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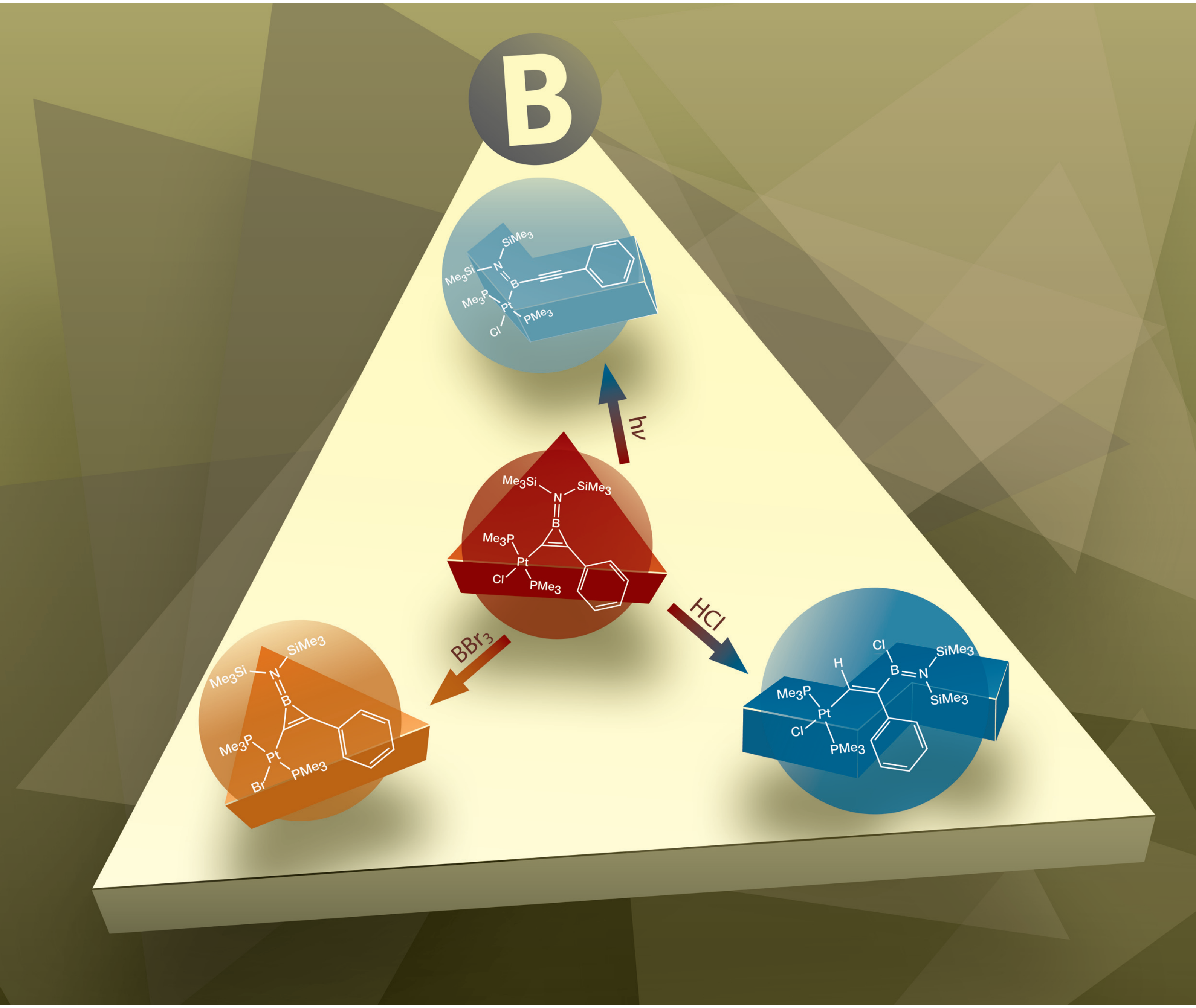

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PAPER

Reactivity of a platinum-substituted borirene†

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We report on (i) the reactivity of the title compound *trans*-[Cl(PMe$_3$)$_2$Pt{μ-BN(SiMe$_3$)$_2$C=C}Ph] (**1**), which underwent a photochemical rearrangement reaction to afford the platinum boryl complex *trans*-[Cl(PMe$_3$)$_2$PtBN(SiMe$_3$)$_2$C≡CPh] (**2**), (ii) a ring-opening reaction by chemoselective boron–carbon bond cleavage resulting in the amino(vinyl)borane *trans*-[Cl(PMe$_3$)$_2$PtCH=C(BClN-(SiMe$_3$)$_2$)Ph] (**3**), and (iii) a Cl–Br ligand exchange on the platinum atom yielding the Br-derivate *trans*-[Br(PMe$_3$)$_2$Pt{μ-BN(SiMe$_3$)$_2$C=C}Ph] (**4**). All compounds were fully characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction analysis.

Introduction

Borirenes, the smallest boron heterocycles, which are isoelectronic with cyclopropenium cations and thus exhibit 2π stabilization,[1] boroles, which possess 4π electrons and might be considered as the smallest neutral antiaromatic boracycles,[2] and borepines, which are isoelectronic with tropylium cations,[3] have attracted tremendous interest with regard to their potential Hückel aromaticity/antiaromaticity. In addition, functionalized boron-containing π-conjugated systems have gained much attention due to their promising applications as electronic materials.[4]

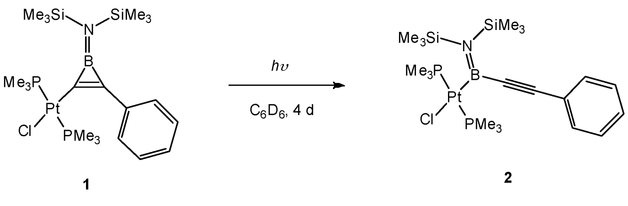
However, synthetic approaches to borirenes are scarce, and most of them represent time-consuming, low yielding protocols, which are difficult to reproduce and/or restricted in scope.[5] In 1984, Pues and Berndt reported on the reaction of (trimethyl-stannyl)alkynes with 1,2-di-*tert*-butyl-1,2-dichlorodiborane, Cl$_2$B$_2$*t*Bu$_2$, which afforded 1-*tert*-butylborirene in acceptable yield.[5] Later on, in 1987, Eisch *et al.* developed the photoisomerization of diaryl(arylethynyl)boranes, which allowed for the isolation and structural characterization of the corresponding borirenes, thus proving the theoretically predicted extensive 2π delocalization over the BCC three-membered ring, as indicated by the shortening of the endocyclic B–C bonds.[5b]An alternative route is given by [2 + 1] cycloaddition reactions of borylenes (:B–R) with alkynes. This strategy was first realized by Pachaly and West in 1984, and the resulting borirene species were characterized spectroscopically.[5d] However, the (triphenylsilyl)borylene employed in these experiments was generated photochemically under rather harsh conditions (−196 °C, hydrocarbon matrix). A much more convenient approach was disclosed in 2005 in our laboratories, that is the borylene transfer.[6] In this case, terminal borylene complexes [(OC)$_5$M=B=N(SiMe$_3$)$_2$] derived from group 6 metals (M = Cr, Mo, W), which can be prepared on a gram scale and can be handled under standard inert atmosphere conditions without difficulty,[7] act as powerful sources of borylenes. The borylene transfer from the coordination sphere of the metal onto C≡C triple bonds of alkynes,[8] and more recently on transition metal σ-alkynyl complexes,[9] thus provides straightforward and selective access to differently substituted borirenes. Besides the functionalization of C≡C triple bonds,[7–9] the borylene transfer protocol has also been applied to the synthesis of new transition metal borylene complexes,[10] metathesis reactions,[11] and the insertion of the :B–R fragment into olefinic C–H bonds.[12] The reactivity of borirenes can be summarized as follows: (1) ring-opening *via* cleavage of one endocyclic B–C bond (*vide infra*);[13,14] (2) photochemically induced metal borirene–boryl transformations (*vide infra*).[9b]

Recently, we presented preliminary results on the synthesis of platinum-substituted borirenes *via* borylene transfer.[9a] Herein, we report the results of our reactivity studies on the title compound **1** with respect to photochemical rearrangement, ring-opening, and Cl–Br ligand exchange at the platinum centre.

Results and discussion

Photochemical rearrangement

Pale yellow benzene-D$_6$ solutions of the platinum borirene *trans*-[Cl(PMe$_3$)$_2$Pt{μ-BN(SiMe$_3$)$_2$C=C}Ph] (**1**) were irradiated under dry argon at room temperature (Scheme 1). The reaction was



Scheme 1 Synthesis of [Cl(PMe$_3$)$_2$PtBN(SiMe$_3$)$_2$CCPh] (**2**).

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monitored by multinuclear NMR spectroscopy, which revealed gradual consumption of the starting materials and the quantitative formation of a new boron- and phosphorous-containing species with ^{11}B and ^{31}P NMR resonances at δ 48.8 and δ 15.8 ($^1J_{\mathrm{Pt,P}}$ = 3085 Hz), respectively. However, in contrast to the photoisomerization of the related iron borirene, which was completed within 5 h, full conversion required 4 days in the case of **1**.

The product of the photochemical rearrangement, that is the platinum (alkynyl)boryl complex *trans*-[Cl(PMe$_3$)$_2$PtBN(SiMe$_3$)$_2$C≡CPh] (**2**), was isolated by crystallization from a toluene–hexane mixture at −30 °C as an analytically pure, colorless crystalline solid in 65% yield. The spectroscopic data of **2** in solution are in good agreement with the proposed structure. In particular, two sharp signals for the nitrogen-bound trimethylsilyl groups at δ 0.64 and 0.70 with a relative intensity of 1 : 1 in the ^{1}H NMR spectrum at room temperature indicate a significantly enlarged rotational barrier about the boron–nitrogen bond, which is a consequence of the BCC ring-opening and a more pronounced B═N π-contribution. Furthermore, the resonance at δ 48.8 in the ^{11}B NMR spectrum falls in the expected range for a platinum boryl complex.[15] Single crystals of **2** suitable for X-ray diffraction analysis were obtained by cooling a solution of **2** in toluene–hexane to −35 °C. **2** crystallizes in the monoclinic space group $P2_1/c$, and a graphical representation of the molecular structure in the solid state is depicted in Fig. 1. Even though the quality of the crystals was satisfactory, extensive disorder of the whole boryl substituent precludes any detailed discussion of the structural parameters within this moiety. However, the data unambiguously confirm the presence of a square-planar platinum boryl species with the anticipated connectivity derived from spectroscopy in solution.

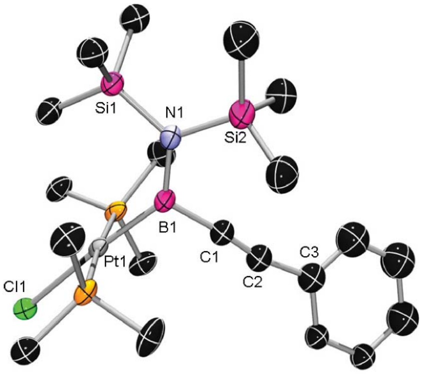
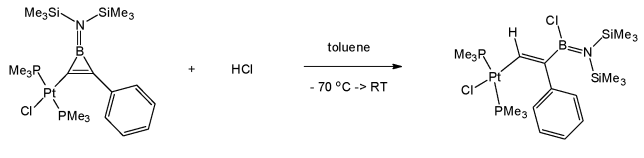


Fig. 1 Molecular structure of **2** in the solid state. Only the major disorder component is shown. Hydrogen atoms, disorder of the boryl substituent, and co-crystallized solvent molecules are omitted for clarity. Due to the extensive disorder of the whole boryl substituent, a discussion of the structural parameters is not possible.

Chemoselective boron–carbon bond cleavage

Borirenes, which are substituted exclusively by organic functionalities, are known to undergo ring-opening reactions by cleavage of one endocyclic B–C bond, initiated by weak Brønsted acids such as water, methanol, or ethanol,[13] or by hydroboration with 9-borabicyclo-[3.3.1]nonane (9-BBN).[14] Hence, we investigated the reactivity of the transition metal substituted borirene **1** towards HCl as a typical protic reagent. A pale yellow solution of **1** in toluene was treated with equimolar amounts of HCl dissolved in benzene at −70 °C. After work up, **3** could be isolated by crystallization from hexane at − 30 °C as an analytically pure, colorless crystalline solid in 38% yield (Scheme 2).



Scheme 2 Ring-opening of platinum-substituted borirene **1** with HCl.

The spectroscopic data of **3** in solution are in agreement with the proposed structure. In particular, the ^{1}H NMR spectrum features one triplet at δ 9.77 ($^3J_{\mathrm{P,H}}$ = 4.6 Hz) for an olefinic proton, thus confirming the boron–carbon bond cleavage. Interestingly, despite the BCC ring-opening, the rotational barrier of the B═N bond is not significantly increased, as indicated by the presence of only one resonance at δ 0.28 for the nitrogen-bound SiMe$_3$ group. Furthermore the ^{11}B NMR resonance at δ 44.8 is shifted to higher frequency by 12 ppm in comparison to the starting material **1** (δ 32.0).

Single crystals suitable for X-ray diffraction analysis were obtained by cooling a saturated hexane solution of **3** to −35 °C. The molecule crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit, both featuring very similar structural parameters. As the geometry of both subunits is identical within experimental error, only one set of data will be discussed in the following (Fig. 2). The results of the X-ray diffraction analysis confirm the C1–B1 bond cleavage with addition of a proton to C1 and attack of the nucleophile Cl$^-$ at the boron centre. The C1–C2 distance (1.357(10) Å) and the C2–B1 distance (1.557(11) Å) are in the expected ranges for C–B single and C═C double bonds, respectively, and are comparable to those determined recently for the ring-opening product of a metal-free borirene with 9-BBN (C1–C2 1.369(2) Å; C2–B1 1.575(2) Å).[14]

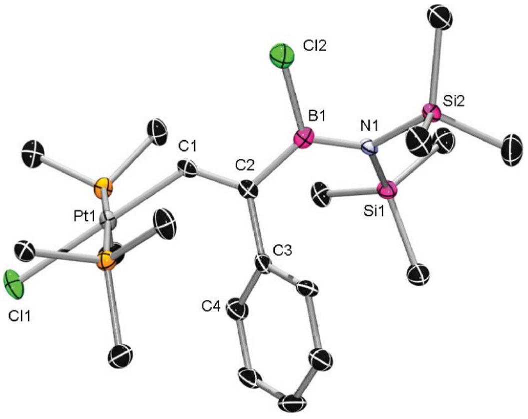


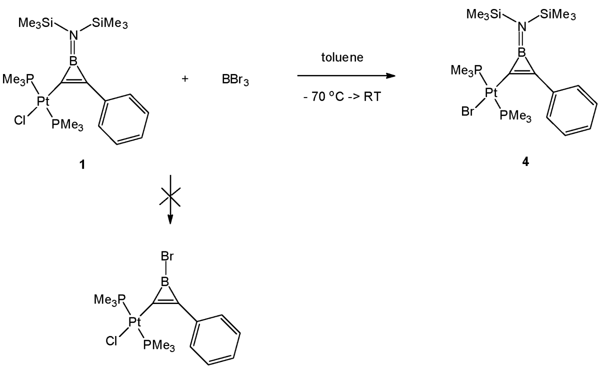
Fig. 2 Molecular structure of **3** in the solid state. Hydrogen atoms and the second independent molecule in the asymmetric unit are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–C11.993(7), C1–C2 1.357(10), C2–B1 1.557(11), B1–N1 1.424(10), C2–C3 1.505(10), B1–Cl2 1.810(9), C2–B1–Cl2 114.7(6), C2–B1–N1 128.0(7), N1–B1–Cl2 117.2(6), B1–N1–Si1 121.1(5), B1–N1–Si2 118.3(5), Si1–N1–Si2 120.6(3), C1–C2–C3 120.6(7), B1–C2–C3 117.8(6), B1–C2–C1 121.5(7).

The sums of angles around B1 (Σ = 359.9°) and N1 (Σ = 360.0°) document a planar coordination geometry for both atoms. The B1–N1 separation distance of 1.424(10) Å is similar to that in **1** (1.428(7) Å).

The Si1–N1–B1–C2 torsion angle of 38.91° suggests a reduced B═N π-contribution, which is presumably a result of an additional Cl–B π-interaction in combination with the pronounced steric congestion imposed by the bulky $N(SiMe_3)_2$ and Ph moieties. Moreover, the cleavage of the B1–C1 bond is accompanied by a slight increase of the Pt1–C1 separation (**3**: 1.993(7) Å; **1**: 1.974(5) Å).

Cl–Br ligand exchange at the platinum centre

Finally, we investigated whether the exocyclic B–N bond can be cleaved by boron tribromide to afford the platinum-substituted bromoborirene as shown in Scheme 3. Thus, a toluene solution of **1** was reacted with one equivalent of BBr_3 at −70 °C. The reaction was monitored by multinuclear NMR spectroscopy, which indicated the formation of a new boron- and phosphorous-containing species featuring resonances at δ 32.6 and δ −19.1 in the ^{11}B and ^{31}P NMR spectrum, respectively. After work up, an analytically pure, colorless crystalline solid was isolated by crystallization from hexane at – 30 °C.



Scheme 3 Synthesis of *trans*-[Br(PMe$_3$)$_2$Pt{μ-BN(SiMe$_3$)$_2$C═C}Ph] (**4**).

Unexpectedly, ^{1}H NMR spectroscopy provided clear evidence for the presence of nitrogen-bound trimethylsilyl groups (δ 0.47), which is inconsistent with the anticipated molecular structure of the product. Since the chemical shift of the ^{11}B NMR resonance remains almost unaffected by this chemical transformation (δ 32.0 for **1** *vs.* δ 32.6 for **4**), we reasoned that a Cl–Br ligand exchange reaction has occurred with retention of the overall structure of the BCC ring.

The formation of **4** was ascertained by X-ray diffraction analysis (Fig. 3). **4** crystallizes in the monoclinic space group $P2_1/n$. As shown in Table 1, the overall geometry of **4** strongly resembles that of the chloro precursor **1**, particularly with respect to the lengths of the endocyclic (C1–C2 1.367(4) Å; C1–B1 1.485(4) Å; C2–B1 1.488(4) Å) and exocyclic bonds (B═N 1.431(4) Å), which suggests extensive 2π delocalization within the BCC ring. In addition, the phenyl ring and the boracyclopropene unit adopt a slightly staggered arrangement, as indicated by a dihedral angle of 9.64°.

Table 1 Selected bond lengths [Å] of **1** and **4**

	1	4
Pt1–C1	1.974(5)	1.970(3)
C1–C2	1.374(7)	1.367(4)
B1–C1	1.511(8)	1.485(4)
B1–C2	1.482(8)	1.488(4)
B1–N1	1.428(7)	1.431(4)

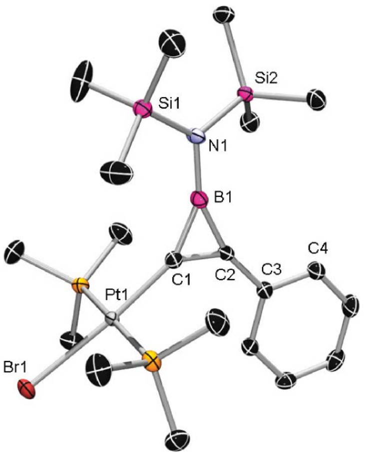


Fig. 3 Molecular structure of **4** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–C1 1.970(3), C1–C2 1.367(4), C2–C3 1.462(4), C1–B1 1.485(4), C2–B1 1.488(4), B1–N1 1.431(4), Pt1–C1–C2 142.2(2), Pt1–C1–B1 154.8(2), B1–C1–C2 62.72(19), C3–C2–C1 135.8(2), C3–C2–B1 161.7(2), B1–C2–C1 62.53(19), C1–B1–C2 54.76(18), N1–B1–C1 151.0(3), N1–B1–C2 154.0(3), Si1–N1–B1 118.21(19), Si2–N1–B1 114.86(19), Si1–N1–Si2 126.90(13).

Conclusions

We have presented the results of our reactivity studies on the platinum substituted (amino)borirene **1** upon UV irradiation, that is the migration of the borylene unit from the C≡C triple bond to the metal–carbon σ-bond with concomitant formation of an alkynylboryl complex (**2**). Moreover, the title compound **1** underwent a ring-opening reaction upon treatment with HCl, thus affording the new amino(vinyl)borane complex **3**, which was formed by selective cleavage of the B1–C1 bond. It should be mentioned that this is the first example of a ring-opening reaction of an asymmetric borirene. When treated with BBr_3, no cleavage of the boron–nitrogen bond in **1** was observed, but a Br–Cl ligand exchange on the platinum atom occurred, thus enabling the isolation of the Br-derivate **4**.

Experimental

General considerations

All manipulations were performed either under dry argon or *in vacuo* using standard Schlenk line and glovebox techniques. Solvents (toluene, benzene, hexane) were purified by distillation under dry argon from appropriate drying agents (sodium and sodium wire, respectively), and stored under the same inert gas atmosphere over molecular sieves. NMR spectra were acquired on a Bruker Avance 500 (^{1}H: 500.133; ^{11}B: 160.472; ^{13}C: 125.777 MHz) NMR spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to external TMS *via* the residual proton signal of the solvent (^{1}H)

or the solvent itself (^{13}C). ^{11}B{^{1}H} NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. ^{31}P{^{1}H} NMR spectra were referenced to 85% H_3PO_4. Microanalyses for C, H, and N were performed on either a Carlo Erba model 1106 or a LecoCHNS-932 Elemental Analyzer. BBr_3 was used as a 0.40 mol L^{-1} solution in hexane. HCl was used as a 0.24 mol L^{-1} solution in benzene. The platinum-substituted borirene *trans*-[Cl(PMe$_3$)$_2$Pt{μ-BN(SiMe$_3$)$_2$C═C}Ph] (**1**) was prepared according to the literature procedure.[9a] NMR spectroscopic experiments were performed in quartz or J. Young NMR tubes. The light source was a Hg/Xe arc lamp (400–550 W) equipped with IR filters, irradiating at 210–600 nm.

Synthesis of compound 2 (rearrangement)

In a 5 mm quartz NMR tube, a pale-yellow solution of **1** (40 mg, 0.06 mmol) in 0.8 mL of C_6D_6 was irradiated for 4 d at room temperature. The volatile components were removed under vacuum, and the yellow residue was extracted with 2 mL of hexane. The light yellow filtrate was concentrated to about 1 mL in volume, and stored at −30 °C overnight to yield colourless crystals of **2**. Evaporation of the filtrate afforded a second crop of analytically pure crystalline material (26 mg, 65%). ^{1}H NMR: δ = 0.64 (s, 9 H, Si(CH$_3$)$_3$), 0.70 (s, 9 H, Si(CH$_3$)$_3$), 1.47 (m, 18 H, P(CH$_3$)$_3$), 7.60 (d, $^3J_{\text{H-H}}$ = 7.0 Hz, 2H, CH-*o* of C$_6$H$_5$), 7.17 (t, $^3J_{\text{H-H}}$ = 7.4 Hz, 2H, CH-*m* of C$_6$H$_5$), 7.12 (t, $^3J_{\text{H-H}}$ = 7.3 Hz, 1H, CH-*p* of C$_6$H$_5$); ^{13}C{^{1}H} NMR: δ = 5.34 (s, Si(CH$_3$)$_3$), 6.21 (s, Si(CH$_3$)$_3$), 43.66 (m, P(CH$_3$)$_3$), 125.48 (s, c-*i* of C$_6$H$_5$), 128.63 (s, CH-*p* of C$_6$H$_5$), 128.80 (s, CH-*m* of C$_6$H$_5$), 130.66 (s, CH-*o* of C$_6$H$_5$), B–C═C not detected; ^{11}B{^{1}H} NMR: δ = 48.8 (s); ^{31}P{^{1}H} NMR: δ = −15.8 ($^1J_{\text{Pt,P}}$ = 3085 Hz); Elemental analysis (%) calcd. for $C_{20}H_{41}BNP_2Si_2ClPt$: C 36.67, H 6.31, N 2.14; found: C 37.65, H 6.35, N 2.99.

Synthesis of compound 3 (ring opening)

A pale yellow solution of **1** (50 mg, 0.076 mmol) in 3 mL of toluene was cooled to −70 °C and treated with a benzene solution of HCl (0.32 mL, *c* = 0.24 mmol mL^{-1}, 0.076 mmol). After warming to ambient temperature (*ca.* 1 h), the reaction mixture was filtered through a filter pipette in a glovebox and the filtrate evaporated to dryness. The pale yellow residue was extracted with 2 mL of hexane. After standing at ambient temperature for 1 h, the filtrate became turbid and was filtered again through a filter pipette, concentrated to about 1 mL in volume, and stored at −30 °C overnight to yield colourless crystals of **3** (20 mg, 38%). ^{1}H NMR: δ = 0.28 (s, 18 H, Si(CH$_3$)$_3$), 1.05 (vt, $^2J_{\text{P-H}}$ + $^4J_{\text{P-H}}$ = 7.6 Hz, 18 H, P(CH$_3$)$_3$), 8.09 (dd, $^3J_{\text{H-H}}$ = 8.2 Hz, $^4J_{\text{H-H}}$ = 1.2 Hz, 2H, CH-*o* of C$_6$H$_5$), 7.21 (t, $^3J_{\text{H-H}}$ = 7.7 Hz, 2H, CH-*m* of C$_6$H$_5$), 7.07 (t, $^3J_{\text{H-H}}$ = 7.4 Hz, 1H, CH-*p* of C$_6$H$_5$), 9.77 (t, $^3J_{\text{H-P}}$ = 4.6 Hz, 1H, HC═C); ^{13}C{^{1}H} NMR: δ = 3.90 (s, Si(CH$_3$)$_3$), 13.19 (m, P(CH$_3$)$_3$), 147.58 (s, c-*i* of C$_6$H$_5$), 126.00 (s, CH-*p* of C$_6$H$_5$), 127.59 (s, CH-*m* of C$_6$H$_5$), 130.16 (s, CH-*o* of C$_6$H$_5$), 166.10 (t, $^2J_{\text{P-C}}$ = 9.1 Hz, Pt-CH), B–C═C not detected; ^{11}B{^{1}H} NMR: δ = 44.8 (s); ^{31}P{^{1}H} NMR: δ = −16.2 ($^1J_{\text{Pt,P}}$ = 2769 Hz); Elemental analysis (%) calcd. for $C_{20}H_{42}BNP_2Si_2Cl_2Pt$: C 34.74, H 6.12, N 2.02; found: C 34.73, H 5.69, N 2.24.

Synthesis of compound 4 (Cl–Br exchange)

A pale yellow solution of **1** (50 mg, 0.076 mmol) in 3 mL of toluene was cooled to −70 °C and treated with a hexane solution of BBr_3 (0.19 mL, *c* = 0.40 mmol mL^{-1}, 0.076 mmol). After warming to ambient temperature (*ca.* 1 h), the reaction mixture was filtered through a filter pipette in a glovebox and the filtrate evaporated to dryness. The pale yellow residue was extracted with 2 mL of hexane. The filtrate was concentrated to about 1 mL in volume, and stored at −30 °C overnight to yield colourless crystals of **4** (8 mg, 15%). ^{1}H NMR: δ = 0.47 (s, 18 H, Si(CH$_3$)$_3$), 1.13 (m, 18 H, P(CH$_3$)$_3$), 8.43 (dd, $^3J_{\text{H-H}}$ = 8.1 Hz, $^4J_{\text{H-H}}$ = 1.3 Hz, 2H, CH-*o* of C$_6$H$_5$), 7.37 (t, $^3J_{\text{H-H}}$ = 7.7 Hz, 2H, CH-*m* of C$_6$H$_5$), 7.20 (t, $^3J_{\text{H-H}}$ = 7.4 Hz, 1H, CH-*p* of C$_6$H$_5$); ^{13}C{^{1}H}NMR: δ = 2.39 (s, Si(CH$_3$)$_3$), 13.03 (m, P(CH$_3$)$_3$), 133.17 (s, c-*i* of C$_6$H$_5$), 127.25 (s, CH-*p* of C$_6$H$_5$), 127.34 (s, CH-*m* or CH-*o* of C$_6$H$_5$), 127.66 (s, CH-*o* or CH-*m* of C$_6$H$_5$), *C* bonded to boron not detected; ^{11}B{^{1}H} NMR: δ = 32.6 (s); ^{31}P{^{1}H} NMR: δ = −19.1 ($^1J_{\text{Pt,P}}$ = 2703 Hz); Elemental analysis (%) calcd. for $C_{20}H_{41}BBrNP_2PtSi_2$: C 34.34, H 5.91, N 2.00; found: C 35.40, H 6.08, N 2.01.

Crystallographic data

The crystal data of **2–4** were collected on a Bruker X8PEX diffractometer with a CCD area detector and multi-layer mirror monochromated Mo$_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the SHELX software package (G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

Crystal data for 2 (rearrangement)

$C_{20}H_{41}BClNP_2PtSi_2$, M_r = 698.09, colourless plate, 0.29 × 0.15 × 0.04 mm^3, monoclinic space group $P2_1/c$, a = 9.4809(6) Å, b = 9.6771(6) Å, c = 33.348(2) Å, β = 91.352(3)°, V = 3058.7(3) Å^3, Z = 4, ρ_{calcd} = 1.516 g cm^{-3}, μ = 4.870 mm^{-1}, F(000) = 1404, T = 100(2) K, R_1 = 0.0490, wR_2 = 0.1127, 6243 independent reflections [$2\theta \le$ 52.78°] and 303 parameters.

Crystal data for 3 (ring opening)

$C_{20}H_{42}BCl_2NP_2PtSi_2$, M_r = 691.47, colourless plate, 0.12 × 0.085 × 0.025 mm^3, monoclinic space group $P2(1)/c$, a = 16.3309(9) Å, b = 9.2064(5) Å, c = 39.750(2) Å, α = 90.00°, β = 91.016(3)°, γ = 90.00°, V = 5975.4(6) Å^3, Z = 8, ρ_{calcd} = 1.537 g cm^{-3}, μ = 5.071 mm^{-1}, F(000) = 2752, T = 100(2) K, R_1 = 0.0719, wR_2 = 0.1130, 12 819 independent reflections [$2\theta \le$ 54.32°] and 547 parameters.

Crystal data for 4 (Cl–Br exchange)

$C_{20}H_{41}BBrNP_2PtSi_2$, M_r = 699.47, colourless block, 0.30 × 0.24 × 0.17 mm^3, monoclinic space group $P2_1/n$, a = 8.9084(5) Å, b = 21.5491(11) Å, c = 15.4872(8) Å, β = 106.388(2)°, V = 2852.3(3) Å^3, Z = 4, ρ_{calcd} = 1.629 g·cm^{-3}, μ = 6.524 mm^{-1}, F(000) = 1376, T = 100(2) K, R_1 = 0.0262, wR_2 = 0.0481, 7106 independent reflections [$2\theta \le$ 56.72°] and 265 parameters.

Acknowledgements

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