Electronic Supplementary Information

Borylene-Based Functionalization of Pt Alkinyl Complexes by Photochemical Borylene Transfer from $[(OC)_5Cr{=}BN(SiMe_3)_2]$

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1) Experimental details on the crystal structure determinations of compound 4:

The crystal data of **4** were collected on a Bruker X8APEX 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 idealised positions and were included in structure factors calculations.

Crystal data for **4**: $C_{20}H_{41}BClNP_2PtSi_2$, $M_r = 655.01$, colourless needle, 0.21×0.09×0.09 mm^3, Monoclinic space group $P2_1/c$, $a = 13.670(4)$ Å, $b = 19.510(6)$ Å, $c = 21.795(6)$ Å, $\beta = 92.514(12)°$, $V = 5807(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.498$ g·cm^{-3}, $\mu = 5.125$ mm^{-1}, $F(000) = 2608$, $T = 100(2)$ K, $R_1 = 0.0360$, $wR^2 = 0.0912$, 14305 independent reflections [$2\theta \leq 56.66°$] and 529 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-**742461**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure of 4:

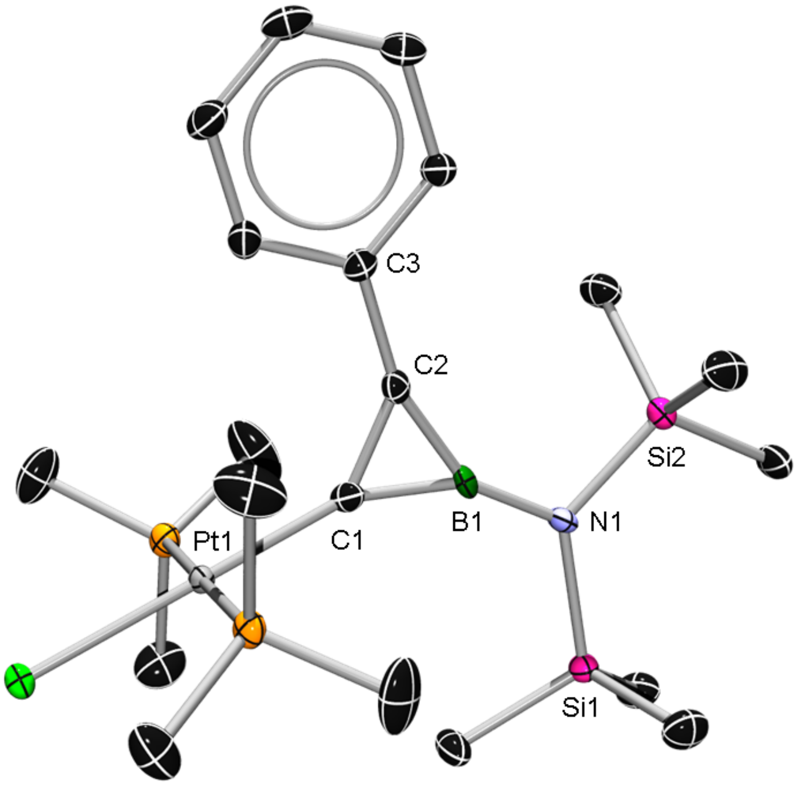

Fig. 1 Molecular structure of **4** in the solid-state. Selected bond lengths [Å] and angles [^{o}] for one of two independent molecules in the asymmetric unit, which feature very similar structures: C1-C2 1.374(7), C1-B1 1.511(8), C2-B1 1.482(8), B1-N1 1.428(7), Pt1-C1 1.974(5), C2-C3 1.466(7), N1-Si1 1.757(5), N1-Si2 1.754(5), C1-C2-B1 63.7(4), B1-C1-C2 61.6(4), C1-B1-C2 54.6(3), C1-B1-N1 153.9(5), C2-B1-N1 151.4(5), B1-C1-Pt1 157.3(4), C2-C1-Pt1 140.9(4), B1-N1-Si1 119.3(4), Si1-N1-Si2 125.2(3).

2) Experimental section

General Remarks: All manipulations were performed either under dry argon or in Vacuo using standard Schlenk line and glovebox techniques. Solvents (THF, ether, benzene and hexane were purified by distillation under dry argon from sodium and stored under the same inert gas over molecular sieves. NMR spectra were acquired on Varian Unity 500 (^{1}H: 499.834; ^{11}B: 160.364; ^{13}C: 125.697 MHz) or Bruker Avance 500 (^{1}H: 500.133; ^{11}B: 160.472; ^{13}C: 125.777 MHz) NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protio solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} spectra were referenced to external $BF_3{\cdot}OEt_2$ and TMS, respectively. NMR probe temperatures were calibrated using a MeOH standard for VT NMR spectroscopic studies. UV-vis were recorded in hexane. UV-vis absorption spectra were obtained on a Jasco V-660 spectrophotometer using standard 1 cm width quartz cells. Microanalyses were performed on a Leco CHNS-932 Elemental Analyzer. $Na_2[Cr(CO)_5]$[1], and $Cl_2B(SiMe_3)_2$[2] were prepared according to the literature. Borylene complexe $[(OC)_5CrBN(SiMe_3)_2]$ (**1**)[3], $Pt(PMe_3)_2Cl_2$[4] and Pt alkinyl complexe $[Cl(PMe_3)_2Pt\text{-}C{\equiv}CPh]$ (**3**)[5] were synthesized as reported in the literature. NMR spectroscopic experiments were performed in quartz NMR tubes. The light source was a Hg/Xe arc lamp (400-550 W) equipped with IR filters, irradiating at 210-600 nm. Large-scale experiments were performed in a 150-mL Schlenk flask equipped with a quartz cooling jacket into which a Hg lamp (125 W) was inserted vertically.

$ClPt(PMe_3)_2\{\mu\text{-}(BNSiMe_3)_2C{=}C\}Ph$ (4): In a 5 mm quartz NMR tube, a pale-yellow solution of **1** (48 mg, 0.10 mmol) and **3** (36 mg, 0.10 mmol) in 1.5 mL of THF was irradiated for 7 h at room temperature. The volatile components were removed under vacuum, and the brown residue was extracted with 8 mL of hexane. The light yellow filtrate was stored at -60 °C overnight to yield colourless crystals of **4**. Evaporation of the filtrate afforded a second crop of analytically pure crystalline material (35 mg, 53%). ^{1}H-NMR: δ = 0.46 (s, 18H, $Si(CH_3)_3$), 1.08 (m, 18 H, $P(CH_3)_3$), 8.39 (m, 2H, CH-*o* of C_6H_5), 7.36 (m, 2H, CH-*m* of C_6H_5), 7.18 (m, 1H, CH-*p* of C_6H_5); ^{13}C{^{1}H}-NMR: (*C* bonded to boron not detected), 3.78 (s, $Si(CH_3)_3$), 13.60 (m, $P(CH_3)_3$), 129.28 (s, c-*i* of C_6H_5), 125.39 (s, CH-*p* of C_6H_5), 128.08 (s, CH-*p* or CH-*m* of C_6H_5), 128.23 (s, CH-*p* or CH-*m* of C_6H_5); ^{11}B{^{1}H}-NMR: δ = 32.01(s); ^{31}P{^{1}H}-NMR: δ = -16.23 ($^{1}J_{Pt,\,P}$ = 3377 Hz); elemental analysis (%) calcd. for

$C_{20}H_{41}BNP_2Si_2ClPt$: C 36.67, H 6.31, N 2.14; found; C 36.68, H 6.32, N 2.44.

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