

## Reversible Activation

## Reversible Activation and Transfer of White Phosphorus by Silyl-Stannylene

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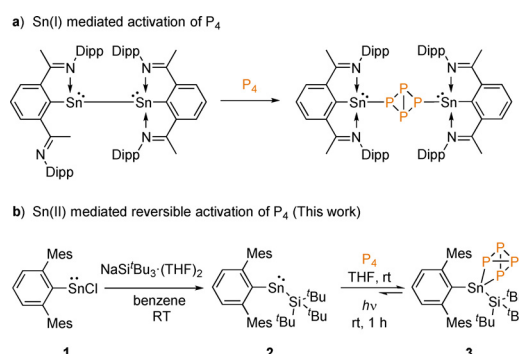
Dedicated to Professor Manfred Scheer on the occasion of his 65th birthday

**Abstract:** Use of a silyl supported stannylene ( $^{Mes}TerSn(Si^tBu_3)$  [ $^{Mes}Ter = 2,6-(2,4,6-Me_3C_6H_2)_2C_6H_3$ ]) enables activation of white phosphorus under mild conditions, which is reversible under UV light. The reaction of a silylene chloride with the activated  $P_4$  complex results in facile P-atom transfer. The computational analysis rationalizes the electronic features and high reactivity of the heteroleptic silyl-substituted stannylene in contrast to the previously reported bis(aryl)stannylene.

Organophosphorus compounds offer unique structural and electronic properties and therefore have gained considerable attention in the past decades.<sup>[1]</sup> Their synthesis classically involves the energy intensive and hazardous chlorination of white phosphorus ( $P_4$ ).<sup>[1d,e]</sup> As an alternative, the activation of  $P_4$  under mild conditions and subsequent transformation to organic molecules presents an attractive approach towards  $P_4$  utilization.<sup>[1a-c,e,f]</sup> To date, a plethora of examples for transition metal mediated  $P_4$  activation has been achieved.<sup>[1b,e]</sup> Very recently, in an elegant study Wolf and co-workers demonstrated the photocatalytic transformation of  $P_4$  to aryl phosphines and phosphonium salts by use of an iridium catalyst.<sup>[2]</sup> In contrast to transition metals, activation of  $P_4$  with main group elements is limited to only a handful of

examples,<sup>[1a,c,f,3]</sup> and catalytic utilization of  $P_4$  with main group compounds remains so far elusive.

Recently, low valent heavier group 14 carbene homologues, namely tetrylenes ( $[R_2E:] E = Si, Ge$ ), which are in the + II oxidation state, have given new impetus to the field of  $P_4$  activation.<sup>[4]</sup> Examples of both silylenes<sup>[4a,c,d,f,5]</sup> and germynes have been reported to activate  $P_4$ .<sup>[4b]</sup> Notably, a diaryl germylene [ $^{Mes}Ter_2Ge:$ ], ( $^{Mes}Ter = 2,6-(2,4,6-Me_3C_6H_2)_2C_6H_3$ ) provided the first main group mediated reversible activation of the P–P bond in  $P_4$ .<sup>[4b]</sup> This is an important discovery, as reversibility is a key step towards main group mediated catalysis.<sup>[6]</sup> To the best of our knowledge, there is only one example of a dimeric, low-valent  $Sn^I$  complex for the controlled activation of  $P_4$  (Scheme 1a), whereas such reactivity is unknown for the heavier tetrylene analog, stannylene [ $R_2Sn$ ].<sup>[7]</sup>



**Scheme 1.** Activation of  $P_4$  with low-valent tin complexes (Dipp = 2,6- $^iPr_2C_6H_3$ , Mes = 2,4,6- $Me_3C_6H_2$ ).

Stannylenes present themselves as ideal candidates for bond activation and catalysis, due to the increased stability of the + II oxidation state compared to the lighter group 14 tetrylenes.<sup>[8]</sup> It has previously been shown that the  $Sn^{II}$ - $Sn^{IV}$  redox couple can be manipulated by use of strongly  $\sigma$ -donating boryl ligands to enable dihydrogen activation.<sup>[8c]</sup> Therefore, we postulated that use of electropositive silyl groups, which have been widely employed as stabilizing ligands in low valent main group chemistry,<sup>[9]</sup> may enable the activation of strong bonds.

Our study began with the targeted isolation of the sterically demanding homoleptic bis(silyl)stannylene [ $(Si^tBu_3)_2Sn$ ]. However, various attempts to isolate [ $(Si^tBu_3)_2Sn$ ] was unsuccessful in our hands. Thus, our attention turned to the synthesis of a heteroleptic silyl

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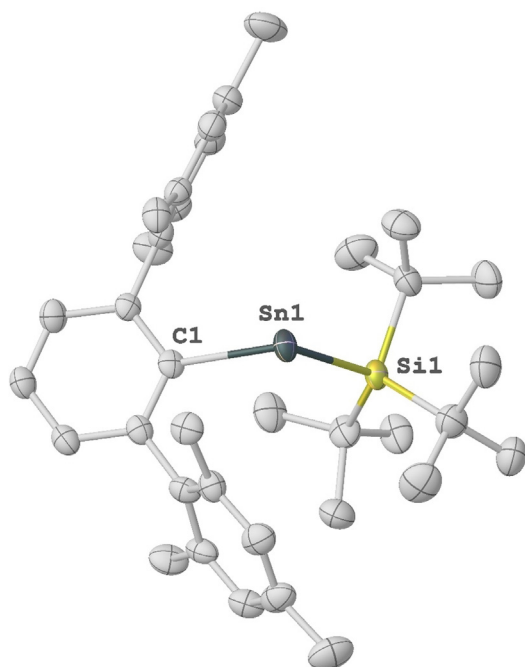
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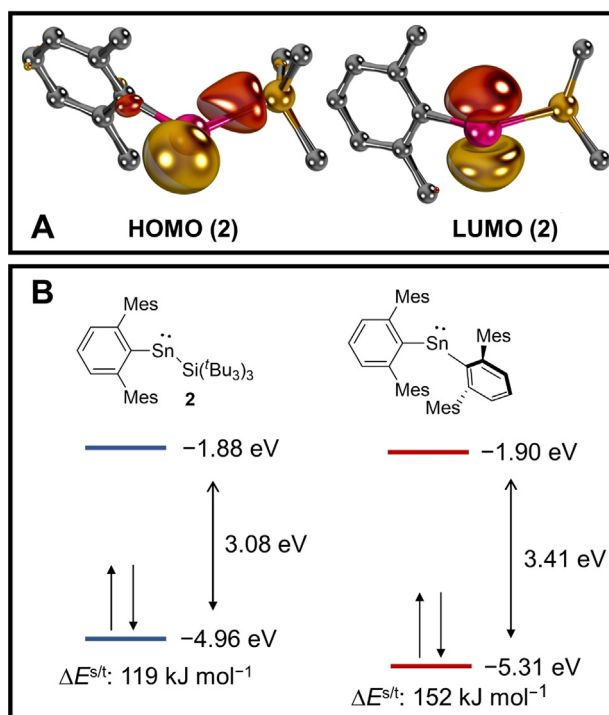
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substituted stannylene. The heteroleptic silyl stannylene **2** [<sup>Mes</sup>TerSn(Si<sup>t</sup>Bu<sub>3</sub>)] was isolated via treatment of chlorostannylene **1** [<sup>Mes</sup>TerSnCl] with one equivalent of NaSi<sup>t</sup>Bu<sub>3</sub>·(THF)<sub>2</sub>. Compound **2** was isolated in 80 % yield as a dark blue solid (Scheme 1b) and is soluble in polar solvents such as tetrahydrofuran, but poorly soluble in nonpolar organic solvents such as benzene or toluene. The <sup>119</sup>Sn{<sup>1</sup>H} NMR spectrum of compound **2** showed a characteristic signal for the tin center at δ 197 ppm, which is significantly upfield in comparison to **1** (562 ppm) and the bis(aryl)stannylene (<sup>Mes</sup>Ter)<sub>2</sub>Sn (1971 ppm).<sup>[8e,10]</sup> This indicates an electron rich Sn<sup>II</sup> center, which can be attributed to the substituent effect (Si<sup>t</sup>Bu<sub>3</sub> vs. <sup>Mes</sup>Ter). In the <sup>29</sup>Si NMR spectrum a distinct signal was observed at 94.7 ppm for the silicon atom of Si<sup>t</sup>Bu<sub>3</sub>. The calculation of NMR shifts for heavy elements represents a challenge due to spin-orbit coupling effects and limitations of common basis sets/ effective core potentials (ECP).<sup>[11]</sup> Nevertheless, calculations at the PBE0-D3/def2-TZVPP//PBE0-D3/def2-SVP level of theory with the def2-ECP reproduce the order of the <sup>119</sup>Sn NMR shifts (**1**: -170 ppm; **2**: -314 ppm; (<sup>Mes</sup>Ter)<sub>2</sub>Sn: 664 ppm) and hence corroborate a comparably electron rich Sn<sup>II</sup> atom in **1**.

Single crystal X-ray diffraction (SC-XRD) analysis confirmed the identity of compound **2**, with the two-coordinate Sn center bound by one Si<sup>t</sup>Bu<sub>3</sub> and *m*-terphenyl group (Figure 1). The ∠ C1-Sn1-Si1 bond angle in **2** is 113.50(14)° and falls within the range of aryl substituted two-coordinate Sn<sup>II</sup> complexes (96.9–117.6°).<sup>[12]</sup> Notably, two-coordinate stannylenes [R<sub>2</sub>Sn] with broad bond angles (∠ R-Sn-R = 112 to 118°) have been shown to activate a wide range of small molecules.<sup>[8c-e]</sup>



**Figure 1.** Molecular structure of compound **2** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Si1–Sn1 2.6981(17), Sn1–C1 2.217(5), C1–Sn1–Si1 113.50(14).



**Figure 2.** Frontier orbitals of **2** (A), their energies and vertical singlet/triplet gap  $\Delta E^{s/t}$  (B, left) and comparison with <sup>Mes</sup>Ter<sub>2</sub>Sn (B, right) as obtained at the PBE0-D3/def2-TZVPP//PBE0-D3/def2-SVP level of theory.

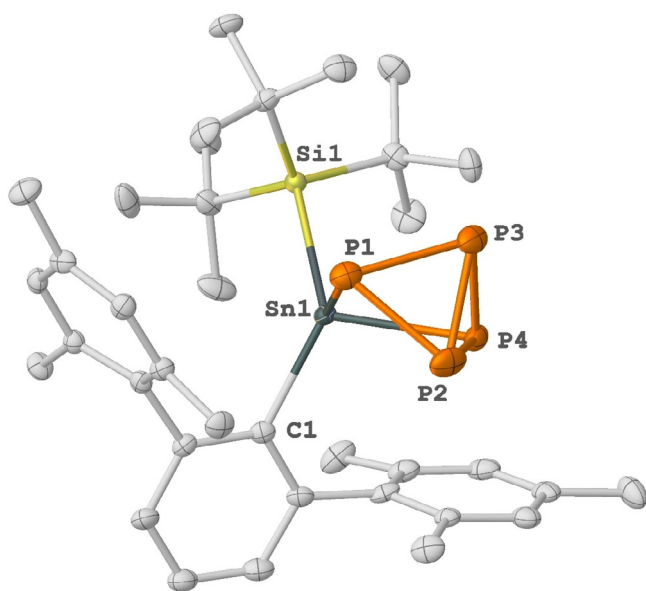
To understand the electronic structure of **2**, we performed a computational analysis. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of **2** (Figure 2A) are centered at the Sn moiety and represent the filled *p<sub>x</sub>*- and empty *p<sub>z</sub>*-orbitals of the tin center. The two frontier orbitals are separated by 3.08 eV ( $\Delta E^{s/t} = 119 \text{ kJ mol}^{-1}$ ; Figure 2B, left), which is considerably smaller than for the reported diaryl stannylene (<sup>Mes</sup>Ter<sub>2</sub>Sn, 3.41 eV;  $\Delta E^{s/t} = 152 \text{ kJ mol}^{-1}$ ; Figure 2B, right) and suggests higher reactivity for the former. Most salient, whilst the energy levels of the LUMOs are essentially equivalent (**2**, -1.88 eV; <sup>Mes</sup>Ter<sub>2</sub>Sn, -1.90 eV), the HOMO of **2**, associated with the *p<sub>x</sub>* orbital and showing overlap with the Si atom, is much higher in energy (**2**, -4.96 eV; <sup>Mes</sup>Ter<sub>2</sub>Sn, -5.31 eV). This corroborates that enhanced  $\sigma$ -donation from the silyl substituent considerably enhances the nucleophilicity of **2** in relation to the bis(aryl)-substituted congener, whereas the electrophilicity of both compounds should be similar.

Encouraged by the computational results, we hypothesized whether compound **2** may activate P<sub>4</sub>. A trial NMR scale reaction of **2** with P<sub>4</sub> at room temperature afforded an immediate color change from blue to blue-green and a yellow solution was obtained within 15 min. Multinuclear NMR analysis confirmed the quantitative conversion of **2** to a tin polyphosphide complex. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum revealed resonances for three distinct <sup>31</sup>P nuclei (X, A and B) at  $\delta_X = 134.3$ ,  $\delta_A = -211.9$  and  $\delta_B = -278.2$  ppm. Interestingly, the downfield resonance signal  $\delta_X$  is split into a doublet of doublets (<sup>1</sup>J(P<sub>X</sub>,P<sub>A</sub>) = 159.0, <sup>1</sup>J(P<sub>X</sub>,P<sub>B</sub>) = 154.8 Hz) while each of the two up-field signals show a doublet of triplets (<sup>1</sup>J-

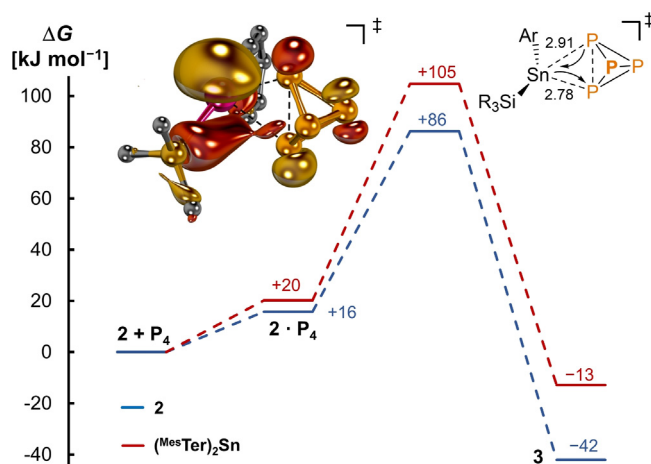
( $P_X, P_A$ ) = 159.0,  $^1J(P_A, P_B)$  = 160.7 Hz), indicating an  $ABX_2$  type splitting pattern. This observation is in line with the isovalent  $[LSiP_4, L = \beta\text{-diketiminate}]$  complex reported by Driess and co-workers.<sup>[4a]</sup> The  $^{119}\text{Sn}$  spectrum of **3** exhibits a triplet resonance at  $\delta = 26.3$  ppm ( $^1J_{\text{Sn-P}} = 323.8$  Hz), which is upfield compared to **1** and falls in the range of known tin polyphosphide complexes ( $\delta = +130.4$  to  $-1540.0$  ppm).<sup>[13]</sup> Notably, tin polyphosphide complexes are typically generated by salt metathesis reactions with the metal polyphosphide and stannylene.<sup>[13a-c,14]</sup> Based on these observations, compound **3** is proposed to contain a coordinated  $P_4$  unit at the Sn center. Repetition of this reaction on a preparative scale enabled the isolation of compound **3** [ $^{\text{Mes}}\text{TerSn}(P_4)\text{Si}^t\text{Bu}_3$ ] as a yellow solid in 91% yield. Thus, facile access to a tin polyphosphide, directly from  $P_4$ , presents an attractive route in  $P_4$  utilization.

SC-XRD of **3** confirmed the coordination of  $^{\text{Mes}}\text{TerSn}(Si^tBu_3)$  across the  $P_4$  unit yielding a tetrahedral tin center with a tricyclic  $\text{SnP}_4$  core (Figure 2). Notably, regioselective activation of  $P_4$  at main group centers is rare.<sup>[1a,c]</sup> Compound **3** is isostructural to the reported  $LSiP_4$  and  $(m\text{-Ter})_2\text{GeP}_4$  complexes (Figure 3).<sup>[4a,b]</sup> In **3**, two Sn-P bond lengths are almost identical (Sn1-P1 2.5714(7) and Sn1-P4 2.5767(7) Å) and fall within the range of Sn-P single bonds.<sup>[13b,c,14]</sup> The exterior P-P bond length of the tetrahedron is P3-P2 2.1638(10) Å, which is slightly shorter than the P-P bond length adjacent to the Sn center (P4-P2 2.2282(9) to P4-P3 2.2158(10) and P2-P1 2.2341(10) Å). Interestingly, in compound **3** the C1-Sn1-Si1 bond angle ( $124.77(5)^\circ$ ) is wider than in **2** ( $113.50(14)^\circ$ ).

Further calculations at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP level of theory with consideration of solvation effects (SMD) shed further light on both the



**Figure 3.** Molecular structures of compound **3** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [ $^\circ$ ]: Si1–Sn1 2.6960(7), Sn1–C1 2.223(2), Sn1–P1 2.5714(7), Sn1–P4 2.5767(7), P2–P3 2.1638(10), P4–P3 2.2158(10), P4–P2 2.2282(9), P2–P1 2.2341(10), P3–P1 2.2260(10), C1–Sn1–Si1  $124.77(5)$ .

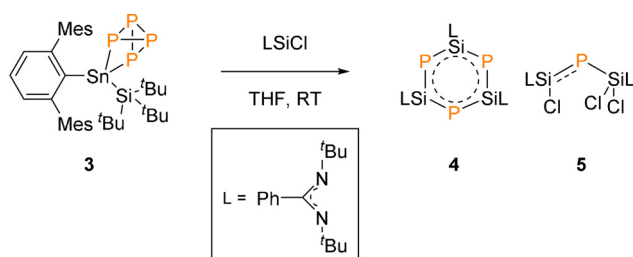


**Figure 4.** Gibbs free energy profile for  $P_4$  activation by  $^{\text{Mes}}\text{TerSn}(Si^tBu_3)$  **2** [blue —] and  $(^{\text{Mes}}\text{Ter})_2\text{Sn}$  [red —] obtained at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP level of theory and bond lengths, given in Å, as well as HOMO of transition state. Mesityl and  $tBu$  substituents as well as hydrogen atoms are omitted for clarity.

kinetics as well as thermodynamics of the conversion of **2** to **3** compared to the bis(aryl)stannylene system (Figure 4). The barrier for the former ( $\Delta G^\ddagger = +86$  kJ mol $^{-1}$ ) was found to be 19 kJ mol $^{-1}$  lower than for the latter ( $\Delta G^\ddagger = +105$  kJ mol $^{-1}$ ). Accordingly, orbital overlap in the asymmetric (Sn-P1: 2.91 Å; Sn-P2: 2.78 Å) transition state further corroborates a dominating nucleophilic interaction in the overall ambiphilic activation step. This highlights the influence of the electropositive silyl group on the  $\text{Sn}^{\text{II}}$  center in enabling the activation of  $P_4$  in contrast to the bis(aryl) system and corroborates our overall design principle.

Interestingly, on storage of a  $[D_8]\text{THF}$  solution of compound **3** under light for one day, it reverted to the blue-green color of compound **2**. Multinuclear NMR analysis ( $^1\text{H}$  and  $^{31}\text{P}$  NMR) suggested the presence of both compounds **3** and **2** in solution, as well as free  $P_4$ . The conversion of **3** to **2** is further facilitated by using a UV light source with a range of (300–400 nm) with the liberation of  $P_4$  observed after 1 h due to the characteristic color change (yellow (**3**) to blue-green (**2**)) and confirmed by multinuclear NMR ( $^{31}\text{P}$  and  $^1\text{H}$ ). Indeed, time-dependent DFT (TD-DFT) calculations corroborate that the transitions to the  $S_2$  state ( $f^{\text{osc}} = 0.11$ ), experimentally observed at 351 nm (Figure S12), relates to a transition from an essentially Sn- $P_4$  bonding- to a Sn- $P_4$  antibonding orbital (Figure S17). Whilst quantitative conversion of **3** to **2** was not achieved, even after prolonged irradiation, this study pointed towards the reversible addition of  $P_4$  across the  $\text{Sn}^{\text{II}}$  center. The low conversion of **3** to **2** is attributed to the facile activation of  $P_4$  with **2**, as the equilibrium of this reaction (cf. Figure 4) should be entirely on the product side in contrast to  $(^{\text{Mes}}\text{Ter})_2\text{Sn}$  ( $\Delta G = -42$  kJ mol $^{-1}$  vs.  $-13$  kJ mol $^{-1}$ ). Additionally, the barrier for activation of  $P_4$  is low ( $\Delta G^\ddagger = +86$  kJ mol $^{-1}$ ), consistent with a fast reaction at room temperature. Notably, compound **2** demonstrates the first example of reversible P-P bond activation with low valent tin compounds.





**Scheme 2.** P<sub>4</sub> transfer reaction.

Encouraged by the reversible activation of P<sub>4</sub>, we were interested to see if **3** could be used as a P<sub>4</sub> transfer reagent. In a similar fashion to that reported by Scheer and co-workers, on treatment of **3** with three equivalent of silylene chloride ([PhC(N<sup>t</sup>Bu)<sub>2</sub>SiCl]) the yellow solution immediately turned to orange (Scheme 2).<sup>[15]</sup> The <sup>31</sup>P NMR spectrum revealed a mixture of phosphorus containing compounds, however, distinct resonance signals were observed for compound **4** [(PhC(N<sup>t</sup>Bu)<sub>2</sub>SiP)<sub>3</sub>] (crude yield = 10%) and **5** [(PhC(N<sup>t</sup>Bu)<sub>2</sub>SiCl)P(SiCl<sub>2</sub>{PhC(N<sup>t</sup>Bu)<sub>2</sub>)]<sub>2</sub>, at -244.1 and -183.5 ppm, respectively (crude yield = 45%).<sup>[15,16]</sup>

In summary, we have reported for the first time the reversible P-P bond activation by a heteroleptic stannylene **2**. Both experimental and computational investigations revealed the effectiveness of the silyl ligand in order to tune and enhance the reactivity of low valent Sn<sup>II</sup> center. Additionally, transfer of P<sub>4</sub> to organic molecules has been demonstrated and further functionalization reactivity is currently under investigation in our lab.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** main group · P<sub>4</sub> activation · reversible activation · small molecule activation · tetraenes

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