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Reactivity of Pt(0) bromosilylene complexes towards ethylene†

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The base-free carbazolyl bromosilylene RSiBr (R = 1,8-bis(3,5-di-*tert*-butyl-phenyl)-3,6-di-*tert*-butyl-carbazolyl) reacts with (η^2-C_2H_4)Pt(PPh_3)$_2$ and Pt(PCy_3)$_2$ to form platinasilacyclobutane R(Br)Si(C_2H_4)Pt(PPh_3)$_2$ (1) and silylene platinum complex R(Br)SiPt(PCy_3)$_2$ (2), respectively. When silylene complex 2 is treated with C_2H_4, the six-membered metallasilacycle R(Br)Si(C_2H_4)$_2$Pt(PCy_3)$_2$ (3) is obtained. All compounds are characterised by XRD and multinuclear NMR spectroscopy.

Silylenes are the heavier congeners of carbenes and consequently, they are strong σ-donors. The isolation of silylene transition metal complexes has been synthetically targeted since the discovery of carbene complexes in the 1960s.[1] Additionally, silylene transition metal species attracted considerable attention as proposed intermediates in catalytic transformations of organosilicon compounds.[2]

Recently, amidinato silylenes with tri- coordinated Si atoms were demonstrated to form stable complexes. As they can be readily incorporated in various ligand scaffolds, this field has seen rapid development.[3–13]

Platinum complexes, in particular, have been known to catalyse silane dehydropolymerization,[14] hydrosilylation[15] or substituent redistribution reactions on silicon[16] since the 1970s. However, the isolation of a platinum silylene complex remained until in 1993, the cationic Fischer-type complex [*trans*-(Cy_3P)$_2$(H)Pt=Si(SEt)$_2$][BPh_4] (**I**) was synthesised by Tilley and Rheingold *via* anion abstraction from a platinum silyl precursor (Scheme 1).[17] Later, Tilley spectroscopically showed that the silylene complex [(dippe)Pt(H)=SiMes_2][MeB(C_6F_5)$_3$] (**II**) could be generated through the 1,2-migration of hydrogen from silicon to platinum.[18] Subsequently in 1998, the group succeeded in the preparation and crystallographic characterisation of the first neutral platinum silylene complex [Mes_2Si=Pt(PCy_3)$_2$] (**III**). In this approach, the transient silylene [Mes_2Si] was generated *via* photolysis of trisilane Mes_2Si(SiMe_3)$_2$ and trapped with Pt(PCy_3)$_2$.[19,20] A variety of heterobimetallic and multinuclear platinum complexes with bridging silylenes were published by the group of Osakada.[21–25] With the discovery of stable silylenes,[26] the direct coordination of free silylenes to unsaturated transition metal fragments became another option to access silylene metal complexes.[27] For instance, Iwamoto and Kira employed the bulky dialkylsilylene $R^H{}_2$Si (R^H = 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl) in reactions with Pt(0) bis(phosphane) compounds to generate silylene platinum complexes [$R^H{}_2$Si = Pt(PL_2)] (L = Me or Cy) (**IV**).[28] Related compounds were synthesised by Iwamoto and Kato, respectively and studied regarding their catalytic activity in hydrosilylation and isomerisation reactions.[29–33] A homoleptic platinum(0) complex containing two bis(guanidinato) silylene ligands was obtained by Tacke *via* reduction of a Pt(II) precursor.[34] The first complexes of base-free halosilylenes were reported by Sasamori and Tokitoh who prepared sterically congested 1,2-dibromodisilenes which, upon treatment with Pt(PCy_3)$_2$ dissociated and formed the bromosilylene platinum complex [Bbt(Br)Si=Pt(PCy_3)$_2$] (**V**) (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl).[35] Such halosilylene ligands may serve as precursors for further functionalisation by metathesis. We have reported on the base-free halosilylenes RSiX (X = Br, I), in which the use of a sterically demanding carbazole scaffold R (R = 1,8-bis(3,5-di-*tert*-butyl-phenyl)-3,6-di-*tert*-butyl-carbazolyl) facilitates the stabilisation of the reactive silicon centre.[36] In this contribution we report on the coordination behaviour of the carbazolyl bromosilylene towards platinum complexes and their reactivity towards ethylene.

As the first Pt(0) source (η^2-C_2H_4)Pt(PPh_3)$_2$ was chosen since the silylene should be capable of replacing C_2H_4 as a ligand at the Pt(0) centre. (η^2-C_2H_4)Pt(PPh_3)$_2$ was reacted with one molar equivalent of carbazolyl bromosilylene at room temperature for 12 hours. The formation of a new product (**1**)

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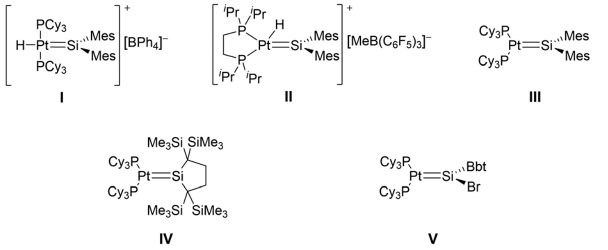
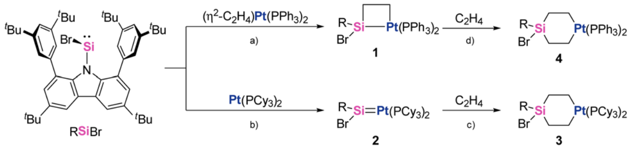


Scheme 1 Examples of platinum silylene complexes (R = Me or Cy).

could be observed judging from the ^{1}H, ^{29}Si and ^{31}P NMR spectra of the reaction mixture (Scheme 2). However, the significant high-field shift of the ^{29}Si NMR resonance from 129.2 ppm in RSiBr to −35.9 ppm in the reaction mixture indicated the presence of a tetra-coordinated silicon atom rather than three-fold coordination. Orange crystals were obtained from a concentrated toluene solution *via* vapour diffusion with *n*-pentane.

Structure elucidation by X-ray diffraction revealed that compound **1** features a four-membered platinasilacyclobutane core with a tetra-coordinated silicon atom (Fig. 1). Thus, it formally constitutes the product of a [2+2] cycloaddition between R(Br)Si=Pt(PPh$_3$)$_2$ and C$_2$H$_4$. Four-membered platinasilacycles were first isolated by Osakada two decades ago, though these compounds were synthesised from silyl platinum precursors and mostly contain unsaturated C–C bonds.[37–39] More recently, a structurally related nickelasilacycle was reported by Driess.[40] Compound **1** exhibits a Si–Pt bond length of 2.3065(7) Å which is comparable to that in a similar platinasilacycle reported by Osakada (2.367(3) Å).[37] The C1–C2 distance (1.560(4) Å) is elongated relative to (η^2-C$_2$H$_4$)Pt(PPh$_3$)$_2$ (1.43(2) Å)[41] but compares well to the respective bond distance in Driess' nickelasilacyclobutane (1.556(3) Å).[40] Within the metallacycle of **1**, the two planes, defined by the Si–Pt–C1 and Pt–Si–C2 atoms, intersect at an angle of 17.1(1)° and as further judged from the bond angles, the square exhibits a twisted conformation. Accordingly, the square-planar coordination environment at platinum and the tetrahedral geometry at silicon are slightly distorted. The Si–N bond length (1.793(2) Å) is only marginally shortened relative to the starting material RSiBr (1.801(2) Å).[36]



Scheme 2 Synthesis of compounds **1–4** starting from RSiBr. Reaction conditions: (a) toluene, RT, 12 h; (b) toluene, RT, sonication 15 min; (c) toluene, 1 atm C$_2$H$_4$, RT, 12 h; (d) C$_6$D$_6$, 1 atm C$_2$H$_4$, 80 °C, 72 h.

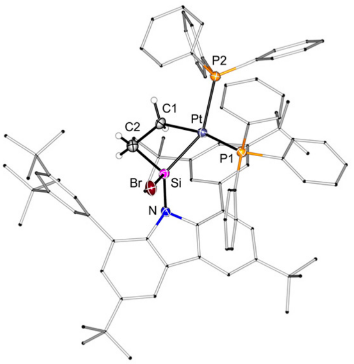


Fig. 1 Molecular structure of **1** in the solid state. Hydrogen atoms and ellipsoids of the carbazole ligand and the Ph$_3$ units are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si–Pt 2.3065(7), C1–C2 1.560(4), Pt–C1 2.143(3), Si–C2 1.853(3), Si–N 1.793(2), Si–Br 2.2880(8), Si–Pt–C1 64.64(8), C1–Pt–P2 88.11(8), P2–Pt–P1 102.93(2), P1–Pt–Si 103.25(2), C2–Si–Pt 91.97(9), Pt–Si–N 127.27(8), N–Si–Br 106.04(8), Br–Si–C2 109.31(10), Pt–C1–C2 107.6(2), C1–C2–Si 88.1(2).

Platinasilacyclobutane **1** was further characterised by multinuclear NMR spectroscopy (Fig. 2). The ^{29}Si NMR resonance is found in the characteristic region for Si(IV) compounds at −35.9 ppm as a doublet signal with coupling to one phosphorus nucleus ($^2J_{\mathrm{SiP1}}$ = 263 Hz) and a set of ^{195}Pt satellites ($^1J_{\mathrm{SiPt}}$ = 1510 Hz). Since the two phosphorus nuclei are magnetically non-equivalent, the ^{31}P NMR spectrum exhibits a doublet of doublets at 26.4 ppm arising from P1–P2 coupling ($^2J_{\mathrm{P1P2}}$ = 10 Hz) and two different phosphorus-platinum couplings ($^1J_{\mathrm{P1Pt}}$ = 1505 Hz, $^1J_{\mathrm{P2Pt}}$ = 2076 Hz). Accordingly, the ^{195}Pt NMR spectrum shows a doublet of doublets at −4617.7 ppm with the respective coupling constants.

We next probed the reactivity of bromosilylene RSiBr towards Pt(PCy$_3$)$_2$. Here, no potentially reactive moiety is precoordinated to the platinum fragment and the reaction should lead to the targeted silylene complex R(Br)SiPt(PCy$_3$)$_2$. Both compounds were mixed as solids and toluene was added. Upon sonication for 15 minutes the solution changed its colour from yellow to bright orange. In this case, the character-

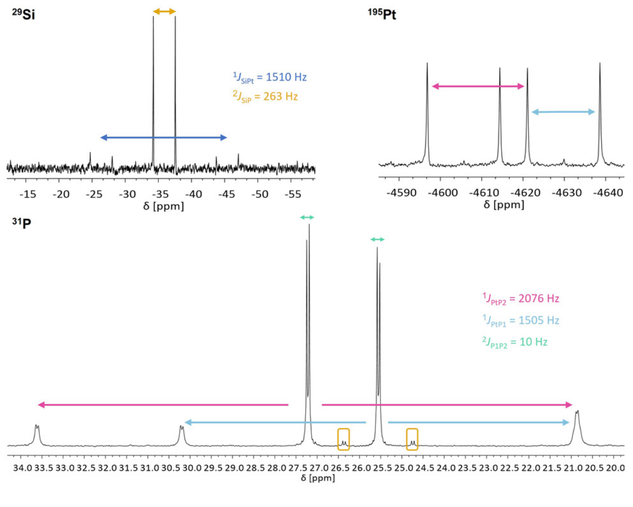


Fig. 2 Multinuclear NMR spectra of **1** in C$_6$D$_6$.

istic down-field shift of the ^{29}Si NMR resonance from 129.2 to 235.5 ppm suggested the formation of silylene platinum complex **2**. Orange crystals of **2** were obtained from immediate concentration of the reaction solution and storage at −40 °C for 24 hours, alongside yellow crystals which were identified as $Pt(PCy_3)_2$.

The molecular structure of complex **2** was determined by X-ray diffraction (Fig. 3). The Si–Pt distance of 2.1858(5) Å is shorter than in previously reported platinum silylene complexes (**I**, **III–V**, 2.21–2.27 Å), indicating Si–Pt double bond character in the solid state.[17,19,28,35] Judging from the bond angles around silicon, the silylene ligand adopts a Y-shaped geometry. Such an arrangement was also observed for Tilley's $[Mes_2Si{=}Pt(PCy_3)_2]$ (**III**), while bromosilylene complex **V** shows a T-shaped arrangement.[19,35] Summation of angles around Si and Pt confirms planarity for both atoms. The plane of the silylene ligand, defined by the Br, N and Si atoms and the coordination plane of platinum, defined by the Pt, P1 and P2 atoms, intersect at an angle of 83°. An ideal dihedral angle of 90° for π-donation from platinum to silicon is thus closely approached. In contrast, reported values for this angle were 69° in $[Mes_2Si{=}Pt(PCy_3)_2]$ (**III**) and 72° in $[Bbt(Br)Si{=}Pt(PCy_3)_2]$ (**V**), most probably due to the greater steric congestion in these complexes.[19,35] The Si–N bond in **2** (1.8218(16) Å) is elongated compared to the starting material RSiBr (1.8018(14) Å).[36] This might be attributed to π-donation from Pt d-orbitals to the silylene p-orbital upon which the p–p-interaction between the carbazole-N and the Si atom decreases. Moreover, in platinum complex **2** the silicon atom is bent out of the plane, spanned by the carbazole unit, by approximately 73°, while in RSiBr the Si atom is situated in the carbazole plane between the two arene units.

The multinuclear NMR spectra of $R(Br)SiPt(PCy_3)_2$ (**2**) are displayed in Fig. 4. The ^{29}Si NMR resonance can be found in the characteristic low-field region at 235.5 ppm as a triplet signal with coupling to the phosphorus nuclei ($^2J_{SiP}$ = 147 Hz) and a set of ^{195}Pt satellites ($^1J_{SiPt}$ = 3570 Hz). The corresponding ^{31}P NMR singlet resonance is obtained at 59.8 ppm ($^1J_{PPt}$ = 3833 Hz), while in the ^{195}Pt NMR, the triplet signal arises at −4644.9 ppm. NMR spectroscopic parameters of compound **2** compare well to bromosilylene platinum complex **V** (δ_{Si} = 298.11 ppm, $^2J_{SiP}$ = 137 Hz, $^1J_{SiPt}$ = 3660 Hz, $^1J_{PPt}$ = 3300 Hz).[35] Relative to the silylene complexes **I–IV**, the ^{29}Si NMR resonance of **2** is high-field shifted (*cf.* δ_{Si} = 309–394 ppm), while the $^1J_{SiPt}$ value is larger (*cf.* **I–III** $^1J_{SiPt}$ = 1305–2973 Hz).[17–19,28] Judging from these parameters the silylene RSiBr should exhibit enhanced σ-donor as well as π-acceptor character as compared to carbon-substituted silylene ligands.

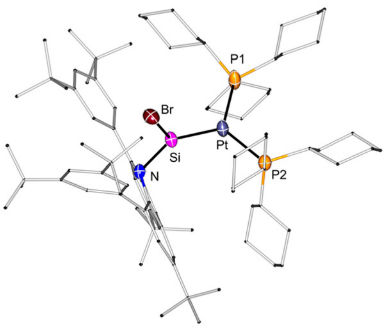


Fig. 3 Molecular structure of **2** in the solid state. Hydrogen atoms and ellipsoids of the carbazole ligand and the Cy$_3$ units are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si–Pt 2.1858(5), Pt–P1 2.3061(6), Pt–P2 2.2882(5), 1.853(3), Si–N 1.821(2), Si–Br 2.2657(6), Si–Pt–P1 121.07(2), Si–Pt–P2 117.54(2), P1–Pt–P2 120.83(2), N–Si–Pt 135.80(6), N–Si–Br 102.58(5), Br–Si–Pt 119.90(2).

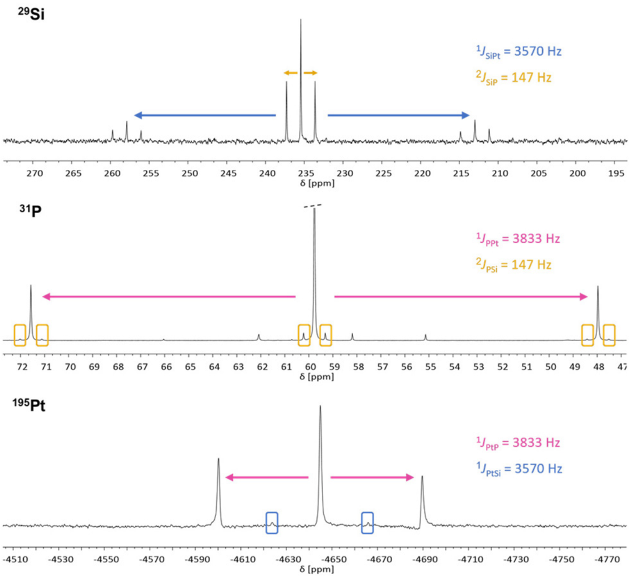
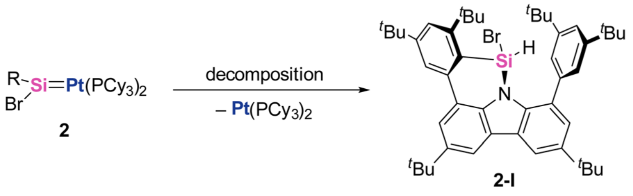


Fig. 4 Multinuclear NMR spectra of **2** in C$_6$D$_6$.

The UV-vis spectrum of silylene complex **2** in hexane solution exhibits an absorption band at 393 nm as well as several bands below 360 nm, explaining the yellow-orange colour of the compound. This is in accord with the spectra observed by Tokitoh, but here, no weak absorption in the range of 560 nm could be found.[35]

Bromosilylene platinum complex **2** decomposes in solution within one day at room temperature forming free $Pt(PCy_3)_2$ and a silicon-containing decomposition product (**2-I**) which was characterised by NMR spectroscopy (Scheme 3). While this compound could not be isolated from the mixture, independent structural proof could be obtained and allowed identifi-



Scheme 3 Decomposition of **2** to **2-I**.

cation (see ESI†). The insertion of the silicon atom into a C–H bond of the flanking arene groups might be attributed to an increased acidity of the silicon atom upon coordination to the metal fragment. A possible mechanism for the decomposition proceeds *via* the π-coordination of one of the flanking arene moieties to the low-coordinated silicon centre. Subsequently, the C–H bond may be activated at Si and the Pt complex can dissociate readily, as a Si(IV) compound is generated.

However, if complex **2** is freshly prepared and exposed to one atmosphere of C_2H_4, a colour change from orange to light yellow is observed after stirring at ambient temperature for 12 hours. Colourless crystals were grown from a concentrated *n*-heptane solution and the X-ray experiment confirmed the presence of the six-membered platinasilacycle $R(Br)Si(C_2H_4)_2Pt(PCy_3)_2$ (**3**). The insertion of π-systems into Pt–silylene bonds has already been described in 2015, though it has been demonstrated with bridging silylene ligands.[24] The molecular structure of compound **3** is depicted in Fig. 5. During the reaction, two molecules of C_2H_4 are added to the Si–Pt double bond, resulting in a cyclohexane type core with chair conformation and two C–C single bonds (1.557(11) Å and 1.537(11) Å). An early example of a six-membered Si–Pt-metallacycle was already isolated in 1992 within attempts to trap transient silylene species by reacting silyl platinum precursors with acetylene.[16] Later, one platinasilacyclohexane type structure was crystallographically characterised among the work on cyclic Si–Pt compounds by Osakada.[37] The Si–C (1.846(9) Å and 1.850(9) Å) and Pt–C (2.093(9) Å and 2.132(8) Å) bond distances in **3** show similar values to those reported for the literature known compound (Si–C(sp^3) 1.863(5) Å, Pt–C(sp^3) 2.148(5) Å).[37] However, because Osakada's metallacyle also comprises sp^2-hybridised carbon atoms, further structural parameters are not compared at this stage. The Si–N bond in complex **3** (1.783(7) Å) is shorter than in the starting material **2** which might be due to electron donation from the carbazole-N atom into the p-type orbital at silicon upon dissociation of the Si–Pt bond. As judged from the bond angles, the expected tetrahedral coordination geometry around the silicon atom is only slightly deformed. At platinum, the P1–Pt–P2 angle is widened to 108.96(9)°, resulting in a distorted square-planar coordination environment.

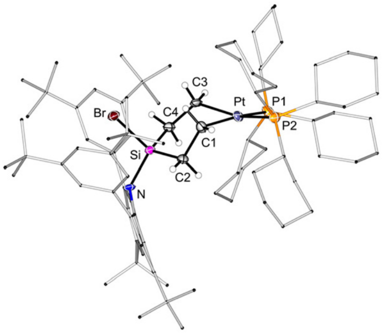


Fig. 5 Molecular structure of **3** in the solid state. Hydrogen atoms and ellipsoids of the carbazole ligand and the Cy_3 units are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. The program SQUEEZE was used to remove electron contribution of disordered solvent molecules.[42] Selected bond lengths [Å] and angles [°]: Si–C2 1.846(9), Si–C4 1.850(9), C1–C2 1.557(11), C3–C4 1.537(11), Pt–C1 2.093(9), Pt–C3 2.132(8), Si–N 1.783(7), Si–Br 2.237(2), N–Si–C2 109.5(4), C2–Si–C4 107.5(4), C4–Si–Br 105.7(3), Br–Si–N 109.1(3), C1–Pt–P2 86.0(3), P2–Pt–P1 108.96(9), P1–Pt–C3 86.0(3), C3–Pt–C1 81.7(4).

The ^{29}Si NMR resonance of $R(Br)Si(C_2H_4)_2Pt(PCy_3)_2$ (**3**) is found at 15.5 ppm. In the ^{31}P NMR experiment, the magnetically equivalent ^{31}P nuclei give rise to one signal at 21.0 ppm with ^{195}Pt satellites that display P–Pt coupling of $^1J_{PPt}$ = 1641.8 Hz. The corresponding ^{195}Pt NMR resonance is obtained as a triplet signal at −4655.5 ppm.

After isolating compound **3**, we wondered if the four-membered platinasilacyle **1** could also be expanded to a cyclohexane-like structure by insertion of another molecule of ethylene into the Pt–Si bond. Thus, **1** was reacted under one atmosphere of C_2H_4 for 72 hours at 80 °C. Judging from the NMR spectra, an analogous platinasilacyclohexane (**4**) formed, as the spectra closely resemble those of compound **3**. The ^{31}P NMR spectrum of **4** exhibits a singlet resonance at 26.8 ppm with a phosphorus platinum coupling constant of $^1J_{PPt}$ = 1761.7 Hz.

In summary, we have shown the distinct reactivity of stable bromosilylene RSiBr towards two Pt(0) compounds. With $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$, the platinasilacyclobutane-like product **1** is obtained. In contrast, the reaction of RSiBr with adduct-free $Pt(PCy_3)_2$ yields platinum silylene complex **2** which features a short Si–Pt bond and a down-field shifted ^{29}Si NMR resonance of 235 ppm. Though complex **2** is unstable in solution, it can be trapped *via* reaction with C_2H_4 to give six-membered platinasilacycle **3**. The four-membered platinasilacyle **1** can further be expanded by insertion of another molecule of C_2H_4 into the Si–Pt bond, yielding platinasilacyclohexane **4**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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