VIP Borylene Complexes

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Stepwise Intermetal Borylene Transfer: Synthesis and Structure of Mono- and Dinuclear Cobalt–Borylene Complexes**

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Free borylenes are elusive, highly reactive species that are not accessible under ambient conditions but can be generated and effectively stabilized in the coordination sphere of transition metals, thus yielding a variety of borylene complexes.[1] The close relationship of this class of compounds with ubiquitous transition-metal carbonyl complexes is reflected by the fact that BR ligands adopt the same bonding pattern (i.e. ligand→metal σ and metal→ligand π bonding) and coordination modes (terminal,[2] doubly[3] or triply bridging,[4] and semi-bridging[5]) as their CO counterparts. Of particular interest are terminal borylene complexes, since very recently it was demonstrated that such compounds serve as potential sources for elusive BR species, thus allowing for unprecedented borylene-based functionalization of organic substrates.[6] Access to these compounds is commonly achieved by salt elimination reactions between dianionic metal carbonylates and suitable dihaloboranes, or in the case of cationic borylene complexes, by halide abstraction from appropriate haloboryl precursors. Both methods, however, are severely limited in scope and have only been successfully applied to Group 6 metals,[7] iron,[8] and most recently, platinum.[9]

In order to provide more general access to terminal borylene complexes, we have started to investigate intermetal borylene transfer[10] and succeded in the isolation of unprecedented mononuclear vanadium[11] and tetranuclear rhodium[12] borylene species, which cannot be obtained by the aforementioned conventional syntheses. Herein, we describe the stepwise borylene transfer from tungsten to cobalt, which proceeds via an unprecedented heterodinuclear intermediate to furnish the first cobalt borylene complexes.

Photolysis of equimolar amounts of $[(OC)_5W{=}BN(SiMe_3)_2]$ (**1**) and $[(\eta^5\text{-}C_5H_5)Co(CO)_2]$ (**2**) in toluene for 6 h results in the formation of the heterodinuclear borylene-bridged complex $[(\eta^5\text{-}C_5H_5)(OC)Co\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ [**3**; Eq. (1)]. After recrystallization from hexane, **3** was isolated as air- and moisture-sensitive dark red crystals in 40% yield.

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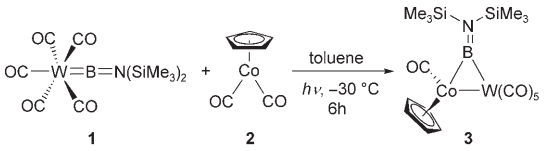
The $^{11}B\{^1H\}$ NMR spectrum of **3** displays a broad singlet at $\delta = 103$ ppm ($\omega_{1/2} = 488$ Hz), which is shifted downfield



(1)

with respect to that of the starting material **1** ($\delta = 87$ ppm),[7a] as expected for the formation of a bridged borylene complex.[1b] The ^1H NMR spectrum shows one new singlet for the trimethylsilyl group at $\delta = 0.22$ ppm, which is deshielded in comparison to that of the borylene precursor **1** ($\delta = 0.12$ ppm).[7a]

The proposed constitution of **3** was confirmed by single-crystal X-ray diffraction (Figure 1).[13] Crystals of **3** were obtained by cooling a concentrated hexane solution to −35 °C; the complex crystallizes in the monoclinic space group $P2_1/n$.

In the solid state, the $\{W(CO)_5\}$ and $\{(\eta^5\text{-}C_5H_5)Co(CO)\}$ fragments are linked by a bridging borylene ligand $BN(SiMe_3)_2$. The W1–B1 bond (2.434(3) Å) is considerably elongated in comparison to that of the corresponding terminal borylene complex **1** (2.151(7) Å),[7a] in agreement with the increased coordination number of the boron center.

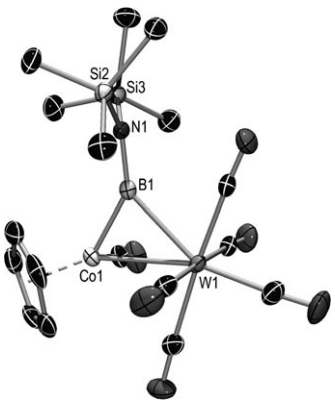
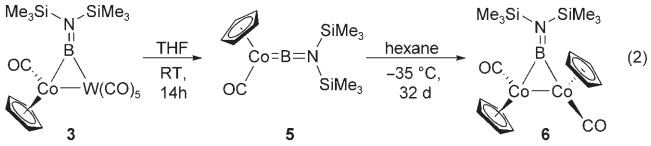


Figure 1. Molecular structure of **3** in the solid state. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths [Å] and angles [°]: B1–Co1 1.913(3), B1–W1 2.434(3), B1–N1 1.387(3), Co1–W1 2.816(4); W1-B1-N1-Si2 78.80(3), W1-B1-N1-Si3 66.40(3), N1-B1-Co1: 141.96(19), N1-B1-W1 138.32(17), B1-Co1-W1 58.26(3), B1-W1-Co1 41.95(6).

The Co1–B1 bond length (1.913(3) Å) is similar to analogous distances found in complexes featuring three-coordinate boron atoms linked to cobalt centers, such as $[(Me_3P)_3Co(Bcat)_2]$ (cat = $C_6H_6O_2$; 1.945(2), 1.970(3) Å).[14] The Si2-B1-Si3 plane is twisted by 72° with respect to the Co1-B1-W1 plane. This effect is probably due to the presence of the bulky Me_3Si groups, as already observed in the borylene-bridged complex $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}]$ (**4**; 53(1)°). The increased B1–N1 bond length of 1.412(4) Å in **4** indicates a less effective π interaction between the nitrogen atom and the boron atom.[15] However, the B1–N1 bond (1.387(3) Å) of **3** is only slightly longer than that observed in the corresponding terminal borylene complex **1** (1.338(3) Å),[7a] thus indicating significant double-bond character in the boron–nitrogen linkage.

Since compound **3** can be viewed as an intermediate of borylene transfer from tungsten to cobalt, the completion of this desired transmetalation was attempted [Eq. (2)].

The terminal borylene complex $[(\eta^5\text{-}C_5H_5)(CO)Co{=}B{=}N(SiMe_3)_2]$ (**5**) was obtained with surprising ease by dissolving



(2)

3 in THF. ^{11}B NMR spectroscopy of the reaction mixture revealed gradual consumption of **3** and concomitant formation of **5**, which was complete after 14 h at ambient temperature. After isolation and purification, **5** was obtained as an analytically pure dark orange oil in 70% yield.

The ^1H NMR spectrum of **5** displays one singlet for the trimethylsilyl group at $\delta = 0.21$ ppm, which is slightly shielded with respect to that of the bridged precursor **3** ($\delta = 0.22$ ppm). The $^{11}B\{^1H\}$ NMR spectrum of **5** features an upfield-shifted resonance at $\delta = 79$ ppm, suggesting the formation of a terminal borylene species. The CO ligand is terminally coordinated in solution, as demonstrated by the presence of a band at $\tilde{\nu} = 1929\ cm^{-1}$ in the IR spectrum of **5** in toluene.

Owing to the oily consistency of **5**, it was not possible to obtain single crystals suitable for X-ray diffraction. However, further convincing evidence for the proposed formulation stems from the computed ^{11}B NMR shift of **5** at $\delta = 83$ ppm,[16] which resembles the experimental value and is in agreement with a terminal borylene complex.

Complex **5** proved to be surprisingly unstable in solution, as ascertained by ^{11}B NMR spectroscopy, which indicated the formation of a new boron-containing product even under mild conditions (hexane at −35 °C). Complete conversion to the new product was accomplished after about 32 days, at which point red crystals of $[\{(\eta^5\text{-}C_5H_5)(OC)Co\}_2(\mu\text{-}BN(SiMe_3)_2]$ (**6**) could be isolated. The rather moderate yield of 29% for **6** is in agreement with its formation in a nonstoichiometric reaction.[17]

The $^{11}B\{^1H\}$ NMR spectrum of **6** exhibits a deshielded broad singlet at $\delta = 106$ ppm (cf. $\delta = 79$ ppm for **5**), which indicates the formation of a new borylene-bridged complex. The ^1H NMR spectrum displays a new singlet for the trimethylsilyl group at $\delta = 0.30$ ppm, which is deshielded in comparison to that of the terminal borylene precursor **5** ($\delta =$ 0.21 ppm).

The molecular structure of **6** was conclusively determined by performing a single-crystal X-ray diffraction analysis.[13] The complex crystallizes in the monoclinic space group *C*2/c.

Figure 2 illustrates that two $\{(\eta^5\text{-}C_5H_5)Co(CO)\}$ units are linked through a metal–metal bond and a bridging borylene ligand. The boron atom and both cobalt atoms form an

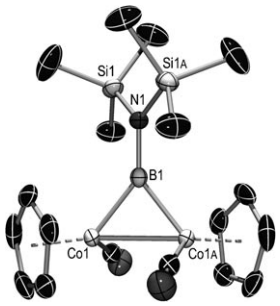


Figure 2. Molecular structure of **6** in the solid state. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths [Å] and angles [°]: B1-Co1 1.952(2), B1-N1 1.404(3), Co1-Co1A 2.493(5); Co1-B1-N1-Si1 54.42(2), N1-B1-Co1 140.32(5), B1-Co1-Co1A 50.32(5), Co1-B1-Co1A 79.35(10).

isosceles triangle with B–Co bonds lengths of 1.952(2) Å and a Co–Co bond length of 2.493(5) Å. The molecular geometry closely resembles that of the methylene-bridged cobalt complex $[(\mu\text{-}CH_2)\{(\eta^5\text{-}C_5H_4Me)Co(CO)\}_2]$. In this case, the Co–Co distance of 2.497(1) Å also indicates the presence of a metal–metal bond, consistent with the effective atomic number (EAN) rule and the description of this class of compounds as dimetallacyclopropanes.[18]

The overall geometry of the exocyclic amino group of **6**, comprising a trigonal-planar nitrogen atom, a B–N distance of 1.404(3) Å, and a dihedral angel between the Si1-B1-Si1A and Co1-B-Co1A planes of 54.42(2)°, resembles that of the aforementioned complex **4**.[15]

The first cobalt borylene species reported herein underline the importance of borylene-transfer reactions for the synthesis of BR-containing products, which are not available by any other more conventional route. Moreover, the full characterization of a novel mixed-metal borylene complex provides convincing evidence that intermetal borylene transfer proceeds via heterodinuclear intermediates, that is, according to an associative process and not by prior dissociation of the borylene ligand.

Experimental Section

All manipulations were conducted either under an atmosphere of dry argon inside a glovebox or employing standard Schlenk techniques.

3: A dark red solution of **1** (0.30 g, 0.61 mmol) and **2** (0.07 mL, 0.61 mmol) in toluene (15 mL) was photolyzed at −30 °C for 6 h. The solvent of the dark red reaction mixture was removed in vacuo, and the resulting dark red solid was dissolved in hexane (2 mL). After

filtration, the solution was cooled to −35 °C, thus yielding dark red crystals of **3** (0.12 g, 40 %). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.59$ (s, 5H, C_5H_5), 0.22 ppm (s, 18H, Me); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta = 198.04$ (CO), 197.20 (CO), 191.40 (CO), 98.13 (C_5H_5), 3.90 ppm (Me), ^{11}B{^{1}H} NMR (64 MHz, C_6D_6, 25 °C): $\delta = 103$ ppm (s, $\omega_{1/2} = 488$ Hz). IR (toluene): $\tilde{\nu} = 2060$, 1969, 1923, 1854 cm^{-1} (C≡O). Elemental analysis (%) calcd for $C_{17}H_{23}BCoNO_6Si_2W$: C 31.55, H 3.58, N 2.16; found: C 31.62, H 3.58, N 2.16.

5: Solid **3** (0.10 g, 0.15 mmol) was dissolved in THF (1 mL) and allowed to react at ambient temperature for 14 h. The solvent was removed in vacuo, and the resulting dark red oil was dissolved in hexane (2 mL). After filtration, all volatiles were removed in vacuo, and **5** was isolated as an analytically pure dark orange oil (0.04 g, 70 %). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.80$ (s, 5H, C_5H_5), 0.21 ppm (s, 18H, Me); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta =$ 201.49 (CO), 82.77 (C_5H_5), 3.26 ppm (Me), ^{11}B{^{1}H} NMR (64 MHz, C_6D_6, 25 °C): $\delta = 79$ ppm (s, $\omega_{1/2} = 43$ Hz). IR (toluene): $\tilde{\nu} = 1929$ cm^{-1} (C≡O). Elemental analysis (%) calcd for $C_{12}H_{23}BCoNOSi_2$: C 44.59, H 7.17, N 4.33; found: C 44.03, H 6.89, N 4.48.

6: Compound **5** (0.05 g, 0.15 mmol) was dissolved in hexane (1 mL) and stored at −35 °C for 32 d to yield a dark red crystalline solid. The solid was dissolved in hexane (2 mL) with subsequent filtration, and the dark red solution was cooled to −35 °C. Complex **6** was isolated as red crystals (0.02 g, 29 %). ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C, TMS): $\delta = 4.71$ (s, 10H, C_5H_5), 0.34 ppm (s, 18H, Me); ^{13}C{^{1}H} NMR (126 MHz, [D$_8$]THF, 25 °C): $\delta = 212.74$ (CO), 87.89 (C_5H_5), 4.47 ppm (Me), ^{11}B{^{1}H} NMR (64 MHz, [D$_8$]THF, 25 °C): $\delta = 106$ ppm (s, $\omega_{1/2} = 320$ Hz). IR (toluene): $\tilde{\nu} = 1982$, 1938 cm^{-1} (C≡O). Elemental analysis (%) calcd for $C_{18}H_{28}BCo_2NO_2Si_2$: C 45.49, H 5.94, N 2.95; found: C 45.49, H 5.92, N 2.94.

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[1] a) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882 – 1898; *Angew. Chem. Int. Ed.* **1998**, *37*, 1786 – 1801; b) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1 – 51; c) H. Braunschweig, *Adv. Organomet. Chem.* **2004**, *51*, 163 – 192; d) H. Braunschweig, M. Colling, *Eur. J. Inorg. Chem.* **2003**, 393 – 403; e) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535 – 559; f) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380 – 5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254 – 5274.

[2] H. Braunschweig, D. Rais, *Heteroat. Chem.* **2005**, *16*, 566 – 571.

[3] a) H. Braunschweig, M. Colling, *J. Organomet. Chem.* **2000**, *614–615*, 18 – 26; b) H. Braunschweig, K. Radacki, D. Rais, F. Seeler, K. Uttinger, *J. Am. Chem. Soc.* **2005**, *127*, 1386 – 1387.

[4] H. Braunschweig, C. Burschka, M. Burzler, S. Metz, K. Radacki, *Angew. Chem.* **2006**, *118*, 4458 – 4461; *Angew. Chem. Int. Ed.* **2006**, *45*, 4352 – 4355.

[5] H. Braunschweig, D. Rais, K. Uttinger, *Angew. Chem.* **2005**, *117*, 3829 – 3832; *Angew. Chem. Int. Ed.* **2005**, *44*, 3763 – 3766.

[6] a) H. Braunschweig, T. Herbst, D. Rais, F. Seeler, *Angew. Chem.* **2005**, *117*, 7627 – 7629; *Angew. Chem. Int. Ed.* **2005**, *44*, 7461 – 7463; b) S. Aldridge, W. Clegg, J. K. Day, R. W. Harrington, D. L. Kays (née Coombs), *Angew. Chem.* **2006**, *118*, 3593 – 3596; *Angew. Chem. Int. Ed.* **2006**, *45*, 3513 – 3516.

[7] a) H. Braunschweig, U. Englert, C. Kollann, *Angew. Chem.* **1998**, *110*, 3355 – 3357; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179 – 3180; b) H. Braunschweig, M. Colling, C. Kollann, K. Merz, K. Radacki, *Angew. Chem.* **2001**, *113*, 4327 – 4329; *Angew. Chem. Int. Ed.* **2001**, *40*, 4198 – 4200; c) H. Braunschweig, K. Radacki, D. Scheschkewitz, G. R. Whittell, *Angew. Chem.* **2005**, *117*, 1685 – 1688; *Angew. Chem. Int. Ed.* **2005**, *44*, 1658 – 1661.

[8] a) S. Aldridge, D. L. Coombs, C. Jones, D. J. Willock, *J. Am. Chem. Soc.* **2003**, *125*, 6356 – 6357; b) A. H. Cowley, V. Lomeli, A. Voigt, *J. Am. Chem. Soc.* **1998**, *120*, 6401 – 6402.

[9] H. Braunschweig, K. Radacki, K. Uttinger, *Angew. Chem.* **2007**, *119*, 4054 – 4057; *Angew. Chem. Int. Ed.* **2007**, *46*, 3979 – 3982.

[10] H. Braunschweig, M. Colling, C. Kollann, B. Neumann, H. G. Stammler, *Angew. Chem.* **2001**, *113*, 2359 – 2361; *Angew. Chem. Int. Ed.* **2001**, *40*, 2298 – 2300.

[11] H. Braunschweig, M. Colling, C. Hu, K. Radacki, *Angew. Chem.* **2003**, *115*, 215 – 218; *Angew. Chem. Int. Ed.* **2003**, *42*, 205 – 208.

[12] H. Braunschweig, M. Forster, K. Radacki, *Angew. Chem.* **2006**, *118*, 2187 – 2189; *Angew. Chem. Int. Ed.* **2006**, *45*, 2132 – 2134.

[13] The crystal data for **3** and **6** were collected on a Bruker APEX diffractometer with a CCD area detector and graphite-monochromated $Mo_{K\alpha}$ radiation. The structure was solved by using direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen, **1997**), and expanded by using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for **3**: $C_{17}H_{23}BCoNO_6Si_2W$, $M_r = 647.13$, dark red blocks, $0.30 \times 0.20 \times 0.18$ mm^3, monoclinic, space group $P2_1/n$, $a =$ 8.7338(7), $b = 18.0672(16)$, $c = 14.9079(13)$ Å, $\beta = 94.976(2)°$, $V = 2343.5(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.834$ Mg m^{-3}, $\mu = 5.745$ mm^{-1}, $F(000) = 1256$, $T = 173(2)$ K, $R_1 = 0.0167$, $wR^2 = 0.0756$, 4631 independent reflections ($2\Phi \leq 52.14°$) and 262 parameters. Crystal data for **6**: $C_{18}H_{28}BCo_2NO_2Si_2$, $M_r = 475.26$, red blocks, $0.35 \times 0.34 \times 0.31$ mm^3, monoclinic, space group $C2/c$, $a =$ 16.7951(11), $b = 9.4145(5)$, $c = 15.4860(9)$ Å, $\beta = 119.303(4)°$, $V = 2135.3(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.478$ Mg m^{-3}, $\mu = 1.678$ mm^{-1}, $F(000) = 984$, $T = 100(2)$ K, $R_1 = 0.0230$, $wR^2 = 0.0612$, 2121 independent reflections ($2\Phi \leq 52.24°$) and 119 parameters. CCDC-645674 (**3**) and CCDC-645673 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] a) K. C. Lam, W. H. Lam, Z. Lin, T. B. Marder, N. C. Norman, *Inorg. Chem.* **2004**, *43*, 2541 – 2547; b) J. F. Corrigan, C. Dai, T. B. Marder, N. C. Norman, G. Stringer, N. J. Taylor, *J. Organomet. Chem.* **1996**, *513*, 273 – 275; c) C. J. Adams, R. A. Baber, A. S. Batsanov, G. Braham, J. H. P. Charmant, M. F. Haddow, J. A. K. Howard, W. H. Lam, Z. Lin, T. B. Marder, N. C. Norman, A. G. Orpen, *Dalton Trans.* **2006**, 1370 – 1373.

[15] H. Braunschweig, C. Kollann, U. Englert, *Eur. J. Inorg. Chem.* **1998**, 465 – 468.

[16] Both geometry and NMR spectra were computed at the B3LYP/6-31G(d,p) level with Stuttgart RSC basis for Co and W.

[17] Two equivalents of **5** form the dinuclear species **6** with formal loss of one equivalent of the borylene $BN(SiMe_3)_2$. Data from NMR spectroscopy did not provided conclusive evidence as to the fate of this fragment.

[18] R. G. Bergman, K. H. Theopold, *J. Am. Chem. Soc.* **1983**, *105*, 464 – 475.

