Borylene-based functionalization of Pt–alkynyl complexes by photochemical borylene transfer from $[(OC)_5Cr{=}BN(SiMe_3)_2]$†

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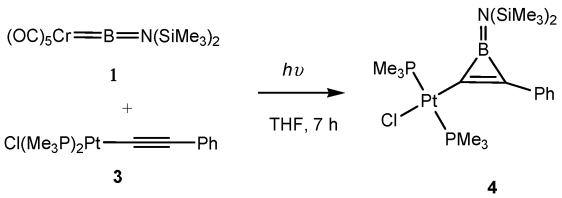
Photochemical borylene transfer from $[(OC)_5Cr{=}BN(SiMe_3)_2]$ to the platinum σ-alkynyl complex $[Cl(PMe_3)_2Pt{-}C{\equiv}CPh]$ gave facile access to the first transition metal–borirene complex. The title compound has been fully characterized in solution and by X-ray crystallography.

Since the first practical synthetic route to group 6 metal borylene complexes $[(OC)_5M{=}BN(SiMe_3)_2]$ (M = Cr, **1**; Mo, **2**) was developed in 1998,[1] the reactivity of these species has been the focus of intense research.[2] Most notably, these compounds have turned out to be convenient sources for the borylene fragment ":B–X", a hypovalent, highly reactive species that was only obtained under drastic conditions and which cannot be isolated as a free molecule.[3] Thus, $BN(SiMe_3)_2$ and related borylene moieties can be efficiently transferred to other transition metals[2g,4] or main-group-element substrates, such as alkenes[5] and alkynes.[6] The latter provides a facile access to borirenes, which are isoelectronic with cyclopropenium cations, and thus constitute the smallest boron heterocycle that might exhibit 2π-aromatic stabilization.[7] Moreover, boron-based π-conjugated systems have attracted much attention due to their interesting photophysical properties and their potential applications as electronic materials.[8] Following these important results, we turned our attention to the analogous borylene transfer to transition metal–alkynyl complexes, to obtain such frameworks involving d-block metals. Platinum–alkynyls were chosen as substrates for borylene transfer reactions, as these complexes also represent an important class of organometallics for optical and opto-electronic applications.[9] Herein, we report the preliminary results of borylene transfer to the platinum–alkynyl $[Cl(PMe_3)_2Pt{-}C{\equiv}CPh]$ (**3**), which leads to the first platinum-substituted borirene.

The title compound **4** was obtained upon photolysis of a pale yellow solution of **1** in the presence of an equimolar amount of platinum–alkynyl **3** for 7 h under dry argon at room temperature (Scheme 1). The reaction was monitored by multinuclear NMR spectroscopy, which revealed gradual consumption of the starting materials, and quantitative



Scheme 1 Synthesis of borirene **4** by photochemically-induced borylene transfer to Pt–alkynyl complex **3**.

formation of a new boron- and phosphorous-containing compound, as indicated by the presence of a new resonance at δ = 32.0 ppm in the $^{11}B\{^1H\}$ NMR spectrum, and at δ = −16.2 ppm ($^1J_{Pt,P}$ = 3377 Hz) in the $^{31}P\{^1H\}$ NMR spectrum (see the ESI†). The former signal is in the expected range for a borirene product.[6a,b,10]

The platinum-substituted amino borirene **4** was isolated by filtration of the reaction mixture and subsequent crystallization from hexanes at −60 °C as an analytically pure, colourless solid in 53% yield. At ambient temperature, the ^1H NMR signal of the nitrogen-bound $SiMe_3$ groups appears as a singlet, implying rapid rotation around the B–N bond.[6b]‡ However, at −75 °C the ^1H NMR spectrum clearly shows two signals for the nitrogen-bound trimethylsilyl groups, which are separated by 40 Hz. From 500 MHz VT ^1H NMR spectroscopy, the barrier to rotation about the boron–nitrogen bond was determined to have a value of $\Delta G^{\neq -}$ = 45.2 kJ mol^{-1} at the coalescence temperature of −55 °C, which is in good agreement with previously reported data for borirenes with a conjugated spacer [1,4-bis-{(μ-$(BNSiMe_3)_2$($SiMe_3C{=}C$)}C_6H_4] (38.7 kJ mol^{-1}) and the bis(borirene) [{(μ-$(BNSiMe_3)_2$-($SiMe_3C{=}C$)}$_2$] (43.1 kJ mol^{-1}).[6b] These values are significantly smaller than those commonly observed for aminoboranes of the general formula $R_2N{=}BR_2$ (71–100 kJ mol^{-1}),[11] thus supporting the presence of 2π-aromatic stabilization within the boron-containing 3-membered ring with incorporation of the p_z-orbital at boron, which reduces the B–N π-contribution.

Single crystals of **4** were grown from hexane *via* evaporation at room temperature. The result of the X-ray crystal structure analysis is displayed in Fig. 1.† The molecule crystallizes in the monoclinic space group $P2_1/c$, with two independent molecules in the asymmetric unit.‡ Both independent molecules, denoted as molecules **A** and **B**, feature very similar structures. The distances within the BCC-ring (C2–B1 = 1.482(8) Å (**A**), 1.487(8) Å (**B**), C1–B1 = 1.511 (8) Å (**A**), 1.502(8) Å (**B**), C1–C2 = 1.374(7) Å (**A**), 1.372(7) Å (**B**)) are comparable to those of previously reported structurally characterized aminoborirenes, which indicates the extensive delocalization of the two electrons over a three-center bonding molecular

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† Electronic supplementary information (ESI) available: Experimental details of all X-ray crystal structure determinations and a figure of the molecular structure of **4**. Experimental section including the syntheses, full characterization, and spectroscopic data of all compounds. CCDC reference number 742461. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b915926f

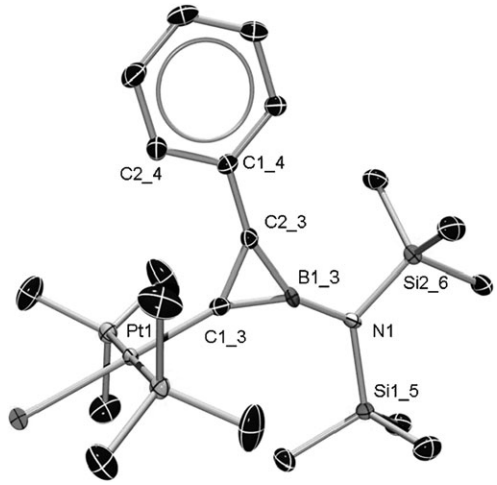

Fig. 1 The molecular structure of $ClPt(PMe_3)_2\{\mu\text{-}(BNSiMe_3)_2C{=}C\}Ph$ (**4**) in the solid state.

orbital comprised of the p_z-atomic orbitals of boron and carbon.[6] Consistent with the result from VT ^{1}H NMR spectroscopy, a slightly elongated B–N separation of 1.428(7) Å (**A**), 1.421(7) Å (**B**), which matches those of previously reported aminoborirenes, indicates a weaker π-interaction between the boron and nitrogen centers. The distance between Pt1, which is in square-planar arrangement, and the sp^2-hybridized C1 (1.974(5) Å (**A**), 1.973(5) Å (**B**)) is slightly elongated in comparison to that between Pt and the sp-hybridized carbon in *trans*,*trans*-$[(Ph_3P)_2(Cl)Pt{-}C{\equiv}C{-}Pt(PPh_3)_2(Cl)]$ (1.958(4) Å).[12]

UV-vis spectra of the Pt–alkynyl precursor **3** and the borirene **4** were recorded in hexane solution (Fig. 2).† The optical properties and electronic structures of Pt–alkynyl complexes have been well studied throughout the literature.[13] In comparison, the UV-vis spectra of **3** exhibit similar absorption bands between 250 and 300 nm, with vibronic contributions particularly from the C≡CPh ligand.[13b] In contrast, the spectra of the Pt-substituted borirene **4** display broad, featureless absorptions with maxima occurring at higher energies. Furthermore, most likely due to the organometallic substituent, the absorption maximum (λ_{max} = 247 nm) of **4** is somewhat blue-shifted with respect to those of previously reported main-group borirene compounds (257–276 nm).[6b]

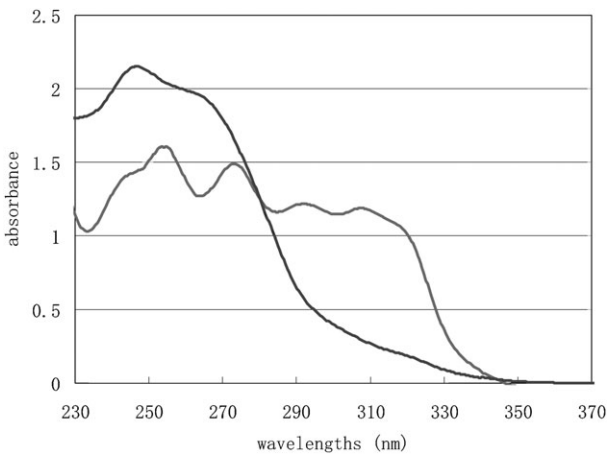

Fig. 2 UV-visible spectra of compound **3** (gray) and **4** (black) in hexane.

In summary, exploiting the ability of compounds **1** and **2** as convenient sources of the borylene moiety under standard conditions, we have reported the first successful borylene-based functionalization of metal–alkynyl complexes by photochemical borylene transfer. Structural and spectroscopic data of the Pt–borirene complex **4** indicate extensive π-delocalisation within the boron heterocycle. Studies targeting the transfer of the borylene unit to alkynyl complexes with different metals and to metal–alkynyl polymers are currently under way.

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Notes and references

‡ 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), b = 19.510(6), c = 21.795(6) Å, β = 92.514(12)°, V = 5807(3) Å^3, Z = 8, ρ_{calcd} = 1.498 g cm^{-3}, μ = 5.125 mm^{-1}, $F(000)$ = 2608, T = 100(2) K, R_1 = 0.0360, wR^2 = 0.0912, 14 305 independent reflections [$2\theta \leq 56.66°$] and 529 parameters.

Spectroscopic data for **4**: ^{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); $^{13}C\{^1H\}$ 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); $^{11}B\{^1H\}$ NMR: δ = 32.01(s); $^{31}P\{^1H\}$ NMR: δ = −16.23 ($^1J_{Pt,P}$ = 3377 Hz).

1 (*a*) H. Braunschweig, C. Kollann and U. Englert, *Angew. Chem.*, 1998, **110**, 3355 (*Angew. Chem., Int. Ed.*, 1998, **37**, 3179); (*b*) B. Blank, H. Braunschweig, M. Colling-Hendelkens, C. Kollann, K. Radacki, D. Rais, K. Uttinger and G. Whittel, *Chem.–Eur. J.*, 2007, **13**, 4770.

2 (*a*) H. Braunschweig and M. Colling, *J. Organomet. Chem.*, 2000, **614–615**, 18; (*b*) H. Braunschweig and M. Colling, *Eur. J. Inorg. Chem.*, 2003, 393; (*c*) H. Braunschweig, *Adv. Organomet. Chem.*, 2004, **51**, 163; (*d*) H. Braunschweig and D. Rais, *Heteroat. Chem.*, 2005, **16**, 566; (*e*) H. Braunschweig, C. Kollann and D. Rais, *Angew. Chem., Int. Ed.*, 2006, **45**, 5254; (*f*) S. Aldridge and D. L. Coombs, *Coord. Chem. Rev.*, 2004, **248**, 535; (*g*) C. E. Anderson, H. Braunschweig and R. D. Dewhurst, *Organometallics*, 2008, **27**, 6381.

3 (*a*) P. L. Timms, *J. Am. Chem. Soc.*, 1967, **89**, 1629; (*b*) P. L. Timms, *Acc. Chem. Res.*, 1973, **6**, 118; (*c*) B. Pachaly and R. West, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 454.

4 (*a*) H. Braunschweig, M. Colling, C. Kollann, B. Neumann and H.-G. Stammler, *Angew. Chem.*, 2001, **113**, 2359 (*Angew. Chem., Int. Ed.*, 2001, **40**, 2298); (*b*) H. Braunschweig, M. Colling, C. Hu and K. Radacki, *Angew. Chem.*, 2003, **115**, 215 (*Angew. Chem., Int. Ed.*, 2003, **42**, 205); (*c*) H. Braunschweig, M. Forster and K. Radacki, *Angew. Chem.*, 2006, **118**, 8036 (*Angew. Chem., Int. Ed.*, 2006, **45**, 2132); (*d*) H. Braunschweig, M. Forster, K. Radacki, F. Seeler and G. Whittell, *Angew. Chem.*, 2007, **119**, 5304 (*Angew. Chem., Int. Ed.*, 2007, **46**, 5212); (*e*) H. Braunschweig, M. Forster, T. Kupfer and F. Seeler, *Angew. Chem.*, 2008, **120**, 6070 (*Angew. Chem. Int. Ed.*, 2008, **47**, 5981).

5 H. Braunschweig, R. D. Dewhurst, T. Herbst and K. Radacki, *Angew. Chem.*, 2008, **120**, 6067 (*Angew. Chem., Int. Ed.*, 2008, **47**, 5978).

6 (*a*) H. Braunschweig, T. Herbst, D. Rais and F. Seeler, *Angew. Chem.*, 2005, **117**, 7627 (*Angew. Chem., Int. Ed.*, 2005, **44**, 7461); (*b*) H. Braunschweig, T. Herbst, D. Rais, S. Ghosh, T. Kupfer, K. Radacki, A. Crawford, R. Ward, T. Marder, I. Fernández and G. Frenking, *J. Am. Chem. Soc.*, 2009, **131**, 8989; (*c*) H. Braunschweig, I. Fernández, G. Frenking, K. Radacki and F. Seeler, *Angew. Chem.*, 2007, **119**, 5307 (*Angew. Chem., Int. Ed.*, 2007, **46**, 5215).

7 (*a*) M. E. Volpin, Y. D. Koreshkov, V. G. Dulova and D. N. Kursanov, *Tetrahedron*, 1962, **18**, 107. For INDO calculations, see: (*b*) C. U. Pittman, A. Kress, T. B. Patterson, P. Walton and

L. D. Kispert, *J. Org. Chem.*, 1974, **39**, 373; (*c*) N. L. Allinger and J. H. Siefert, *J. Am. Chem. Soc.*, 1975, **97**, 752. For *ab initio* calculations, see: (*d*) K. Krogh-Jespersen, D. Cremer, J. D. Dill, J. A. Pople and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 2589.

8 (*a*) N. Matsumi and Y. Chujo, in *Contemporary Boron Chemistry, Spec. Publ. No. 253*, ed. M. G. Davidson, A. K. Hughes, T. B. Marder and K. Wade, Royal Society of Chemistry, Cambridge, 2000, pp. 51–58; (*b*) C. D. Entwistle and T. B. Marder, *Angew. Chem.*, 2002, **114**, 3051 (*Angew. Chem., Int. Ed.*, 2002, **41**, 2927); (*c*) F. Jäkle, *J. Inorg. Organomet. Polym. Mater.*, 2005, **15**, 293; (*d*) D. Gabel, in *Science of Synthesis: Houben-Weyl Methods of Molecular Transformation*, ed. D. Kaufmann, D. S. Matteson, G. T. Verlag, Thieme, Stuttgart, 2005, vol. 6, p. 1277.

9 (*a*) J. Kavandi, J. Callis, M. Goutermann, G. Khalil, D. Wright, E. Green, D. Burns and B. McLachlan, *Rev. Sci. Instrum.*, 1990, **61**, 3340; (*b*) P. T. Furuta, L. Deng, S. Garon, M. E. Thompson and J. M. Frechet, *J. Am. Chem. Soc.*, 2004, **126**, 15388.

10 C. Habben and A. Meller, *Chem. Ber.*, 1984, **117**, 2531.

11 C. Brown, R. H. Cragg, T. J. Miller and D. O. Smith, *J. Organomet. Chem.*, 1983, **244**, 209.

12 K. Sünkel, U. Birk and C. Robl, *Organometallics*, 1994, **13**, 1679.

13 (*a*) C.-Y. Wong, C.-M. Che, M. C. W. Chan, J. Han, K.-H. Leung, L. D. Philips, K.-Y. Wong and N. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 13997; (*b*) L. A. Emmert, W. Choi, J. A. Marshall, J. Yang, L. A. Meyer and J. A. Brozik, *J. Phys. Chem. A*, 2003, **107**, 11340; (*c*) E. R. Batista and R. L. Martin, *J. Phys. Chem. A*, 2005, **109**, 9856; (*d*) T. M. Cooper, D. M. Krein, A. R. Burke, D. G. McLean, J. E. Rogers and J. E. Stagle, *J. Phys. Chem. A*, 2006, **110**, 13370.