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# **New Horizon of Organosilicon Chemistry**

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## Synthesis, characterisation and complexation of phosphino disilenes<sup>†</sup>

# Marco Hartmann, Abdishakur Haji-Abdi, Kai Abersfelder, Peter R. Haycock, Andrew J. P. White and David Scheschkewitz\*

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The treatment of disilenide Tip<sub>2</sub>Si=Si(Tip)Li (1, Tip = 2,4,6-/Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) with *P*-chloro phosphines affords the phosphino disilenes (**2a-d**; **a**: R = Ph, **b**: R = 'Pr, **c**: R = Cy, **d**: R = 'Bu), which were characterised by multinuclear NMR spectroscopy for **2a-d** and a single crystal X-ray diffraction study in case of **2c**. As an alternate synthetic method, the diphenyl derivative **2a** could also be prepared by reaction of LiPPh<sub>2</sub> with the thermally unstable iododisilene, Tip<sub>2</sub>Si=Si(Tip)I (**3**), which in turn was obtained by oxidation of **1** with stoichiometric amounts of iodine. Providing the first example for a Si=Si bond with an iodo functionality, disilene **3** was fully characterised by multinuclear NMR and X-ray diffraction. The thermal rearrangement of phosphine disilene **2a** *via* a C-H insertion reaction yields the diastereomeric mixture of a 1-phospha-2,3-disilaindane **4**. The structure of the *cis*-diastereomer of **4** was determined by X-ray diffraction. Finally, the synthesis of first transition metal complex of **2a** and **2b** by their coordination to the [Pd(PCy<sub>3</sub>)] fragment is reported. The solid state structure of complex **5a** reveals  $\eta^2$ -coordination of the Si=Si bond of the phosphino disilene **2a** with an intermediate bonding mode between  $\pi$ -complex and metallacyclopropane rather than coordination of the phosphino group.

#### Introduction

Vinyl-substituted phosphorus derivatives find applications in organic synthesis and catalysis.<sup>1</sup> Vinyl phosphines (**A**) are isoelectronic neutral versions of the anionic allyl ligands and as such have attracted considerable interest as precursors for various complexes featuring the related anionic phosphaallyl ligands.<sup>2</sup> The coordination modes of neutral vinyl phosphines on the other hand range from the usual  $\eta^3$ -mode of the isomeric all-carbon analogue (**B**),<sup>3</sup> to  $\eta^1$ -coordinating ligands,<sup>4</sup> where the C–C double bond can act as a hemilabile donor protecting a vacant coordination site (**C**).<sup>5</sup>



Despite sharing the same group of the periodic table with carbon, silicon is—in terms of electronegativity and size—much more akin to the group 15 element phosphorus. The coordination behaviour of disilenes is therefore, though qualitatively similar (Dewar–Chatt–Duncanson model),<sup>6</sup> quantitatively very different from that of alkenes. The higher HOMO and lower LUMO of the Si–Si double bond<sup>7</sup> account for both stronger  $\sigma$ -donation to the metal and stronger  $\pi$ -back donation from the metal to the ligand, which explains the prevalence of the metallacyclopropane binding mode in most disilene complexes (**D**).<sup>8</sup> In fact, only two

examples of genuine  $\pi$ -coordination of a Si–Si double bond (E) were observed by Kira and Iwamoto *et al.* in the complexes comprising the 12-electron transition metal fragment, [Cy<sub>3</sub>PPd].<sup>9</sup>

We therefore considered phosphino-substituted disilenes attractive synthetic targets. They could reasonably be expected to exhibit a versatile coordination behaviour including  $\eta^3$ -allyl type bonding, hemilabile modes, and  $\eta^2$ -modes effected by coordination of the Si=Si bond with either  $\pi$ -complex or metallacyclopropane character.

In general, however, the synthesis of disilenes with heterosubstitution is a non-trivial task. Until recently only a few examples have been reported, none of which concerned phosphorus.<sup>10</sup> Besides, these procedures are mainly based on the dimerisation of silylene fragments and as such unsuitable for the selective introduction of just one hetero-substituent. Two methods emerged in the meantime that allow for the selective incorporation of one functional substituent. The first is based on addition chemistry to the Si–Si triple bond of a disilyne granting a straightforward access to amino and boryl-substituted disilenes.<sup>11</sup> The second method relies on formal nucleophilic substitution reactions by disila analogues of vinyl anions, *i.e.* disilenides, which afforded zirconium, boron, and tin-substituted derivatives.<sup>12</sup>

Here, we report that treatment of lithium disilenide  $1^{13}$  with the appropriate *P*-chloro phosphines indeed provides a convenient access to the first phosphino disilenes **2a–d**. In addition, in case of **2a**, we report on an alternate synthetic approach employing an umpolung strategy and its isomerisation upon heating. For **2a** and **2b**, first transition metal complexes are reported, prepared by reaction with  $[Pd(PCy_3)_2]$  as an electron-poor transition metal fragment. All compounds were characterised by multinuclear NMR spectroscopy in solution; solid state structures were confirmed by X-ray diffraction on single crystal of one representative example of each class of compounds.

Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London, SW7 2AZ, UK. E-mail: d.scheschkewitz@ imperial.ac.uk; Fax: +44 (0)20 7594 5804; Tel: +44(0)20 7594 7473 † CCDC reference numbers 768711 (2c), 768712 (3), 768713 (4), and 769675 (5). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00180e

#### Experimental

#### General

All manipulations were carried out in oven-dried glassware under an atmosphere of argon or nitrogen using Schlenk-type techniques or in a glovebox. Solvents were dried and freed of oxygen by reflux for at least two days in the presence of the appropriate reagent. Disilenide 1 was synthesized with two coordinating molecules of 1,2-dimethoxyethane according to our published procedure.13 Chlorophospines were purchased from Sigma-Aldrich and distilled tube-to-tube under argon prior to use. NMR spectra were recorded at room temperature on a Bruker Avance 500 (1H: 500.13 MHz, 13C: 125.77 MHz, 29Si: 99.37 MHz, <sup>31</sup>P: 202.46 MHz). Chemical shifts are reported relative to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si) and H<sub>3</sub>PO<sub>4</sub>, 85% (<sup>31</sup>P, external). UV/vis spectra were recorded on a Shimadzu UV Mini 1240 photometer. Melting points were determined in closed NMR tubes under argon and are uncorrected. Microanalyses on crystallised samples on sufficient spectroscopic purity were carried out with a vario MICRO elemental analyser from Elementaranalysensysteme GmbH.

#### Synthesis

General procedure for the preparation of phosphino disilenes, 2a–d. At room temperature 1.17 mmol of the appropriate chlorophosphane were added dropwise to a solution of 1.00 g (1.17 mmol) of disilenide 1 in 10 mL of toluene. Stirring was maintained for 4 h before all volatiles were removed in vacuum. The residue was digested with 20 mL of pentane and LiCl separated by filtration. Removal of the solvent afforded the product in NMR spectroscopic purity.

1-Diphenylphosphino-1,2,2-tris(2',4',6'-triisopropyl-phenyl)disilene, 2a. Orange crystals from hexane (0.46 g, 46%, mp. 135 °C). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 7.60 (t, 4H, Ph-*H*), 7.03 (s), 7.02 (s), 7.01, 7.00, 6.98 (m), 6.97, 6.93 (m) (6H, Tip-H and 6H, Ph-H), 4.27 (br), 3.95 (br), 3.86 (br), 2.78, 2.70, 2.68 (each hept, together 9H, Pr-CH), 1.26, 1.19, 1.14, 1.11, 0.97 (each d, together 54H, <sup>*i*</sup>Pr-*CH*<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 156.16, 155.58, 154.61, 151.28, 151.26 150.93 (Tip- $C_{o/p}$ ), 138.13 (br, d,  $J({}^{13}C, {}^{31}P) = 20.3$  Hz, Ph-*C*H), 134.25 (br, d *J*(C, P) = 18.0 Hz, Ph-*C*H), 127.43 (Ph-*C*H), 135.48 (d, J(C, P) = 15.0 Hz, Tip- $C_i$ ), 133.22 (Tip- $C_i$ ), 131.48 (d,  $J({}^{13}C, {}^{31}P) = 3.0 \text{ Hz}, \text{Tip-}C_i), 122.42, 122.35, 121.95 \text{ (Tip-}CH),$ 38.74, 38.37, 37.73 (br), 34.74, 34.72, 34.50 (Pr-CH), 24.95 (br), 24.51, 24.11, 24.03, 23.95 (<sup>*i*</sup>Pr-CH<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 96.5  $({}^{2}J(Si,P) = 77 \text{ Hz}, SiC_{2}), 54.4 ({}^{1}J(Si,P) = 116 \text{ Hz}, SiCP). {}^{31}P \text{ NMR}$  $(C_6D_6) \delta = -45.7 ({}^1J(Si,P) = 116 \text{ Hz}, {}^2J(Si,P) = 77 \text{ Hz}). \text{ UV/Vis}$ (hexane)  $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 423 nm (18380). Microanalysis calc. for C<sub>57</sub>H<sub>79</sub>Si<sub>2</sub>P: C, 80.41, H, 9.40. found.: C, 80.04, H, 9.50.

**1-Diisopropylphosphino-1,2,2-tris(2',4',6'-triisopropyl-phenyl)disilene, 2b.** orange-yellow solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 7.08, 6.98, 6.97 (each s, 6H, Tip-*H*), 4.03 (br), 2.734, 2.728, 2.73, 2.67 (each hept, together 9H, <sup>1</sup>Pr–C*H*), 2.26 (hept, 2H, P-'Pr–C*H*), 1.61, 1.36, 1.24, 1.19 (br), 1.17, 1.11 (each d, <sup>1</sup>Pr-C*H*<sub>3</sub>), 1.15 (d, P-<sup>1</sup>Pr–C*H*<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 155.57, 155.24, 154.32, 150.88, 150.78, 150.56 (Tip-C<sub>*o*/*p*</sub>), 136.3 (*J*(C, P) = 11.1 Hz, Tip-C<sub>*i*</sub>), 134.11(Tip-C<sub>*i*</sub>), 132.9 (*J*(C,P) = 3.0 Hz, Tip-C<sub>*i*</sub>), 122.29, 122.16 (br) (Tip-CH), 38.0, 37.67 (br), 34.75, 34.68, 34.50 (<sup>1</sup>Pr-CH), 25.71, 25.25 (br), 24.42 (br), 24.09, 24.00 (<sup>1</sup>Pr-CH<sub>3</sub>), 22.97 (v br, P-<sup>*i*</sup>Pr-CH, Tip-<sup>*i*</sup>PrCH<sub>3</sub>, P-<sup>*i*</sup>Pr-CH<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 96.6 (br, <sup>2</sup>J (Si,P) = *ca*. 60 Hz, *Si*C<sub>2</sub>), 53.2 (<sup>1</sup>J (Si,P) = 118 Hz, *Si*CP). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = -21.9 (v br).

1-Dicyclohexylphosphino-1,2,2-tris(2',4',6'-triisopropylphenyl)**disilene**, **2c.** Orange crystals from hexane (0.23 g, 23%, mp. 140 °C). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 7.09 (br), 6.98, 6.97 (br) (each s, 6H, Tip-H), 4.58 (br), 3.99, 3.74 (br, 6H, 'Pr-CH), 2.73, 2.72, 2.67 (each hept, 3H, <sup>i</sup>Pr-CH), 2.10 (br), 1.66 (br), 1.46 (br), 1.42 (br) (20H, Cy-CH<sub>2</sub>), 1.24, 1.19 (br), 1.16, 1.14, 1.11, 0.96 (br) (each d, together 54H, <sup>*i*</sup>Pr-*CH*<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 155.66, 155.23, 154.34, 150.83, 150.74, 150.53 (Tip- $C_{o/p}$ ) 136.38 (br, d, J(C,P) = $10.96 \text{ Hz}, \text{Tip-}C_i$ , 134.22 (br, Tip- $C_i$ ), 132.96 (d, J(C,P) = 1.94 Hz, Tip-C<sub>i</sub>), 122.42, 122.16 (br) (Tip-CH), 37.92, 37.62 (br), 34.73, 34.68, 34.50 (<sup>i</sup>Pr-CH), 33.24, 27.88 (br), 26.63 (Cy-CH<sub>2</sub>), 25.80 (br), 24.49 (br), 24.11, 24.05, 23.99 (<sup>i</sup>Pr-CH<sub>3</sub>, Cy-CH<sub>2</sub>). <sup>29</sup>Si NMR  $(C_6D_6) \delta = 95.4$  (br, <sup>2</sup>J (Si,P) = ca. 60 Hz, SiC<sub>2</sub>), 52.5 (br.,  ${}^{1}J$  (Si,P) = ca. 115 Hz, SiCP).  ${}^{31}P$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = -36.3$  (v br). UV/Vis (hexane)  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 416 nm (18970). Microanalysis calc. for C<sub>57</sub>H<sub>91</sub>Si<sub>2</sub>P: C, 79.30, H, 10.60. found.: C, 79.30, H, 10.90.

1-Di-tert.-butylphosphino-1,2,2-tris(2',4',6'-triisopropyl-phenyl)disilene, 2d. orange-yellow solid. <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta = 7.28$ , 7.10, 7.04, 7.02, 6.93, 6.90 (each s, 6H, Tip-H), 4.77, 4.54, 4.03, 3.94, 3.55 (br, 6H, <sup>i</sup>Pr-CH), 2.76, 2.72, 2.67 (each hept, together 3H, <sup>*i*</sup>Pr-CH), 1.94 (br), 1.58 (br), 1.40 (br), 1.36 (d), 1.30 (d), 1.19 (d), 1.15 (d), 1.11(d), 0.51, 0.44, 0.38 (together 72H,  $CH_3$ ). <sup>13</sup>C NMR ( $C_6D_6$ )  $\delta = 155.82$ , 155.39, 155.14, 155.05, 154.1, 153.92 (br, Tip- $C_o$ ) 150.89, 150.61, 150.37 (Tip- $C_p$ ), 137.3 (J(C,P) =15.3 Hz, Tip- $C_i$ ), 134.5 (J(C,P) = 1.7 Hz Tip- $C_i$ ), 133.2 (J(C,P) =4.0 Hz Tip-C<sub>i</sub>), 123.17, 123.09, 122.98, 122.06, 121.79, 121.50 (br, Tip-CH), 38.88, 38.73, 37.40, 37.02, 36.49, 36.93 (o-<sup>i</sup>Pr-CH), 34.68, 34.67, 34.47 (p- $^{i}$ Pr-CH), 33.61, 33.00 (d,  $^{2}J(C,P) = 15$  Hz, <sup>*t*</sup>Bu–CH<sub>3</sub>), 34.10, 33.90 (<sup>2</sup>J(C,P) = 15 Hz, <sup>*t*</sup>Bu–C<sub>*a*</sub>), 29.72, 26.40, 25.97, 24.97, 24.71, 24.29, 24.17, 24.00 (br) (<sup>i</sup>Pr-CH<sub>3</sub>). <sup>29</sup>Si NMR  $(C_6 D_6) \delta = 98.8 ({}^{1}J(Si,Si) = 143 \text{ Hz}, {}^{2}J(Si,P) = 89 \text{ Hz}, SiC_2), 53.0$  $({}^{1}J(Si,Si) = 143 \text{ Hz}, {}^{1}J(Si,P) = 133 \text{ Hz}, SiCP).{}^{31}P \text{ NMR} (C_6D_6)$  $\delta = 8.9 ({}^{1}J(\text{Si},\text{P}) = 133 \text{ Hz}, {}^{2}J(\text{Si},\text{P}) = 89 \text{ Hz}).$ 

Synthesis of 1-iodo-1,2,2-tris(2',4',6'-triisopropyl-phenyl)disilene, 3. At -80 °C a solution of 0.31 g (1.17 mmol) iodine in 10 mL of toluene was added dropwise to 1.00 g (1.17 mmol) of disilenide 1 in 25 mL of hexane. The purple reaction mixture was brought to room temperature within the course of 2h, during which the colour of the solution changes to orange-red and lithium iodide precipitates. The salts were filtered off and all volatiles removed in vacuum. The residue was dissolved in a minimum amount of hexane. Storing at 0 °C overnight afforded thermally sensitive orange crystals of 3 (0.12 g, 17%). <sup>1</sup>H NMR  $(C_6D_6) \delta = 7.10, 7.07, 6.98$  (each s, each 2 H, Tip-H), 4.40, 4.00, 3.76, 2.74 (br), 2.65 (br) (each hept, together 9H, <sup>i</sup>Pr-CH), 1.38 (br), 1.3 (br), 1.24, 1.18, 1.17, 1.1, 0.96 (each d, together 54H, <sup>*i*</sup>Pr-*CH*<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 155.79, 155.36, 154.20, 152.64, 151.83, 151.16 (Tip-C<sub>o/p</sub>) 135.56, 132.72, 132.68 (Tip-C<sub>i</sub>), 122.41, 122.38, 122.11 (Tip-CH), 39.36, 38.52, 38.36, 34.86, 34.73, 34.57 (<sup>i</sup>Pr-CH), 25.71 (br), 24.51, 24.17 (br), 24.10, 24.04, 23.92 (<sup>*i*</sup>Pr-CH<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 76.8 (S*i*C<sub>2</sub>) (<sup>*i*</sup>J(S*i*/S*i*) = 128 Hz), 51.7 (*Si*CI) ( ${}^{1}J(Si/Si) = 128$  Hz).

**Reaction of iodo disilene 3 with Ph<sub>2</sub>PLi.** At 0 °C "BuLi (156  $\mu$ L, 1.5 M in hexane) were added to a solution of 46.9 mg Ph<sub>2</sub>PH (prepared by reaction of Ph<sub>2</sub>PCl with LiAlH<sub>4</sub> in Et<sub>2</sub>O followed by cautious quenching with degassed H<sub>2</sub>O and distillation) in 5 mL of Et<sub>2</sub>O. After stirring 2 h at room temperature the resulting pale yellow solution was added at -90 °C to a solution of 200 mg (0.25 mmol) of **3** in 10 mL of Et<sub>2</sub>O. The reaction mixture was warmed to room temperature and all solvents were distilled off in vacuum. <sup>1</sup>H and <sup>31</sup>P NMR data: see **2a**. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 96.5 (<sup>2</sup>J(Si,P) = 77 Hz, SiC<sub>2</sub>), 54.4 (<sup>1</sup>J(Si,P) = 116 Hz, SiCP), -41.4 (impurity), -69.1 (impurity).

Thermolysis of 2a. Isolation of a diastereomeric mixture of 1-phenyl-2,2,3-tris(2',4',6'-triisopropylphenyl)-1-phospha-2,3-disilaindane, 4. A solid sample of 100 mg (0.117 mmol) of 2a was melted under argon and kept at 150 °C for 1 h. After cooling, a minimum amount of hexane was added and the sample kept at room temperature overnight yielding colourless crystals suitable for X-ray analysis (68 mg, 68%). In solution two diastereomers are observed in a 72 : 28 ratio. <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta = 7.97$  (t), 7.87, 7.85, 7.74, 7.52, 7.48, 7.26, 7.14, 7.12, 7.05, 6.94, 6.81, 6.77, 6.72, 6.55 (m, Ar-H), 6.01 (s,  ${}^{1}J(Si,H) = 192$  Hz,  ${}^{2}J(Si,H) = 39$  Hz, Si-H, *cis*-4), 5.64 (s,  ${}^{1}J(Si,H) = 191 \text{ Hz}$ ,  ${}^{2}J(Si,H) = 40 \text{ Hz} Si-H$ , *trans*-4), 4.55, 4.41, 4.17, 3.73, 3.41, 3.16, 2.79, 2.68, 2.41 (each hept., 'Pr-CH), 1.47, 1.63, 1.57, 1.53, 1.49, 1.42, 1.39, 1.25, 1.19, 1.14, 1.10, 0.98, 0.93, 0.88, 0.67, 0.57, 0.53, 0.30, 0.28, 0.21 (<sup>*i*</sup>Pr-CH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, RT)  $\delta = \delta = 158.13, 157.15, 155.94, 155.55, 155.05,$ 154.68, 154.38, 154.16, 153.28, 151.13, 150.5, 150.32, 150.18, 147.28, 143.43, 143.34, 135.12, 133.63, 126.08 (Ar-C), 137.84, 137.75, 137.58, 137.43, 136.43, 135.44, 135.28, 135.12, 132.91, 132.79, 130.05, 126.24, 123.58, 123.40, 123.20, 122.85, 122.70, 122.40, 121.40 (Ar-CH), 38.08, 37.07, 36.06, 35.81, 35.76, 35.54, 35.22, 35.16, 34.77, 34.68, 34.63, 34.57, 34.01, 33.77, 31.97, 30.24, 29.03, 28.25, 27.61, 26.94, 25.82, 25.52, 25 40, 25.25, 25.04, 24.77, 24.46, 24.33, 24.11, 24.01, 23.95, 23.86, 23.55, 23.45, 23.27, 23.07, 22.90, 22.15 (<sup>*i*</sup>Pr-CH<sub>3</sub>). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = -8.6$  (<sup>1</sup>J (Si,P) = 49 Hz, SiP, trans-4), -27.0 (<sup>1</sup>J (Si,P) = 35 Hz, SiP, cis-4), -28.2 (<sup>2</sup>J (Si,P) = 20 Hz, trans-4), -40.4 (<sup>2</sup>J (Si,P) = 2 Hz, cis-4). <sup>31</sup>P NMR  $(C_6D_6) \delta = -41.2 (^1J(Si,P) = 35 \text{ Hz}), cis-4), -58.5 (^1J(Si,P) = -58.5)$ 49 Hz,  ${}^{2}J(Si,P) = 20$  Hz, trans-4).

**Thermolysis of 2c.** A sample of 100 mg (0.12 mmol) of **2c** was heated to 140 °C for 1 h. After cooling to room temperature the sample was analysed by NMR spectroscopy. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = 7.1$  (<sup>1</sup>*J* (Si,P) = 91 Hz, minor isomer), -8.5 (<sup>2</sup>*J* (Si,P) = 14 Hz, major isomer), -46.2 (<sup>1</sup>*J* (Si,P) = 62 Hz, major isomer), -59.2 (<sup>2</sup>*J* (Si,P) = 13 Hz, minor isomer). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta = -44.1$  (minor isomer), -56.0 (<sup>1</sup>*J*(Si,P) = 62 Hz, major isomer).

General procedure for the synthesis of phosphino disilene complexes 5a,b. A mixture of 0.3 mmol of  $[Pd(PCy_3)_2]$  and 0.3 mmol of the appropriate phosphino disilene was dissolved in 10 mL of benzene and stirred at room temperature leading to a gradual darkening. The reaction was complete after 18 h at the indicated temperature (5a: 20 °C; 5c: 50 °C) affording a 1:1 mixture of free PCy<sub>3</sub> and 5a or 5b, respectively. The solvent was distilled off in vacuum. Complex 5a was crystallised from hexane as redorange crystals suitable for X-ray diffraction in 10% isolated yield.

 $\eta^2$ -[1-Diphenylphosphanyl-1,2,2-tris(2',4',6'-triisopropyl-phenyl)disileno]-tricyclohexylphospino-palladium(0), 5a. <sup>1</sup>H NMR  $(C_6D_6) \delta = 8.07$  (br), 7.44 (br), 7.04, 7.02, 6.98 (pseudo-t), 5.16, 4.47, 4.16, 4.12, 3.99, 3.72, 2.78, 2.77, 2.72 (each hept, each 1H), 1.92 (br m), 1.74 (br m), 1.67, 1.64, 1.41, 1.35, 1.26, 1.25, 1.23, 1.21, 1.18, 1.17 (each d), 1.10 (br m), 0.99, 0.90, 0.88, 0.56, 0.55, 0.50, 0.42, 0.42 (each d). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 157.08, 154.88, 153.19, 152.89, 152.56, 149.69, 149.32, 148.96, 141.34, 138.77 (br), 137.9 (d), 133.32 (br) 132.51, 129.26 (br), 125.78 (br), 122.69, 122.61, 122.21, 122.12, 121.97, 121.71, 40.48, 37.78, 37.68, 37.56, 37.49, 37.06, 36.60, 34.71, 34.53, 33.52, 33.46, 32.25, 32.18, 31.71, 31.58, 31.36, 31.33, 28.68, 28.16, 28.02, 27.92, 27.82, 26.93, 26.50, 26.45, 26.01, 25.10, 25.03, 24.62, 24.26, 24.12, 24.04, 23.99, 23.74, 23.41.<sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, RT)  $\delta$  = 43.9 (dd, <sup>2</sup>J (Si,P) = 29 Hz, <sup>2</sup>J (Si,P) = 13 Hz), -3.3 (dd, <sup>1</sup>J (Si,P) = 105 Hz,  ${}^{2}J$  (Si,P) = 23 Hz).  ${}^{31}P$  NMR (C<sub>6</sub>D<sub>6</sub>, RT)  $\delta$  = 22.5 (d,  ${}^{3}J(P,P)$  = 3 Hz), 10.0 (PCy<sub>3</sub>), -33.2 (d,  ${}^{3}J(P,P) = 3$  Hz,  ${}^{1}J(P,Si) = 105$  Hz). UV/Vis (hexane)  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 491 nm (3800), 443 (4500).

**η**<sup>2</sup>-[1-Diisopropylphosphanyl-1,2,2-tris(2',4',6'-triisopropyl-phenyl)disileno]-tricyclohexylphospino-palladium(0), 5b. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, RT) δ = 48.0 (dd, <sup>1</sup>J(Si/Si) = 90 Hz, <sup>2</sup>J (Si,P) = 31 Hz, <sup>2</sup>J (Si,P) = 13 Hz), 1.1 (dd, <sup>1</sup>J(Si/Si) = 90 Hz, <sup>1</sup>J (Si,P) = 105 Hz, <sup>2</sup>J (Si,P) = 22 Hz). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, RT) δ = 21.9 (s), 10.0 (PCy<sub>3</sub>), -21.5 (s, <sup>1</sup>J(P,Si) = 105 Hz).

#### X-ray structure determination

The solid state structures of 2c, 3, and  $cis-4\dagger$  (Table 1) were determined on a Bruker SMART Apex II diffractometer equipped with a CCD area-detector and a custom-made cooling device; the structure of 5a on an Oxford diffraction Xcalibur PX Ultra. Absorption corrections based on symmetry equivalent reflections were applied using SADABS.14 The structures were solved using the SHELXTL program package<sup>15</sup> by Direct Methods (2c, 3, 5a) or Patterson synthesis (4). Dynamic or static disorder phenomena were observed in lateral sections of the molecules and accounted for as follows. One cyclohexyl-group of 2c (C52 to C57) was disordered over two positions (ca. 82% and 18% occupancy) and anisotropically refined without restraints. One para-isopropyl groups of 3 (C40 to C42) was refined anisotropically on split positions with restraints applied to (idealised) geometries and the thermal parameters of neighbouring atoms. The same group (C40, C41, C42) showed disorder in case of 4 and was refined anisotropically on split positions with restraints to thermal parameters only. In 5a, the included hexane solvent molecule was found to be disordered about a centre of symmetry. Two unique orientations of ca. 36% and 14% occupancy were identified (two further orientations are generated by the centre of symmetry), their geometries were optimised, and all of the atoms were refined isotropically with the thermal parameters of neighbouring atoms restrained to be similar. All other non-hydrogen atoms (2c, 3, 4, 5a) were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms except for H1 in 3, which was located on the difference electron density map and isotropically refined, were constrained to ideal geometries and refined with fixed isotropic displacement parameters.

Table 1	Data of structure	determinations	by si	ngle crysta	l X-ray	diffraction
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Compound	2c	3	4	$5a \cdot 0.5(C_6H_{14})$
Formula	C <sub>57</sub> H <sub>91</sub> PSi <sub>2</sub>	C45H69ISi2	C57H79PSi2	$C_{78}H_{119}P_{2}PdSi_{2}$
$M/g \text{ mol}^{-1}$	863.45	793.08	851.35	1281.25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	20.8212(12)	23.6013(19)	13.5451(9)	19.87013(7)
b/Å	10.5035(6)	10.7701(9)	20.3454(13)	14.06651(4)
c/Å	26.2637(16)	17.9227(14)	19.0323(12)	27.06129(8)
$\alpha/^{\circ}$	90	90	90	90
$\beta/^{\circ}$	103.603(1)	98.941(2)	97.780(1)	100.9683(3)
$\gamma/^{\circ}$	90	90	90	90
$V/Å^3$	5582.6(6)	4500.4(6)	5196.7(6)	7425.55(4)
Ζ	4	4	4	4
$\rho/\mathrm{g}\mathrm{cm}^{-3}$	1.027	1.171	1.088	1.146
T/K	173	173	173	173
$\theta_{\rm max}/^{\circ}$	25.03	25.03	25.03	72.58
F(000)	1904	1680	1856	2764
λ/Å	0.71073	0.71073	0.71073	1.54184
$\mu/\mathrm{mm}^{-1}$	0.125	0.792	0.134	3.016
Reflections Collected	42316	43109	40563	90750
Unique	9822	7936	9158	14685
Observed $[I > 2\sigma(I)]$	9336	7337	8432	13722
Restraints	0	12	32	97
Parameters	614	481	589	771
$R_{\rm int}$	0.0346	0.0203	0.0330	0.0257
$R_1[I > 2\sigma(I)]$	0.0839	0.0345	0.0645	0.0268
$wR_2$ (all data)	0.1694	0.0846	0.1479	0.0714
GOF on $F^2$	1.283	1.049	1.209	1.061
Largest Diff. Peak, Hole/e Å <sup>-3</sup>	0.701/-0.596	0.756/-0.487	0.469/-0.355	0.340/-0.422

#### **Results and discussion**

#### Synthesis and characterisation of phosphino disilenes

Reaction of one equivalent of the appropriate *P*-chlorophosphines with disilenide 1 in toluene at room temperature afforded the yellow to red-orange phosphino disilenes **2a-d** ( $\mathbf{R} = \mathbf{Ph}$  (**2a**), 'Pr (**2b**), Cy (**2c**), 'Bu (**2d**)) in 95 to 99% purity without further purification (Scheme 1). Despite the high solubility of **2a-d** in all inert organic solvents, **2a** and **2c** could be crystallised at 0 °C from a minimum amount of hexane, which allowed for obtaining meaningful UV/vis data and combustion analysis in these cases.



**Scheme 1** Synthesis of phosphino disilenes **2a-d** (Tip = 2,4,6-triisopropylphenyl, **2a**: R = Ph, **2b**:  $R = {}^{t}Pr$ , **2c**: R = Cy = cyclohexyl, **2d**:  $R = {}^{t}Bu$ ).

All phosphino disilenes **2a-d** show distinct set of two <sup>29</sup>Si NMR doublets due to the coupling with the <sup>31</sup>P nucleus (Table 2). The signals of **2b-c** are considerably broadened, presumably due to hindered rotation around the Si–P bond, which can be expected to lead to the presence of two or more rotamers. The <sup>29</sup>Si chemical shifts, ranging from 52.5 to 54.4 ppm for the phosphorus-bound silicon atom and from 95.4 to 98.8 ppm for the β-Si atom, are fairly independent of the substituents on phosphorus and of the same magnitude as the previously reported monosilyl disilenes. <sup>124,13</sup> The excellent signal-to-noise ration in case of the <sup>29</sup>Si NMR spectrum of the t-butyl derivative **2d** allowed for the observation of <sup>29</sup>Si satellites and thus the determination of the <sup>1</sup>*J*(Si,Si) coupling of

**Table 2** <sup>29</sup>Si and <sup>31</sup>P NMR data of disilenes phosphine disilenes **2a–d**, iododisilene **3**, and complexes **5a,b** (chemical shifts  $\delta$  in ppm and coupling constants in Hz)

Compound	$\delta^{\scriptscriptstyle 29}Si_\alpha$	$\delta^{\scriptscriptstyle 29}Si_\beta$	$^{1}J(Si,Si)$	$\delta^{\scriptscriptstyle 31} P$	$^{1}J(Si,P)$	$^{2}J(Si,P)$
2a	54.4	96.5	а	-45.7	116	76
2b	53.2	96.6	a	-21.9	118	ca. 60
2c	52.5	95.4	a	-36.3	ca. 115	ca. 60
2d	53.0	98.8	143	8.9	133	88
3	51.7	76.8	128	_		_
5a	-3.3	43.9	a	-33.2	105	29
5b	1.1	48.0	90	-21.5	105	31

" Not observed

the Si=Si bond. The value of 143 Hz is smaller than the one observed for tetraaryl disilenes, *e.g.*  $Tip_2Si=Si(Tip)Ph (^1J(Si,Si) = 151.4 Hz)^{16}$  suggesting a larger s-character of the bonding. This observation coincides with a relatively large P,Si coupling constant (Table 2). It may therefore be attributed to a decreased Si–Si double bond character due allylic delocalisation brought about by the planarising effect of the two t-butyl groups at the phosphorus atom.

As to be expected, the <sup>31</sup>P NMR shifts (Table 2) are much more variable, but follow the well known trend associated to the differing steric (and electronic) demand of the groups attached to phosphorus as described by the Tolman cone angle.<sup>17</sup> The constitution of compounds was deduced from the observed coupling patterns in a straightforward manner (though the couplings were partially obscured by the broad signals in case of **2b** and **2c**). Not surprisingly, the <sup>1</sup>J(Si,P) increases with the steric demand of the substituents at phosphorus, because the s-character of the Si–P bond is increased as an sp<sup>2</sup>-like situation is approached. This is particularly obvious in case of the t-butyl derivative **2d** with its relatively small Si,Si coupling constant (*vide supra*).

UV/vis spectroscopy of **2a** and **2c** in hexane solution (the two phosphino disilenes of reliable purity, because obtained in crystalline form) revealed longest wavelength absorptions and extinction coefficients typical of the  $\pi$ - $\pi$ \* transition of triaryl disilenes<sup>12,13,16</sup> ( $\lambda_{max} = 423$  (**2a**), 416 (**2c**) nm;  $\varepsilon = 18400$  (**2a**), 19000 (**2c**) M<sup>-1</sup>cm<sup>-1</sup>).

X-ray diffraction on single crystals of 2c confirmed the structural assignment based on the spectroscopic data (Table 1, Fig. 1). The Si(1)–Si(2) bond distance with 2.1542(11) Å is at the short end of what has been observed for Si=Si bonds. The P-Si distance (P(1)–Si(1) 2.2367(12) Å) is relatively short as well considering the bulk of the substituents. For comparison, the P-Si distance in HC(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>PPh<sub>2</sub>) - arguably with less bulky substituents - has been determined to 2.295 Å.18 The short P-Si bond in 2c is presumably due to the smaller coordination number of Si1, but may in fact also indicate a certain allylic delocalisation in accordance with the NMR spectroscopic findings for the t-butyl derivative 2d. The sums of angles around both silicon atoms are close to the 360° of a trigonal planar coordination environment  $(\sum \text{ angles} = 359.47^{\circ} \text{ (Si(1))}, 358.99^{\circ} \text{ (Si(2))}. \text{ Distortions from})$ planarity are small: the *trans*-bent angles  $\theta$  (derived from the angle between the Si(1)-Si(2) vector and the normal of the planes defined by the silicon atom and the pending atoms) are moderate ( $\theta_{si(1)} =$ 7.7°,  $\theta_{Si(2)} = 8.9^{\circ}$ ), as is the twisting between the two planes ( $\tau =$ 3.5(1)°).



Fig. 1 Structure of 2c in the solid state. Ellipsoids drawn at 50% probability. H atoms and disordered cyclohexyl group omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)-Si(2) 2.1542(11); Si(1)-P(1) 2.2367(12); Si(1)-C(1) 1.898(3); Si(2)-C(16) 1.904(3); Si(2)-C(31) 1.892(3); Si(2)-Si(1)-P(1) 110.51(5); C(52)-P(1)-C(46) 102.6(2); C(46)-P(1)-Si(1) 107.39(12); C(52)-P(1)-Si(1) 108.2(2).

## Synthesis, characterisation and reactivity towards $\mathbf{Ph}_2\mathbf{PLi}$ of an iodo disilene

Even though the syntheses of phosphino disilenes **2a-d** worked well after some optimisation, initial problems with unwanted side reactions prompted us to explore the possibility of an "umpolung" strategy. Recently, Tokitoh *et al.* reported the reaction of a 1,2-dibromo disilene with organyl lithium to afford the mono substitution products.<sup>19</sup> In order to obtain an electrophilic version

of 1, we reacted disilenide 1 with a very slight excess (1.02 eq) of iodine at -80 °C affording orange iodo disilene 3 in spectroscopically almost quantitative yield (Scheme 2).



Scheme 2 Synthesis of iodo disilene 3 and alternate generation of diphenylphosphino disilene 2a by an "umpolung" strategy (Tip = 2,4,6-triisopropylphenyl).

The isolation of **3** from the reaction mixture, however, proved tedious due to the apparent thermal instability of **3**. In solution is decomposes to unidentified brownish products within days even at -30 °C. Nonetheless, we were able to isolate **3** as yellow crystals in 12% yield by crystallisation from hexane. In crystalline form, the orange **3** is persistent at -30 °C.

The <sup>29</sup>Si NMR signals of **3** at 76.8 and 51.7 ppm are assigned to the Tip<sub>2</sub>Si and TipSiI fragments, respectively, on the basis of 2D <sup>29</sup>Si/<sup>1</sup>H correlations. The good signal to noise ratio again allowed for the observation of <sup>29</sup>Si satellite signals and thus the determination of the one-bond coupling constant (<sup>1</sup>*J*(Si, Si) = 128 Hz). The significantly smaller value in comparison to those of phosphino disilene **2d** and other triaryl disilenes<sup>12,13,16</sup> seems to be at odds with Bent's rule that s-character of orbitals tends to be directed towards the more electropositive groups. On the other hand, according to the CGMT model<sup>20</sup> electronegative substituents lead to increased *trans*-bending of the Si=Si bond, and therefore decrease the direct overlap between s-type orbitals.

The structure of **3** in the solid state was determined to address this question (Fig. 2). The Si(1)–Si(2) distance of 2.1914(9) Å is the first indication of a weaker Si=Si bond in accordance with the CGMT model. In line with that observation, the *trans*-bent angles are very large ( $\theta_{Si(1)} = 25.7^{\circ}$ ,  $\theta_{Si(2)} = 30.6^{\circ}$ ). For comparison, the *trans*-bent angles of Tip<sub>2</sub>Si=Si(Tip)Ph were determined to  $\theta_{Si(1)} =$ 23.6° and  $\theta_{Si(2)} = 22.3^{\circ}$ . The Si(1)–I distance of 2.4520(7) Å is of a typical length.



**Fig. 2** Structure of **3** in the solid state. Thermal ellipsoids drawn at 50% probability. H atoms omitted for clarity. Selected bond lengths [Å] and angles[°]:Si(1)–Si(2) 2.1914(9); Si(1)–I(1) 2.4520(7); Si(1)–C(1) 1.874(2); Si(2)–C(16) 1.902(2); Si(2)–C(31) 1.898(2); Si(2)–Si(1)–I(1) 113.86(3); C(1)–Si(1)–I(1) 110.00(7); C(1)–Si(1)–Si(2) 128.20(7); C(31)–Si(2)–C(16) 108.96(9); C(31)–Si(2)–Si(1) 115.81(7); C(16)–Si(2)–Si(1) 124.07(8).

Addition of Ph<sub>2</sub>PLi (prepared by deprotonation of Ph<sub>2</sub>PH with n-butyl lithium) to one equivalent of **3** at -90 °C affords **2a** as the only phosphorus containing product according to the <sup>31</sup>P NMR. The <sup>1</sup>H NMR spectrum contained all characteristic signals of **2a**. However, a significant (apparently phosphorus-free) impurity was detected by <sup>29</sup>Si NMR with signals at -41.4 and -69.1 ppm, which was also observed in the product mixture of the synthesis of the starting material **3** and was therefore possibly carried through from this stage of the synthesis.

Nonetheless, the "umpolung" strategy appears to be a feasible alternative for the introduction of the  $Tip_2Si=SiTip$ -moiety. Given the considerable additional effort, however, this reaction sequence would only be a sensible option if either the nucleophilic functional disilene or the electrophilic substrate is unavailable, hazardous or difficult to access.

#### Thermal rearrangement of phosphino disilenes 2a,c

In the case of a chlorodiphenylsilyl disilene,<sup>12d</sup> we had observed the formation of a trisilaindane derivative upon melting, which was explained by a transient silylene insertion into one of the *ortho*–CH bonds of one of the phenyl groups. Melting of neat **2a** should produce the 1-phospha-2,3-disilaindane in an analogous fashion, invoking a 1,2-phosphino shift to produce a transient silylene intermediate (Scheme 3).<sup>21</sup>



Scheme 3 Thermal rearrangement of 2a to a mixture of diastereomers of CH insertion product 4 (Tip = 2,4,6-triisopropylphenyl).

Thus, keeping a solid sample of diphenylphosphino disilene **2a** at 140 °C for one hour affords a mixture of diastereomers in a 65:35 ratio. Crystallisation from hexane only allows for a marginal enrichment of one of the isomers (72:28) of **4**.

On grounds of their two sets of <sup>29</sup>Si satellites, the <sup>1</sup>H NMR signals at 6.01 (72%) and 5.64 (28%) are identified as due to Si–H groups, tentatively assigned of *cis*- and *trans*-4, respectively. Both signals exhibit virtually identical coupling constants to two <sup>29</sup>Si nuclei (*cis*-4: <sup>1</sup>J(Si,H) = 192 Hz, <sup>2</sup>J = 39 Hz; *trans*-4: <sup>1</sup>J(Si,H) = 191 Hz, <sup>2</sup>J = 40 Hz). Due to the fact that meaningful NOESY spectra could not be obtained, the assignment of the more intense signal to the *cis*-diastereomer is based on the assumption of lower steric strain in *cis*-4 due to reduced 1,3-diaxial interactions. The <sup>29</sup>Si and <sup>31</sup>P NMR spectra of the diastereomeric mixture reveal interesting differences in the coupling constants. The <sup>1</sup>J(Si,P) and <sup>2</sup>J(Si,P) coupling constants are significantly smaller in the major isomer, *cis*-4, than in *trans*-4, suggesting a larger p-character in the P–Si bond (*cis*-4: <sup>1</sup>J (Si,P) = 35 Hz, <sup>2</sup>J(Si,P) = 2 Hz; *trans*-4: <sup>1</sup>J(Si,P) = 49 Hz, <sup>2</sup>J(Si,P) = 20 Hz).

The structure of *cis*-4 determined by X-ray diffraction on single crystals reveals a possible explanation for this observation (Fig. 3). The endocyclic angles at P(1), Si(1), and Si(2) are considerably smaller than the angles in an ideal pentagon ( $108^{\circ}$ ) and thus show a relatively high p-character (C(46)–P(1)–Si(2) 97.97(8)°, C(47)–



**Fig. 3** Structure of *cis*-4 in the solid state. Thermal ellipsoids drawn at 50% probability. H atoms except for H1 and isopropyl groups omitted for clarity. Selected bond lengths [Å] and angles[°]:Si(1)–Si2 2.3601(9); Si(2)–P(1) 2.3075(9); Si(1)–H(1) 1.37(2); Si(1)–C(1) 1.904(2); Si(1)–C(47) 1.889(2); Si(2)–C(16) 1.917(2); Si(2)–C(31) 1.913(2); P(1)–C(46) 1.844(3); P(1)–C(52) 1.849(3); C(47)–Si(1)–Si(2) 97.59(8); P(1)–Si(2)–Si(1) 90.57(3); C(46)–P(1)–Si(2) 97.97(8).

Si(1)–Si(2) 97.59(8)°; P(1)–Si(2)–Si(1) 90.57(3)°). This finding is in line with the usual reluctance of third row elements to hybridise, but only possible due to a strong envelope distortion of the five-membered ring (dihedral angles C(46)–P(1)–Si(2)–Si(1) 29.19(8), C(47)–Si(1)–Si(2)–P(1) 28.92(8)°).

In turn, this distortion brings the phenyl group close together with the *cis*-substituent on the  $\beta$ -silicon atom; a situation, which is much more favourable if this substituent is hydrogen (*cis*-4) rather than a Tip group as in *trans*-4. Conversely, although we were unable to obtain crystals of *trans*-4 the increased 1,3-interactions would presumably flatten the five-membered ring, which would lead to larger endocyclic angles and thus more s-character and larger coupling constants.

The cyclohexyl substituted **2c** similarly undergoes a CHinsertion reaction upon heating, presumably yielding a mixture of two diastereomers as well as suggested by two sets of high-field <sup>29</sup>Si and <sup>31</sup>P NMR signals very similar to that of **4**. Due to noncrystalline nature of the products, however, the constitution of the insertion products remains to be confirmed.

## Complexation of phosphino disilenes 2a,b to a 12-electron palladium fragment

The Pd(0) precursor  $[Pd(PCy_3)_2]$  has previously been used by Kira and co-workers for the synthesis of disilene complexes with a  $\pi$ -complex-like coordination mode of the Si–Si double bond.<sup>9</sup> This encouraged us to apply the same reagent towards phosphino disilenes **2a** and **2b** (Scheme 4).



Scheme 4 Formation of phosphine disilene complexes 5a,b (Tip = 2,4,6-triisopropylphenyl, Cy = cyclohexyl, 2a: R = Ph, 2b: R =  $^{\prime}$ Pr).

Indeed, the reactions of **2a** and **2b** with  $[Pd(PCy_3)_2]$  proceed smoothly at 25 and 50 °C, respectively, with concomitant

elimination of free PCy<sub>3</sub>. The disilene complexes **5a**,**b** are formed in almost quantitative spectroscopic yield. Isolation of pure **5a**,**b**, however, proved to be tedious and only **5a** could be crystallised in approx. 10% yield forming crystals suitable for X-ray diffraction.

The structure of the 5a,b can be readily derived from the spectroscopic data. In particular, the <sup>29</sup>Si NMR is instructive with the two doublets of doublets, each signal being high-field shifted by approximately 50 ppm with respect to the free phosphino disilene ligand (Fig. 4, Table 2). This implies a coordination of the Si=Si bond to the palladium centre. The short relaxation times  $T_1$  of the <sup>29</sup>Si nuclei of **2b** ( $T_1 \approx 1.0$  s for  $\delta = 48.0$  ppm;  $T_1 \approx 1.5$  s for  $\delta = 1.1$  ppm) allowed for the sufficiently rapid accumulation of the <sup>29</sup>Si NMR spectrum and therefore the observation of the <sup>29</sup>Si satellites for **2b**. The thus determined coupling constant of  ${}^{1}J(Si, Si) = 90$  Hz is distinctly smaller than for the free ligand: suggesting considerable backbonding from Pd to the Si=Si  $\pi^*$ orbital. The <sup>29</sup>Si-<sup>31</sup>P couplings constants are significantly smaller as well, which indicates a lower s-character of the P-Si bond implying that the donation from the Si=Si bond to the palladium centre is predominantly effected by s-type orbitals. The <sup>31</sup>P NMR signals of the phophino groups of the disilenes in the complex 5a,b show very similar chemical shifts to that of 2a,b providing a first indication that the phosphorus atom does not directly coordinate to the metal in either complex. The small <sup>31</sup>P-<sup>31</sup>P coupling constant of 3 Hz in 5a (not observed in 5b) supports this interpretation by being more in line with a <sup>3</sup>J than with a <sup>2</sup>J coupling. Apparently, the strong  $\sigma$ -donation by the Si=Si bond as well as the considerable  $\pi$ -backbonding from the Pd centre easily compensates the undoubtedly much more pronounced steric strain imposed by the observed coordination mode, which essentially reflects the low thermodynamic stability of Si–Si  $\pi$ -bonding.



**Fig. 4** <sup>29</sup>Si NMR signals of **5b** showing the doublet of doublet coupling patterns and <sup>29</sup>Si satellites.

The UV/vis spectrum of **5a** shows two considerably overlapping transitions at  $\lambda_{max} = 491$  nm and 443 nm. The extinction coefficients at maximum absorption are both of the same order of magnitude with approximately  $\varepsilon = 4000 \text{ M}^{-1} \text{ cm}^{-1}$ , which is less than a quarter of that of the precursor **2a**. The very broad appearance of the bands prevents further interpretations, but a charge transfer contribution involving the Pd centre can be considered as likely.

The solid state structure of **5a** confirms the structural features deduced from the spectroscopic data (Fig. 5). While the Si=Si moiety coordinates to the Pd centre (Pd–Si(1) 2.3764(4), Pd–Si(2)



Fig. 5 Structure of 5a in the solid state. Thermal ellipsoids drawn at 50% probability. H atoms and isopropyl groups as well as co-crystallised hexane omitted for clarity. Selected bond lengths [Å] and angles[°]:Pd–Si(1) 2.3764(4); Pd–Si(2) 2.3424(4); Pd–P(2) 2.4604(4); Si(1)–Si(2) 2.2569(5); Si(1)–P(1) 2.2696(5); Si(1)–C(1) 1.9145(14); Si(2)–C(16) 1.9027(14); Si(2)–C(31) 1.9194(14); P(1)–C(46) 1.8528(16); P(1)–C(52) 1.8404(15); P(2)–C(58) 1.8561(17); P(2)–C(64) 1.8665(15); P(2)–C(70) 1.8577(16); Si(2)–Pd–Si(1) 57.142(12); Si(1)–Pd–P(2) 156.049(13); Si(2)–Pd–P(2) 140.325(13).

2.3424(4) Å), the pending phosphino group does not participate in the coordination sphere of the transition metal. The coordination environment is similar to that of the disilene  $\pi$ -complexes **6** and **7**.<sup>9</sup>

The much more significant steric congestion in **5a** in concert with the unsymmetrical substitution pattern at the Si=Si bond, however, leads to a few differences with respect to **6**. The two Si-Pd-P angles (Si(1)-Pd-P(2) 156.049(13)°; Si(2)-Pd-P(2) 140.325(13)°) are much closer to one another than what had been observed by Kira for **6** (128.94 and 171.83°).<sup>9</sup>



In addition, while in **6** the P atom of the phosphine ligand lies approximately in the Si–Si–Pd plane, in **5a** the deviation of P(2) from the Si(1)–Si(2)–Pd plane amounts to 0.5953(5) Å. A similar deviation has been found for 1,2-disilacyclohexene complex **7**, in which the [*Z*]-geometry of the Si=Si bond accounts for the necessary discrimination in terms of steric demand. The Si(1)– Si(2) bond of **5a** (compared to **2c** due to the absence of solidstate structural information of **2a**) is elongated from 2.1542(11) to 2.2569(5) Å, hence by 4.8% (**6**: 3.2%; **7**: 1.9%). The bent-back angles  $\theta$  (**5a**:  $\theta_{Si1} = 16.0^{\circ}$ ,  $\theta_{Si2} = 17.2^{\circ}$ , which are another criterion for the degree of  $\pi$ -back-donation, are considerably larger than in **6** ( $\theta_{Si1} = 4.4^{\circ}$ ,  $\theta_{Si2} = 9.7^{\circ}$ ) and **7** ( $\theta_{Si1} = 6.7^{\circ}$ ,  $\theta_{Si2} = 7.2^{\circ}$ ). The sum of observation provides unambiguous prove for a substantial metallacyclopropane character of **5a,b**.

#### Conclusions

We reported two different synthetic access routes to phosphinosubstituted disilenes of type **2**: the first makes use of the established nucleophilic reagent, disilenide **1**; the other route employs the electrophilic iodo disilene **3**, which is the first example of an iodo functionalised disilene. In terms of thermal stability, phosphino disilenes resemble the corresponding chlorosilyl disilenes, previously reported by us. In close analogy to these chlorosilyl disilenes, the phosphino disilenes **2a,c** rearrange into 1-phospha-2,3-disilaindanes upon melting, presumably *via* a transient silylene derivative.

Most importantly, the first transition metal complexes of silicon analogues to vinyl phosphines have established the stark contrast that the Si=Si double bond coordinates in preference to the P-Atom of the phosphino group benefitting from considerable  $\pi$ backdonation despite the coordination to a very electron-poor 12-electron [PdPCy<sub>3</sub>] fragment.

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