sup>Bu) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162.0 MHz, 293 K): δ 34.0 (s, sat, *J*<sub>P-117Sn</sub> = 614 Hz, *J*<sub>P-119Sn</sub> = 647 Hz) ppm. <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 149.2 MHz, 293 K): δ 246.3 (t, *J*<sub>119Sn-P</sub> = 647 Hz).

**SiCl<sub>2</sub>(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (2).** <sup>n</sup>BuLi (1.5 mL, 2.4 mmol, 1.6 M in hexanes) was added to a solution of *o*-{N(H)CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (485 mg, 1.1 mmol) in diethylether (20 mL) at -78 °C. The resulting grey suspension was allowed to reach the room temperature. After stirring for 2 h, SiCl<sub>4</sub> (0.13 mL, 1.1 mmol) was added and the resulting yellow-orange suspension was stirred for 18 h. The solvent was evaporated under reduced pressure and the residue was extracted with hexanes (3 x 10 mL). The filtered solution was evaporated to dryness to give **2** as a pale yellow solid (290 mg, 49 %). Anal. (%) calcd. for C<sub>24</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Si (*M* = 521.56): C, 55.27; H, 8.50; N, 5.37; found: C, 55.40; H, 8.56; N, 5.30. (+)-ESI LRMS: *m/z* = 475.26; calcd. for [*M* - 2 Cl + 2 H + Na]<sup>+</sup> (C<sub>24</sub>H<sub>46</sub>N<sub>2</sub>NaP<sub>2</sub>Si): 475.28. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.1 MHz, 293 K): δ 6.96 (s, 4 H, 4 CH of C<sub>6</sub>H<sub>4</sub>), 3.51 (s, 4 H, 4 CH of 2 PCH<sub>2</sub>), 1.11 (d, <sup>3</sup>*J*<sub>H-P</sub> = 11.9 Hz, 36 H, 12 CH<sub>3</sub> of 4 <sup>t</sup>Bu) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 293

K):  $\delta$  138.2 (s, C of C<sub>6</sub>H<sub>4</sub>), 138.1 (s, C of C<sub>6</sub>H<sub>4</sub>), 119.0 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 109.1 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 37.6 (d,  $J_{C-P}$  = 18.1 Hz, 2 CH<sub>2</sub> of 2 PCH<sub>2</sub>), 31.8 (d,  $J_{C-P}$  = 22.1 Hz, 4 C of 4 <sup>t</sup>Bu), 29.4 (d,  $J_{C-P}$  = 13.1 Hz, 12 CH<sub>3</sub> of 4 <sup>t</sup>Bu) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 293 K):  $\delta$  14.4 (s) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 79.6 MHz, 293 K):  $\delta$  -29.2 (s, br) ppm.

**SiHCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (3).** <sup>n</sup>BuLi (6.5 mL, 10.4 mmol, 1.6 M in hexanes) was added to a solution of *o*-{N(H)CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (2.20 g, 5.2 mmol) in diethylether (30 mL) at -78 °C. The resulting grey suspension was allowed to reach the room temperature and was stirred further for 2 h. Then, HSiCl<sub>3</sub> (0.55 mL, 5.2 mmol) was added and the resulting light orange suspension was stirred for 18 h. The solvent was evaporated under reduced pressure and the residue was extracted into hexanes (2 x 20 mL). The filtrate was vacuum-dried to give **3** as a white solid (1.82 g, 72 %). Anal. (%) calcd. for C<sub>24</sub>H<sub>45</sub>ClN<sub>2</sub>P<sub>2</sub>Si ( $M$  = 487.11): C, 59.18; H, 9.31; N, 5.75; found: C, 59.31; H, 9.36; N, 5.69. (+)-ESI LRMS:  $m/z$  = 435.30; calcd. for [ $M$  - Cl - Me - H]<sup>+</sup> (C<sub>23</sub>H<sub>41</sub>N<sub>2</sub>P<sub>2</sub>Si): 435.25. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.1 MHz, 293 K):  $\delta$  7.32 (t,  $J_{H-P}$  = 9.7 Hz), 7.03–7.01 (m, 2 H, 2 CH of C<sub>6</sub>H<sub>4</sub>), 6.84–6.82 (m, 2 H, 2 CH of C<sub>6</sub>H<sub>4</sub>), 3.56 (dd,  $J_{H-H}$  = 13.5 Hz,  $J_{H-P}$  = 3.1 Hz, 2 H, 2 CH of PCH<sub>2</sub>), 3.31 (m, 2 H, 2 CH of PCH<sub>2</sub>), 1.09 (d,  $J_{H-P}$  = 11.4 Hz, 18 H, 6 CH<sub>3</sub> of 2 <sup>t</sup>Bu), 1.04 (d,  $J_{H-P}$  = 11.0 Hz, 18 H, 6 CH<sub>3</sub> of 2 <sup>t</sup>Bu) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 293 K):  $\delta$  139.9 (s, C of C<sub>6</sub>H<sub>4</sub>), 139.8 (s, C of C<sub>6</sub>H<sub>4</sub>), 119.0 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 108.7 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 37.7 (d,  $J_{C-P}$  = 12.1 Hz, 2 CH<sub>2</sub> of 2 PCH<sub>2</sub>), 32.4 (d,  $J_{C-P}$  = 22.1 Hz, 2 C of 2 <sup>t</sup>Bu), 31.9 (d,  $J_{C-P}$  = 18.1 Hz, 2 C of 2 <sup>t</sup>Bu), 29.6 (m, 12 CH<sub>3</sub> of 4 <sup>t</sup>Bu) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162.0 MHz, 293 K):  $\delta$  18.0 (s) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 79.6 MHz, 293 K):  $\delta$  -30.7 (t,  $J_{Si-P}$  = 11.3 Hz) ppm.

**SiH(HMDS)(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (4).** *Method A:* KHMDs (2.0 mL, 1.0 mmol, 0.5 M in toluene) was added to a solution of SiHCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (487 mg, 1.0 mmol) in toluene (4 mL) at room temperature. The resulting orange suspension was stirred at room temperature for 18 h. Solvents were evaporated under reduced pressure and the residue was extracted into hexanes (2 x 10 mL). The filtrate was vacuum-dried to give **4** as a yellow solid (526 mg, 86 %). *Method B:* LiHMDS (1.0 mL, 1.0 mmol, 1.0 M in hexanes) was added to a solution of SiHCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (487 mg, 1.0 mmol) in toluene (4 mL) at room temperature. The resulting yellow suspension was stirred at 100 °C for 18 h. The solvent was evaporated under reduced pressure and the residue was extracted into hexanes (2 x 10 mL). The filtrate was vacuum-dried to give **4** as a yellow solid (451 mg, 74 %). Anal. (%) calcd. for C<sub>30</sub>H<sub>63</sub>N<sub>3</sub>P<sub>2</sub>Si<sub>3</sub> ( $M$  = 612.05): C, 58.87; H, 10.38; N, 6.87; found: C, 59.10; H, 10.44; N, 6.67. (+)-ESI LRMS:  $m/z$  = 466.29; calcd. for [ $M$  - 2 SiMe<sub>3</sub> + H]<sup>+</sup> (C<sub>24</sub>H<sub>46</sub>N<sub>3</sub>P<sub>2</sub>Si): 466.29. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.1 MHz, 293 K):  $\delta$  7.01–6.93 (m, 4 H, 4 CH of C<sub>6</sub>H<sub>4</sub>), 6.52 (t,  $J_{H-P}$  = 6.2 Hz, 1 H, SiH), 3.75 (d,  $J_{H-H}$  = 13.9 Hz, 2 H, 2 CH of 2 PCH<sub>2</sub>), 3.42 (dd,  $J_{H-H}$  = 13.9 Hz,  $J_{H-P}$  = 4.8 Hz, 2 H, 2 CH of 2 PCH<sub>2</sub>), 1.16 (d,  $J_{H-P}$  = 10.8 Hz, 18 H, 6 CH<sub>3</sub> of 2 <sup>t</sup>Bu), 1.10 (d,  $J_{H-P}$  = 10.5 Hz, 18 H, 6 CH<sub>3</sub> of 2 <sup>t</sup>Bu), 0.62 (s, 9 H, 3 CH<sub>3</sub> of HMDS), 0.06 (s, 9 H, 3 CH<sub>3</sub> of HMDS) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 293 K):  $\delta$  140.3 (s, 2 C of C<sub>6</sub>H<sub>4</sub>), 118.1 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 108.2 (s, 2 CH of C<sub>6</sub>H<sub>4</sub>), 38.3 (d,  $J_{C-P}$  = 18.1 Hz, 2 CH<sub>2</sub> of 2 PCH<sub>2</sub>), 32.5 (d,  $J_{C-P}$  = 24.1 Hz, 2 C of 2 <sup>t</sup>Bu), 31.5 (d,  $J_{C-P}$  = 21.1 Hz,

2 C of 2 <sup>t</sup>Bu), 30.1 (d,  $J_{C-P} = 11.1$  Hz, 6 CH<sub>3</sub> of 2 <sup>t</sup>Bu), 29.9 (d,  $J_{C-P} = 11.1$  Hz, 6 CH<sub>3</sub> of 2 <sup>t</sup>Bu), 5.5 (s, 3 CH<sub>3</sub> of HMDS), 3.8 (s, 3 CH<sub>3</sub> of HMDS) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 293 K): δ 12.7 (s) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 79.6 MHz, 293 K): δ 4.6 (s, HMDS), 3.0 (s, HMDS), -34.1 (t,  $J_{Si-P} = 6.9$  Hz) ppm.

**[Rh{κ<sup>2</sup>Sn,P-SnCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(η<sup>4</sup>-cod)] (5).** Toluene (3 mL) was added to a mixture of Sn(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (54 mg, 0.10 mmol) and [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(η<sup>4</sup>-cod)<sub>2</sub>] (24 mg, 0.05 mmol). The initial orange color changed rapidly to dark red. After stirring at room temperature for 18 h, the solution was vacuum-dried to give **5** as a dark red solid (38 mg, 46 %). Anal. (%) Calcd. for C<sub>32</sub>H<sub>56</sub>ClN<sub>2</sub>P<sub>2</sub>RhSn ( $M = 787.82$ ): C, 48.79; H, 7.16; N, 3.56; found: C, 46.84; H, 6.94; N, 3.34. (+)-ESI LRMS: No spectrum was obtained. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.1 MHz, 293 K): δ 7.14–6.98 (m, 2 H, 2 CH of C<sub>6</sub>H<sub>4</sub>), 6.94–6.80 (m, 2 H, 2 CH of C<sub>6</sub>H<sub>4</sub>), 6.12–5.10 (m, br, 4 H, 4 CH of cod), 3.83–3.61 (m, 3 H, 3 CH of 2 PCH<sub>2</sub>), 2.92 (dd,  $J_{H-H} = 11.6$  Hz,  $J_{H-P} = 9.3$  Hz, 1 H, 1 CH of PCH<sub>2</sub>), 2.41–2.15 (m, br, 1 H of CH<sub>2</sub> of cod), 2.10–1.84 (m, br, 4 H of CH<sub>2</sub> of cod), 1.74–1.60 (m, br, 3 H of CH<sub>2</sub> of cod), 1.36–1.23 (m, 9 H, 3 CH<sub>3</sub> of <sup>t</sup>Bu), 1.17–1.04 (m, 9 H, 3 CH<sub>3</sub> of <sup>t</sup>Bu), 1.05–0.83 (m, 18 H, 6 CH<sub>3</sub> of <sup>t</sup>Bu) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 293 K): δ 144.6 (d,  $J_{C-P} = 20.0$  Hz, C of C<sub>6</sub>H<sub>4</sub>), 144.2 (d,  $J_{C-P} = 13.0$  Hz, C of C<sub>6</sub>H<sub>4</sub>), 116.5 (s, CH of C<sub>6</sub>H<sub>4</sub>), 115.5 (s, CH of C<sub>6</sub>H<sub>4</sub>), 109.5 (s, CH of C<sub>6</sub>H<sub>4</sub>), 108.4 (s, CH of C<sub>6</sub>H<sub>4</sub>), 91.1 (m, CH of cod), 87.4 (m, 2 CH of cod), 85.4 (m, CH of cod), 39.8 (d,  $J_{C-P} = 8.0$  Hz, CH<sub>2</sub> of PCH<sub>2</sub>), 39.3 (d,  $J_{C-P} = 8.0$  Hz, C of <sup>t</sup>Bu), 35.6 (d,  $J_{C-P} = 8.0$  Hz, C of <sup>t</sup>Bu), 35.0 (d,  $J_{C-P} = 30.0$  Hz, CH<sub>2</sub> of PCH<sub>2</sub>), 33.3–32.8 (m, 2 C of 2 <sup>t</sup>Bu), 31.5–29.3 (m, 4 CH<sub>2</sub> of cod + 12 CH<sub>3</sub> of 4 <sup>t</sup>Bu) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.4 MHz, 293 K): δ 86.1 (d, sat,  $J_{P-Rh} = 141$  Hz,  $J_{P-Sn} = 222$  Hz), 64.1 (s, sat,  $J_{P-Sn} = 523$  Hz) ppm.

**[RuCl{κ<sup>2</sup>Sn,P-SnCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(η<sup>6</sup>-cym)] (6).** Toluene (3 mL) was added to a mixture of Sn(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (49 mg, 0.090 mmol) and [Ru<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>2</sub>(η<sup>6</sup>-cym)<sub>2</sub>] (28 mg, 0.045 mmol). The initial orange suspension changed rapidly to dark brown. After stirring at room temperature for 1 h, the solvent was removed under reduced pressure and the solid residue was washed with hexane (3 x 2 mL) and vacuum-dried to give **6** as a dark brown solid (60 mg, 79 %). Anal. (%) Calcd. for C<sub>34</sub>H<sub>58</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>RuSn ( $M = 847.47$ ): C, 48.19; H, 6.90; N, 3.31; found: C, 48.25; H, 6.95; N, 3.28. (+)-ESI LRMS:  $m/z = 845.19$ ; calcd. for  $[M - Cl + MeOH]^+$  (C<sub>35</sub>H<sub>62</sub>ClN<sub>2</sub>P<sub>2</sub>RuSn): 845.21. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.1 MHz, 293 K): δ 7.11–6.97 (m, 2 H, 2 CH of C<sub>6</sub>H<sub>4</sub>), 6.95–6.82 (m, 2 H, 2 CH of C<sub>6</sub>H<sub>4</sub>), 6.21 (d,  $J_{H-H} = 5.9$  Hz, CH of cym), 5.72 (d,  $J_{H-H} = 5.9$  Hz, CH of cym), 5.03 (d,  $J_{H-H} = 5.9$  Hz, CH of cym), 4.71 (d,  $J_{H-H} = 5.9$  Hz, CH of cym), 4.00–3.76 (m, 2 H, 2 CH of 2 PCH<sub>2</sub>), 3.62 (dd,  $J_{H-H} = 11.6$  Hz,  $J_{H-P} = 7.2$  Hz, CH of PCH<sub>2</sub>), 2.93 (dd,  $J_{H-H} = 11.6$  Hz,  $J_{H-P} = 4.7$  Hz, CH of PCH<sub>2</sub>), 2.77 (sept,  $J_{H-H} = 6.9$  Hz, CH of <sup>i</sup>Pr), 1.94 (s, 3 H of CH<sub>3</sub> of cym), 1.42 (d,  $J_{H-P} = 11.3$  Hz, 9 H, 3 CH<sub>3</sub> of <sup>t</sup>Bu), 1.26–1.05 (m, 33 H, 11 CH<sub>3</sub> of <sup>t</sup>Bu and <sup>i</sup>Pr) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 293 K): δ 146.6 (d,  $J_{C-P} = 15.7$  Hz, C of C<sub>6</sub>H<sub>4</sub>), 145.5 (d,  $J_{C-P} = 17.5$  Hz, C of C<sub>6</sub>H<sub>4</sub>), 118.0 (s, C of cym), 116.6 (s, CH of C<sub>6</sub>H<sub>4</sub>), 115.9 (s, CH of C<sub>6</sub>H<sub>4</sub>), 111.5 (s, CH of C<sub>6</sub>H<sub>4</sub>), 107.2 (s, CH of C<sub>6</sub>H<sub>4</sub>), 92.4 (s, C of

cym), 92.1 (t,  $J_{C-P} = 5.1$  Hz, CH of cym), 85.1–84.5 (m, 2 CH of cym), 83.7 (d,  $J_{C-P} = 7.6$  Hz, CH of cym), 40.0 (d,  $J_{C-P} = 5.4$  Hz, CH<sub>2</sub> of PCH<sub>2</sub>), 39.8 (d,  $J_{C-P} = 14.2$  Hz, C of <sup>t</sup>Bu), 39.0 (d,  $J_{C-P} = 15.6$  Hz, C of <sup>t</sup>Bu), 36.6 (d,  $J_{C-P} = 32.8$  Hz, CH<sub>2</sub> of PCH<sub>2</sub>), 33.4 (d,  $J_{C-P} = 16.4$  Hz, C of <sup>t</sup>Bu), 32.5 (d,  $J_{C-P} = 18.7$  Hz, C of <sup>t</sup>Bu), 32.3–30.3 (m, 6 CH<sub>3</sub> of <sup>t</sup>Bu and CH of <sup>i</sup>Pr), 22.8 (s, CH<sub>3</sub> of <sup>i</sup>Pr), 22.0 (s, CH<sub>3</sub> of <sup>i</sup>Pr), 18.5 (s, CH<sub>3</sub> of cym) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 293 K): δ 99.5 (s, sat,  $J_{P-Sn} = 443$  Hz) ppm, 65.0 (s, sat,  $J_{P-Sn} = 494$  Hz) ppm.

**[IrCl{κ<sup>2</sup>Sn,P-SnCl(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}(η<sup>5</sup>-Cp\*)] (7).** Toluene (3 mL) was added to a mixture of Sn(NCH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (49 mg, 0.090 mmol) and [Ir<sub>2</sub>Cl<sub>2</sub>(μ-Cl)<sub>2</sub>(η<sup>5</sup>-Cp\*)<sub>2</sub>] (36 mg, 0.045 mmol). The resulting dark purple suspension was stirred at room temperature for 1 h. The liquid phase was decanted off and the solid was washed with toluene (3 x 2 mL) and vacuum-dried to give **7** as a purple solid (64 mg, 76 %). Anal. (%) Calcd. for C<sub>34</sub>H<sub>59</sub>Cl<sub>2</sub>N<sub>2</sub>IrP<sub>2</sub>Sn ( $M = 939.63$ ): C, 43.46; H, 6.33; N, 2.98; found: C, 43.52; H, 6.51; N, 2.85. (+)-ESI LRMS:  $m/z = 971.22$ ; calcd. for  $[M + MeOH - H]^+$  (C<sub>35</sub>H<sub>62</sub>Cl<sub>2</sub>N<sub>2</sub>IrOP<sub>2</sub>Sn): 971.24. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz, 293 K): δ 6.66–6.40 (m, 4 H, 4 CH of C<sub>6</sub>H<sub>4</sub>), 3.80 (dd,  $J_{H-H} = 12.8$  Hz,  $J_{H-P} = 9.9$  Hz, CH of PCH<sub>2</sub>), 3.49–3.38 (m, 2 H, 2 CH of PCH<sub>2</sub>), 2.89 (dd,  $J_{H-H} = 12.8$  Hz,  $J_{H-P} = 5.4$  Hz, CH of PCH<sub>2</sub>), 1.98 (m, 15 H, 5 CH<sub>3</sub> of Cp\*), 1.49–1.26 (m, 27 H, 9 CH<sub>3</sub> of <sup>t</sup>Bu), 1.16 (d,  $J_{H-P} = 10.9$  Hz, 9 H, 3 CH<sub>3</sub> of <sup>t</sup>Bu) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100.6 MHz, 293 K): δ 145.4 (d,  $J_{C-P} = 16.6$  Hz, C of C<sub>6</sub>H<sub>4</sub>), 145.6 (d,  $J_{C-P} = 14.2$  Hz, C of C<sub>6</sub>H<sub>4</sub>), 115.8 (s, CH of C<sub>6</sub>H<sub>4</sub>), 115.4 (s, CH of C<sub>6</sub>H<sub>4</sub>), 111.6 (s, CH of C<sub>6</sub>H<sub>4</sub>), 106.8 (s, CH of C<sub>6</sub>H<sub>4</sub>), 94.6 (d,  $J_{C-P} = 1.4$  Hz, C of Cp\*), 41.7 (d,  $J_{C-P} = 21.7$  Hz, C of <sup>t</sup>Bu), 39.4–38.6 (m, CH<sub>2</sub> of PCH<sub>2</sub> and C of <sup>t</sup>Bu), 36.5 (d,  $J_{C-P} = 37.6$  Hz, CH<sub>2</sub> of PCH<sub>2</sub>), 33.7 (d,  $J_{C-P} = 16.4$  Hz, C of <sup>t</sup>Bu), 32.9 (d,  $J_{C-P} = 19.7$  Hz, C of <sup>t</sup>Bu), 31.7 (d,  $J_{C-P} = 3.6$  Hz, 3 CH<sub>3</sub> of <sup>t</sup>Bu), 31.2 (d,  $J_{C-P} = 1.8$  Hz, 3 CH<sub>3</sub> of <sup>t</sup>Bu), 30.7 (d,  $J_{C-P} = 9.6$  Hz, 3 CH<sub>3</sub> of <sup>t</sup>Bu), 30.2 (d,  $J_{C-P} = 9.8$  Hz, 3 CH<sub>3</sub> of <sup>t</sup>Bu), 10.8 (d,  $J_{C-P} = 2.5$  Hz, CH<sub>3</sub> of Cp\*) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162.0 MHz, 293 K): δ 63.2 (s, sat,  $J_{P-Sn} = 259$  Hz), 58.7 (s, sat,  $J_{P-Sn} = 350$  Hz) ppm.

**Computational details.** DFT Calculations were carried out using the wB97XD functional,<sup>35</sup> which includes the second generation of Grimme's dispersion interaction correction<sup>36</sup> as well as long-range interactions effects. This functional reproduces the local coordination geometry of transition metal compounds very well and it also corrects the systematic overestimation of non-bonded distances seen for all the density functionals that do not include estimates of dispersion.<sup>37</sup> The Stuttgart-Dresden relativistic effective core potential and the associated basis sets (SDD) were used for the Sn and Ru atoms.<sup>38</sup> The basis set used for the remaining atoms was the cc-pVDZ.<sup>39</sup> The stationary points were fully optimized in gas phase and confirmed as energy minima (all positive eigenvalues) by analytical calculation of frequencies. The orbital analysis was carried out within the NBO framework.<sup>40</sup> All calculations were carried out with the Gaussian09 package.<sup>41</sup> The atomic coordinates of all the DFT-optimized structures are given in the electronic supplementary information.

**X-Ray diffraction analyses:** Crystals of  $1 \cdot C_7H_8$  and  $6 \cdot (C_7H_8)_{0.5}$  were analyzed by X-ray diffraction. A selection of crystal, measurement and refinement data is given in Table S18. Diffraction data were collected on an Oxford Diffraction Xcalibur Onyx Nova single crystal diffractometer with  $CuK\alpha$  radiation. Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.<sup>42</sup> The structures were solved using SIR-97.<sup>43</sup> Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL.<sup>44</sup> All non-H atoms were refined anisotropically except the C atoms of the toluene solvent of  $6 \cdot (C_7H_8)_{0.5}$ , which were kept isotropic due to their tendency to give nonpositive definite or oblate ellipsoids. All H atoms were set in calculated positions and were refined riding on their parent atoms. The toluene molecules found in the unit cell of  $6 \cdot (C_7H_8)_{0.5}$  were disordered about centres of symmetry and were refined with restraints on their geometrical and thermal parameters. The WINGX program system<sup>45</sup> was used throughout the structure determinations. The molecular plots were made with MERCURY.<sup>46</sup> CCDC deposition numbers: 1588313 ( $1 \cdot C_7H_8$ ) and 1588314 ( $6 \cdot (C_7H_8)_{0.5}$ ).

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## Conflicts of interest

There are no conflicts to declare.

## References and notes

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**Table 1.** Relative energies (kcal/mol) of the DFT-optimized “planar” ( $E_{R-pl}$ ) and “non planar” ( $E_{R-npl}$ ) conformers of compounds  $E(NCH_2PR_2)_2C_6H_4$  ( $E = C, Si, Ge, Sn$ ;  $R = tBu, Me$ ).

E	Conformer (R = $tBu$ )	Energy <sup>a</sup>	Conformer (R = Me)	Energy <sup>a</sup>
C	<b>C<sub>tBu-pl</sub></b>	7.63	<b>C<sub>Me-pl</sub></b>	1.37
	<b>C<sub>tBu-npl</sub></b>	0.00	<b>C<sub>Me-npl</sub></b>	0.00
Si	<b>Si<sub>tBu-pl</sub></b>	1.73	<b>Si<sub>Me-pl</sub></b>	3.55
	<b>Si<sub>tBu-npl</sub></b>	0.00	<b>Si<sub>Me-npl</sub></b>	0.00
Ge	<b>Ge<sub>tBu-pl</sub></b>	0.00	<b>Ge<sub>Me-pl</sub></b>	2.85
	<b>Ge<sub>tBu-npl</sub></b>	0.48	<b>Ge<sub>Me-npl</sub></b>	0.00
Sn	<b>Sn<sub>tBu-pl</sub></b>	0.00	<b>Sn<sub>Me-pl</sub></b>	0.28
	<b>Sn<sub>tBu-npl</sub></b>	5.00	<b>Sn<sub>Me-npl</sub></b>	0.00

<sup>a</sup> An energy of 0.00 kcal/mol is assigned to the most stable conformer of each pair.

**Table 2.** NBO second order perturbation analysis of weak P–E donor–acceptor interactions in the “planar” conformers of compounds  $E(NCH_2P^tBu_2)_2C_6H_4$  ( $E = C, Si, Ge, Sn$ ).

Conformer	Donor orbital	Acceptor orbital	E (kcal/mol)
<b>C<sub>tBu-pl</sub></b>	Lp(P) (MO112)	$\sigma^*(C-N)$ (MO191)	0.94
	Lp(P') (MO113)	$\sigma^*(C-N)$ (MO192)	0.94
			<u>Total 1.88</u>
<b>Si<sub>tBu-pl</sub></b>	Lp(P) (MO116)	$\sigma^*(Si-N')$ (MO134)	3.40
	Lp(P) (MO116)	$\sigma^*(Si-N)$ (MO135)	2.02
	Lp(P') (MO117)	$\sigma^*(Si-N')$ (MO134)	2.02
	Lp(P') (MO117)	$\sigma^*(Si-N)$ (MO135)	3.40
		<u>Total 10.84</u>	
<b>Ge<sub>tBu-pl</sub></b>	Lp(P') (MO126)	$\sigma^*(Ge-N)$ (MO137)	4.37
	Lp(P') (MO126)	$\sigma^*(Ge-N')$ (MO138)	2.43
	Lp(P) (MO127)	$\sigma^*(Ge-N)$ (MO137)	2.43
	Lp(P) (MO127)	$\sigma^*(Ge-N')$ (MO138)	4.37
		<u>Total 13.60</u>	
<b>Sn<sub>tBu-pl</sub></b>	Lp(P') (MO121)	$\sigma^*(Sn-N)$ (MO133)	5.82
	Lp(P') (MO121)	$\sigma^*(Sn-N')$ (MO134)	4.85
	Lp(P) (MO122)	$\sigma^*(Sn-N)$ (MO133)	4.83
	Lp(P) (MO122)	$\sigma^*(Sn-N')$ (MO134)	5.84
		<u>Total 21.34</u>	

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The title stannylene presents intramolecular P···Sn interactions and is prone to get inserted into M–Cl bonds to give a  $\kappa^2$ -Sn,P-coordinated chloridostannyl ligand.

