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Facile rotation around a silicon–phosphorus double bond enabled through coordination to tungsten†

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Unprecedented *E/Z* isomerisation of a Si=P bond was observed by temperature dependent NMR spectroscopy. DFT calculations showed that the coordination of phosphasilene to tungsten lowered the rotational barrier from 19.1 to 14.2 kcal mol⁻¹. The thermodynamically more stable phosphinosilylene tungsten complex is formed at elevated temperatures through substituent migration.

It is well known that a π bond is usually not free to rotate. For instance, alkenes have very high activation energies (*cis*-2-butene = 62 kcal mol⁻¹) for rotation around the C=C bond, making them inert against *E/Z*-isomerisation at room temperature.¹ However, this isomerisation energy can be decreased by introducing bulky substituents (*cf.* stilbene = 43 kcal mol⁻¹, bifluorenylidene = 23 kcal mol⁻¹) or using the push–pull effect^{1c} (*cf.* dimethyl[(dimethyl-amino)methylene]malonate = 16 kcal mol⁻¹).

Their higher homologues, disilenes, display relatively low rotation barriers of 26–28 kcal mol⁻¹ at 350 K for the Si=Si bond, which enable *E/Z*-isomerisation.² In the interesting case of tetrakis(trialkylsilyl)-disilenes, rotation around the Si=Si bond becomes possible at room temperature (activation barrier 15.3 kcal mol⁻¹ at 303 K), which is attributed to an effective σ – π conjugation in the transition state.³ It should be noted that additional pathways for *E/Z*-isomerisation of disilenes through dissociation–recombination reactions, disilene–silylsilylene inter-conversions and through irradiation are also viable.⁴ Diphosphenes with a P=P double bond can undergo photoisomerisation from *E*- to *Z*-conformations.⁵ However, to the best of our knowledge no *E/Z*-isomerisation was reported for phosphasilenes (Chart 1). The Si=P bond can be strongly influenced by the introduction of

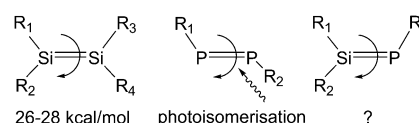


Chart 1 *E/Z*-Isomerisation of compounds containing a double bond.

substituents that can enhance the elemental polarization induced by the different electronegativities of silicon and phosphorus.⁶ The push–pull effect could also be used for decreasing the rotation barrier of the Si=P double bond with the intention to observe *E/Z*-isomerisation of phosphasilenes. In addition, phosphasilenes feature an electron lone pair on phosphorus that can coordinate to transition metals. This coordination behaviour on phosphorus may lead to a lower rotation energy of the Si=P double bond. However, surprisingly, little is known about its coordination to transition metals.⁷

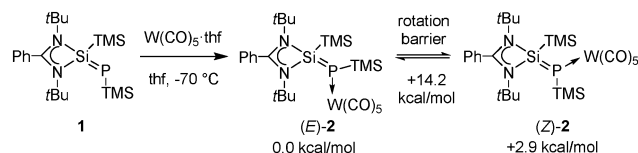
With this in mind, we utilized zwitterionic phosphasilene **1**^{6a} and engaged the electron lone pair on phosphorus in coordination to tungsten (Scheme 1). By this we obtained an even weaker Si=P bond in **2** and a low rotation barrier of only 14.2 kcal mol⁻¹ leading to fast *E/Z*-isomerisation at room temperature.

The phosphasilene tungsten carbonyl complex **2** was synthesized from **1** and W(CO)₅·thf in a very good yield of 92% (Scheme 1). Compound **2** exists as two stable isomers labeled as (*E*)-**2** and (*Z*)-**2**. It should be noted that only (*E*)-**2** is having the proper Si2–Si1–P1–W1 torsion angle of 175.13°, while the isomer referred to as (*Z*)-**2** actually exhibits a Si2–Si1–P1–W1 torsion angle of 38.8°. The rotational isomer with a torsion angle of 0° is higher in energy (6.8 kcal mol⁻¹, see the ESI,† Fig. S24). DFT calculations based on the B97-D/6-31G(d) level of theory revealed that the rotation barrier for the silicon–phosphorus

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† Electronic supplementary information (ESI) available: Details of experimental procedures and characterization methods, NMR spectra, IR spectra, the UV/Vis spectrum, crystallographic and computational details, molecular orbitals and mechanistic schemes. CCDC 1061059 (**2**) and 1061060 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc04247j



Scheme 1 Synthesis and isomerism of complex **2**.



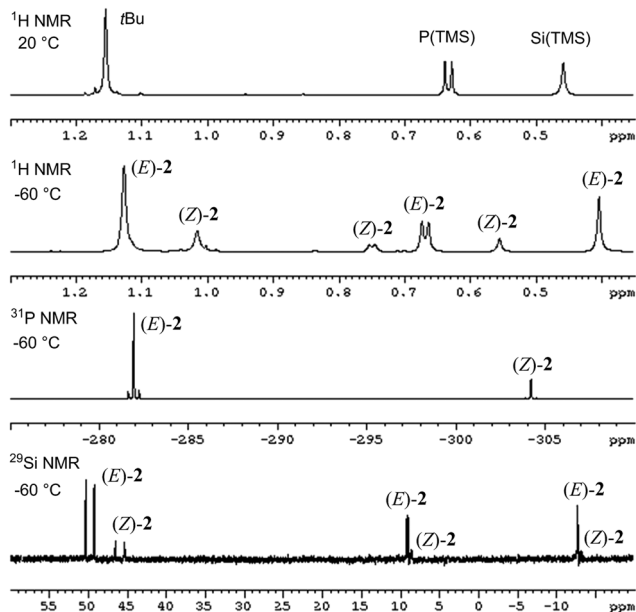


Fig. 1 The dynamic behavior of **2** observed by temperature dependent NMR spectroscopy in toluene- d_6 .

double bond in **2** is $14.2 \text{ kcal mol}^{-1}$, which is feasible at room temperature, but not at low temperature. Indeed, we observed by NMR spectroscopy that the signals belonging to one set at room temperature undergo coalescence and give rise to two sets of signals at $-60 \text{ }^\circ\text{C}$ (Fig. 1). The ratio between (*E*)-**2** and (*Z*)-**2** is 3 : 1 in favor of (*E*)-**2**, which was assigned based on lower thermodynamic stability of (*Z*)-**2** ($2.9 \text{ kcal mol}^{-1}$). The most prominent differences in the NMR shifts of (*E*)-**2** and (*Z*)-**2** were observed for the phosphorus and the silene silicon. The $^{31}\text{P}\{^1\text{H}\}$ NMR signals of **2** ((*E*)-**2**: $\delta = -282.0 \text{ ppm}$, $^1J_{\text{P-W}} = 123 \text{ Hz}$ and (*Z*)-**2**: $\delta = -304.3 \text{ ppm}$, $^1J_{\text{P-W}} = 128 \text{ Hz}$) are upfield shifted from that of **1** ($\delta = -252.9 \text{ ppm}$).^{6a} The low tungsten-phosphorus coupling constants of 123 and 128 Hz are indicative of the strong negative polarization on phosphorus and can be compared to those of (phosphoranylidene phosphine)pentacarbonyltungsten complexes ($102.5\text{--}109.9 \text{ Hz}$).⁸ The silene $^{29}\text{Si}\{^1\text{H}\}$ NMR signals of **2** ((*E*)-**2**: $\delta = 49.8 \text{ ppm}$ ($^1J_{\text{Si-P}} = 106 \text{ Hz}$) and (*Z*)-**2**: $\delta = 45.9 \text{ ppm}$ ($^1J_{\text{Si-P}} = 130 \text{ Hz}$) are downfield shifted from that of **1** ($\delta = 40.5 \text{ ppm}$ ($^1J_{\text{Si-P}} = 191.4 \text{ Hz}$)).^{6a} In addition the silene-phosphorus coupling constant is significantly decreased in **2** compared to **1**, which is all in agreement with the weakened and more polarized Si=P bond in **2**. It is important to note that the NMR signals for the silene silicon and phosphorus are broad at room temperature presumably due to the rotation around this bond. Solid state $^{29}\text{Si}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed that only (*E*)-**2** is present in the solid state. Variable temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR measurements of phosphasilene **1** did not reveal coalescence or two sets of signals at low temperatures down to $-60 \text{ }^\circ\text{C}$, proving experimentally that a rotation around the Si=P bond at r.t. is not applicable for **1**.

X-ray diffraction analysis of single crystals obtained from hexane elucidated the molecular structure of (*E*)-**2** (Fig. 2). The Si1-P1 bond length ($2.158(2) \text{ \AA}$) in (*E*)-**2** is clearly longer than that in **1** ($2.095(3) \text{ \AA}$),^{6a} which confirms further the weakening of the silicon-phosphorus double bond by the coordination of

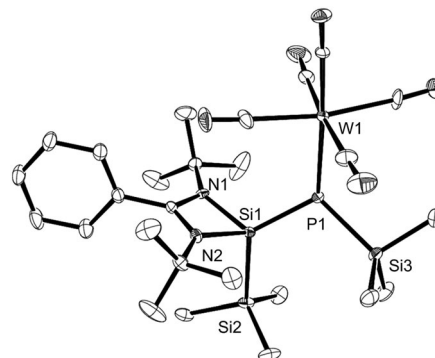


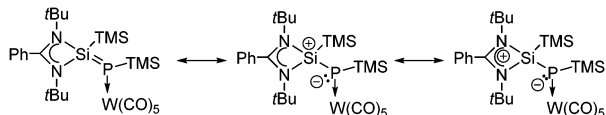
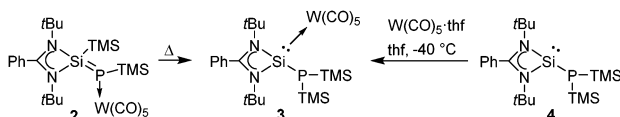
Fig. 2 Molecular structure of compound (*E*)-**2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$) in (*E*)-**2**: Si1-P1 $2.158(2)$, Si1-Si2 $2.369(2)$, P1-Si3 $2.253(2)$, P1-W1 $2.6265(18)$; Si1-P1-W1 $118.82(8)$, Si3-P1-W1 $115.55(8)$.

phosphorus to tungsten. The coordination to gold in the only known phosphasilene complexes with a coordinative bond showed little effect on the Si1-P1 bond lengths ($2.0924(2) \text{ \AA}$ and $2.0917(5) \text{ \AA}$).^{7c} The angles around phosphorus are nearly 120° and the torsion angle Si2-Si1-P1-W1 amounts to 175.13° establishing the η^1 -coordination of the Si=P bond to tungsten. The P1-W1 bond length ($2.6265(18) \text{ \AA}$) is longer than in phosphalkene tungsten complexes ($2.51\text{--}2.54 \text{ \AA}$)⁹ and closer to that of the (phosphoranylidene phosphine)penta-carbonyltungsten complex ($2.603(1) \text{ \AA}$).^{8b} DFT calculations were utilized to understand the molecular structure of (*Z*)-**2**. Only minor differences were found for the interatomic distances in (*Z*)-**2** and (*E*)-**2** (Si1-P1 2.159 \AA and 2.152 \AA and P1-W1 2.663 \AA and 2.648 \AA , respectively).

UV/Vis spectroscopy revealed a red-shift from **1** to **2** ($\lambda_{\text{max}} = 333 \text{ nm}$ and $\lambda_{\text{max}} = 354 \text{ nm}$, respectively), which was also observed for the phosphasilene gold complexes ($8\text{--}10 \text{ nm}$).^{7c} TD-DFT calculations based on the B3LYP/cc-pVTZ//B97-D/6-31G(d) level of theory similarly predicted a red shift for (*E*)-**2** ($\lambda_{\text{max}} = 383 \text{ nm}$, 3.24 eV , oscillator strength 0.050). The UV/Vis transition of (*E*)-**2** occurs mainly from the HOMO to the LUMO (weight 0.55), while the LUMO+1 and LUMO+2 (weight 0.11 and weight 0.15, respectively) play a less significant part (see the ESI,† Fig. S25). The HOMO of (*E*)-**2** (-4.13 eV) is determined by the antibonding combination of the π orbital of the phosphasilene and a filled d-orbital of tungsten. It is higher in energy than the HOMO of **1** (-5.94 eV) marked by the silicon-phosphorus π -bonding orbital which can explain the observed red-shift.^{6e,10} According to NBO analysis, the already very polarized double bond of **1** (silicon: $+0.99$ charge, 21.45% of the π -bond, phosphorus: -0.75 charge, 78.55%)^{6e} gets even further polarized in **2** (silicon: $+1.14$ charge, phosphorus: -0.49 charge), to the extent of being dissected by NBO analysis into an empty orbital on silicon and a lone pair on phosphorus.¹¹ This confirms the increasing importance of zwitterionic resonance structures, also supported by the amidinato ligand and its additional coordination (Scheme 2), which explains the tendency of **2** for *E/Z*-isomerisation.

Though compound **2** is stable at room temperature, at elevated temperatures it undergoes a slow reaction to yield the phosphinosilylene tungsten carbonyl complex **3** (Scheme 3).¹² DFT calculations showed that a stepwise mechanism in contrast to a concerted shift



Scheme 2 Resonance structures of **2**.Scheme 3 Reactivity of **2** and independent synthesis of **3** from **4**.

of the TMS group and $W(CO)_5$ moiety occurs for the transformation of **2** to **3** (see the ESI,† Fig. S26). The first step is the shift of the TMS group, which is also rate determining (transition state: $19.7 \text{ kcal mol}^{-1}$) and thus responsible for the kinetic stability of **2** at room temperature. The formation of **3** from **2** is thermodynamically favoured by $10.1 \text{ kcal mol}^{-1}$ and can be explained by the stronger donor strength of the silylene.¹³ In accordance with the calculated values, no formation of **2** from **3** at elevated temperatures was observed. This is contrasted by the equilibrium between **1** and phosphinosilylene **4** (Scheme 3), which is determined by a smaller thermodynamic difference ($1.9 \text{ kcal mol}^{-1}$ in favour of **1**) and a higher activation barrier ($32.1 \text{ kcal mol}^{-1}$).¹⁴

To date, merely four stable phosphinosilylenes have been reported¹⁵ and their reactivity studies were limited to N_2O , $tBuCOCl$ and $Ni(COD)_2$.^{6d,14,16} Complex **3** was synthesized independently from the parent phosphinosilylene **4** in a moderate to low yield of 30% (Scheme 3).¹⁷ The silylene tungsten complex **3** was thus fully characterized using NMR and IR spectroscopy, mass spectrometry, elemental analysis and single crystal X-ray diffraction. As expected, the $^{29}Si\{^1H\}$ NMR signal of the silylene-silicon in **3** is downfield shifted from that of **4** and the $^1J_{Si-P}$ coupling constant has considerably decreased ($\delta = 70.7 \text{ ppm}$, $^1J_{Si-P} = 134 \text{ Hz}$ and $\delta = 44.0 \text{ ppm}$, $^1J_{Si-P} = 194 \text{ Hz}$, respectively).^{6a} The $^{31}P\{^1H\}$ NMR signal of **3** is slightly downfield shifted from that of **4** ($\delta = -199.4 \text{ ppm}$ and $\delta = -211.0 \text{ ppm}$, respectively).^{6a} The presence of the carbonyl group is evident from $^{13}C\{^1H\}$ NMR spectroscopy ($\delta = 202.0 \text{ ppm}$) and IR spectroscopy ($\nu_{CO} = 2054, 1918, 1905 \text{ cm}^{-1}$). The molecular structure of compound **3** is shown in Fig. 3 and it revealed that the silicon-phosphorus bond length in **3** ($2.249(9) \text{ \AA}$ and $2.237(6) \text{ \AA}$) is shorter than that of **4** ($2.2838(12) \text{ \AA}$).^{6a} The silicon-tungsten bond length in **3** ($2.562(3) \text{ \AA}$ and $2.619(2) \text{ \AA}$) is longer than those of $(PhC\{NtBu\}_2)_2Si(W\{CO\}_5)Cl$ and $(PhC\{NtBu\}_2)Si(W\{CO\}_5)F$ ($2.5086(11) \text{ \AA}$ and $2.4990(8) \text{ \AA}$, respectively)¹⁸ and similar to that of $(PhC\{NiPr\}_2)_2Si(W\{CO\}_5)$ ($2.5803(9) \text{ \AA}$).¹⁹

In conclusion, the coordination of zwitterionic phosphasilene **1** to a tungsten carbonyl complex leads to a more polarized and weaker silicon-phosphorus bond in **2**. Interestingly, it also lowers the rotation barrier of the $Si=P$ bond from $19.1 \text{ kcal mol}^{-1}$ in **1** to $14.2 \text{ kcal mol}^{-1}$ in **2** to allow facile *E/Z*-isomerisation at room temperature. In the presence of the transition metal, the phosphinosilylene complex **3** is thermodynamically preferred to **2**. Both species, **2** and **3**, are versatile building blocks for low-valent silicon compounds due to their labile trimethylsilyl groups^{6a,e,14}

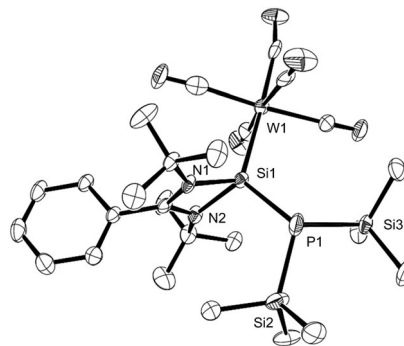


Fig. 3 Molecular structure of compound **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted and only one of the disordered fractions is depicted for clarity. Selected bond lengths (\AA) and angles ($^\circ$) in **3**, values in brackets refer to the other disordered fraction: $Si1-P1$ $2.249(9)$ ($2.237(6)$), $Si1-W1$ $2.562(3)$ ($2.619(2)$), $P1-Si2$ $2.228(13)$ ($2.260(10)$), $P1-Si3$ $2.177(10)$ ($2.375(9)$), $W1-Si1-P1$ $122.0(3)$ ($120.7(2)$).

and the additional stabilization provided by the transition metal. In fact, further reactivity studies are currently under way and shall be reported in due course.

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