

Reversible Activation

Reversible Activation and Transfer of White Phosphorus by Silyl-Stannylene

Debotra Sarkar, Catherine Weetman, Dominik Munz, and Shigeyoshi Inoue*

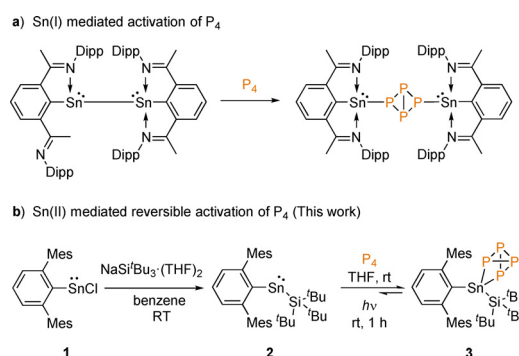
Dedicated to Professor Manfred Scheer on the occasion of his 65th birthday

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.^[1] Their synthesis classically involves the energy intensive and hazardous chlorination of white phosphorus (P_4).^[1d,e] 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.^[1a-c,e,f] To date, a plethora of examples for transition metal mediated P_4 activation has been achieved.^[1b,e] 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.^[2] In contrast to transition metals, activation of P_4 with main group elements is limited to only a handful of

examples,^[1a,c,f,3] 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.^[4] Examples of both silylenes^[4a,c,d,f,5] and germynes have been reported to activate P_4 .^[4b] 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 .^[4b] This is an important discovery, as reversibility is a key step towards main group mediated catalysis.^[6] 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].^[7]



Scheme 1. Activation of P_4 with low-valent tin complexes (Dipp = 2,6- $^{i}Pr_2(C_6H_3)$, Mes = 2,4,6- $Me_3(C_6H_2)$).

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.^[8] It has previously been shown that the Sn^{II} - Sn^{IV} redox couple can be manipulated by use of strongly σ -donating boryl ligands to enable dihydrogen activation.^[8c] Therefore, we postulated that use of electropositive silyl groups, which have been widely employed as stabilizing ligands in low valent main group chemistry,^[9] 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

[*] D. Sarkar, Dr. C. Weetman, Prof. Dr. S. Inoue
Department of Chemistry, WACKER-Institute of Silicon Chemistry
and Catalysis Research Center, Technische Universität München
Lichtenbergstraße 4, 85748 Garching (Germany)
E-mail: s.inoue@tum.de

Dr. C. Weetman
Department of Pure and Applied Chemistry, University of Strathclyde
Glasgow, G1 1XL (UK)

Prof. Dr. D. Munz
Department of Chemistry and Pharmacy, General and Inorganic
Chemistry, Friedrich-Alexander-University Erlangen-Nuremberg
(FAU)

Egerlandstraße 1, 91058 Erlangen (Germany)
and

Inorganic Chemistry: Coordination Chemistry, Saarland University,
Geb. C4.1
66123 Saarbrücken (Germany)

Supporting information and the ORCID identification number(s) for
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substituted stannylene. The heteroleptic silyl stannylene **2** [^{Mes}TerSn(Si^tBu₃)] was isolated via treatment of chlorostannylene **1** [^{Mes}TerSnCl] with one equivalent of NaSi^tBu₃·(THF)₂. 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 ¹¹⁹Sn{¹H} 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 (^{Mes}Ter)₂Sn (1971 ppm).^[8e,10] This indicates an electron rich Sn^{II} center, which can be attributed to the substituent effect (Si^tBu₃ vs. ^{Mes}Ter). In the ²⁹Si NMR spectrum a distinct signal was observed at 94.7 ppm for the silicon atom of Si^tBu₃. 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).^[11] Nevertheless, calculations at the PBE0-D3/def2-TZVPP//PBE0-D3/def2-SVP level of theory with the def2-ECP reproduce the order of the ¹¹⁹Sn NMR shifts (**1**: -170 ppm; **2**: -314 ppm; (^{Mes}Ter)₂Sn: 664 ppm) and hence corroborate a comparably electron rich Sn^{II} 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^tBu₃ 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^{II} complexes (96.9–117.6°).^[12] Notably, two-coordinate stannylenes [R₂Sn] with broad bond angles (∠ R-Sn-R = 112 to 118°) have been shown to activate a wide range of small molecules.^[8c-e]

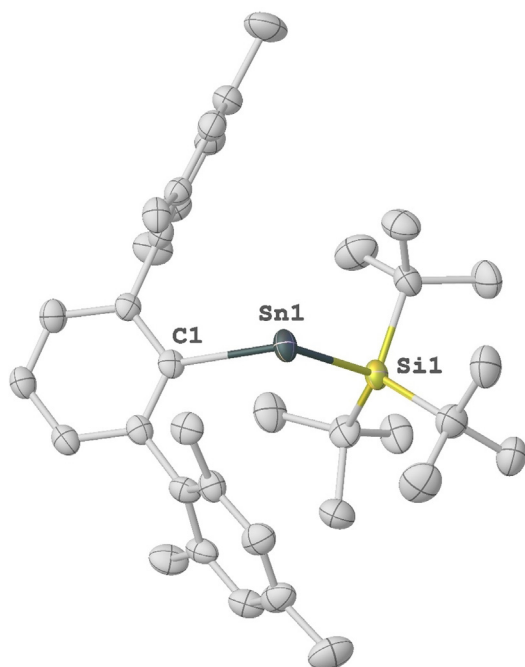


Figure 1. Molecular structure of compound **2** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Si1–Sn1 2.6981(17), Sn1–C1 2.217(5), C1–Sn1–Si1 113.50(14).

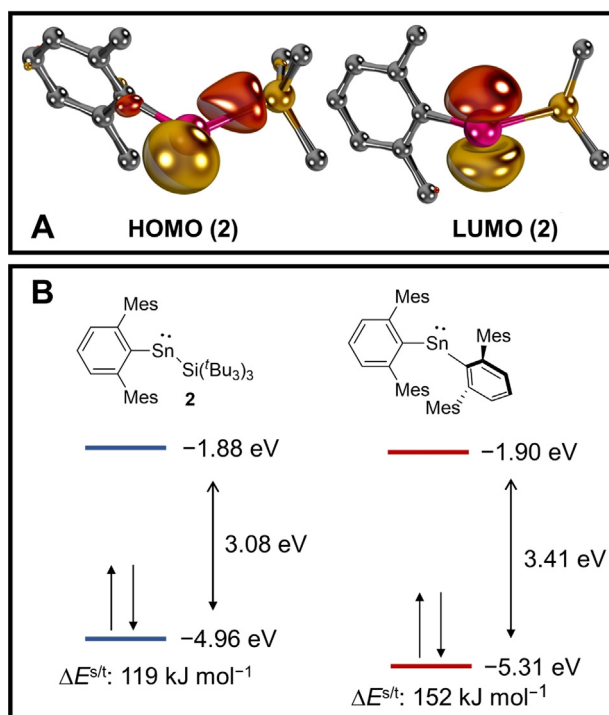


Figure 2. Frontier orbitals of **2** (A), their energies and vertical singlet/triplet gap $\Delta E^{s/t}$ (B, left) and comparison with ^{Mes}Ter₂Sn (B, right) as obtained at the PBE0-D3/def2-TZVPP//PBE0-D3/def2-SVP level of theory.

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_x*- and empty *p_z*-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 (^{Mes}Ter₂Sn, 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; ^{Mes}Ter₂Sn, -1.90 eV), the HOMO of **2**, associated with the *p_x* orbital and showing overlap with the Si atom, is much higher in energy (**2**, -4.96 eV; ^{Mes}Ter₂Sn, -5.31 eV). This corroborates that enhanced σ -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 P₄. A trial NMR scale reaction of **2** with P₄ 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 ³¹P{¹H} NMR spectrum revealed resonances for three distinct ³¹P 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 δ_X is split into a doublet of doublets ($^1J(\text{P}_X, \text{P}_A) = 159.0$, $^1J(\text{P}_X, \text{P}_B) = 154.8$ Hz) while each of the two up-field signals show a doublet of triplets (1J -

(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 $[LSiP_4]$, $L = \beta$ -diketiminate complex reported by Driess and co-workers.^[4a] The ^{119}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).^[13] Notably, tin polyphosphide complexes are typically generated by salt metathesis reactions with the metal polyphosphide and stannylene.^[13a-c,14] 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 SnP_4 core (Figure 2). Notably, regioselective activation of P_4 at main group centers is rare.^[1a,c] Compound **3** is isostructural to the reported $LSiP_4$ and $(m\text{-Ter})_2\text{GeP}_4$ complexes (Figure 3).^[4a,b] 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.^[13b,c,14] 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

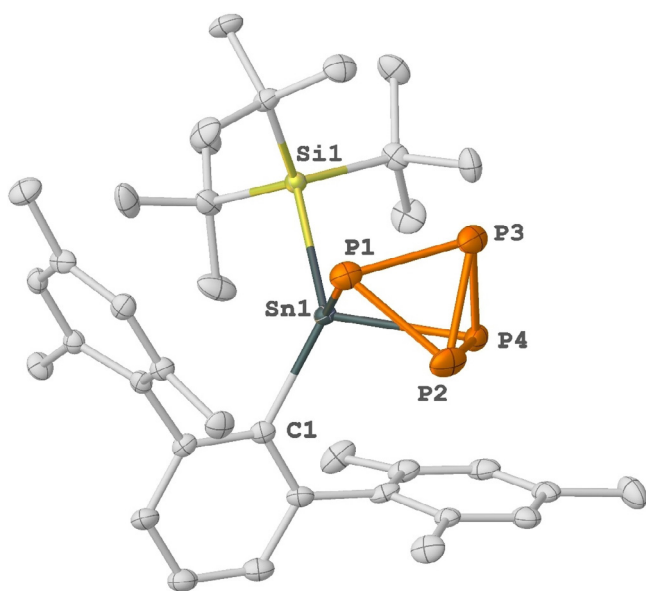


Figure 3. Molecular structures of compound **3** in the solid state. Ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [$^\circ$]: Si1–Sn1 2.6960(7), Sn1–C1 2.223(2), Sn1–P1 2.5714(7), Sn1–P4 2.5767(7), P2–P3 2.1638(10),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

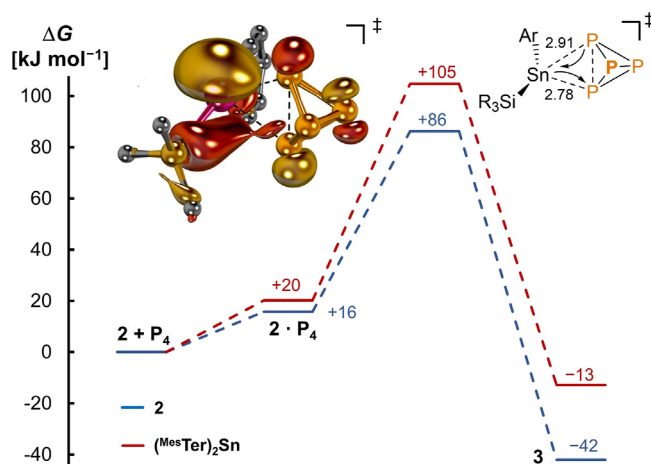
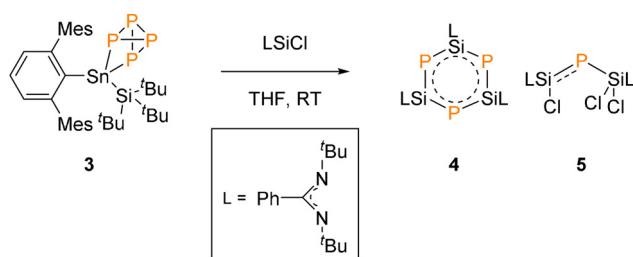


Figure 4. Gibbs free energy profile for P_4 activation by $^{\text{Mes}}\text{TerSn}(Si^tBu_3)$ **2** [blue —] and $(^{\text{Mes}}\text{Ter})_2\text{Sn}$ [red —] obtained at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3/def2-SVP level of theory and bond lengths, given in Å, as well as HOMO of transition state. Mesityl and $t\text{Bu}$ 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 Sn^{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 (^1H and ^{31}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}P and ^1H). 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 Sn^{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. P₄ transfer reaction.

Encouraged by the reversible activation of P₄, we were interested to see if **3** could be used as a P₄ 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^tBu)₂SiCl]) the yellow solution immediately turned to orange (Scheme 2).^[15] The ³¹P NMR spectrum revealed a mixture of phosphorus containing compounds, however, distinct resonance signals were observed for compound **4** [[PhC(N^tBu)₂SiP]₃ (crude yield = 10%) and **5** [[PhC(N^tBu)₂SiCl]P{SiCl₂{PhC(N^tBu)₂}], at -244.1 and -183.5 ppm, respectively (crude yield = 45%).^[15,16]

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^{II} center. Additionally, transfer of P₄ 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 · P₄ activation · reversible activation · small molecule activation · tetrylenes

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