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Intermetallic transfer of unsymmetrical borylene fragments: isolation of the second early-transition-metal terminal borylene complex and other rare species†

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Transition metal borylene complexes of the type [(OC)₅M=BN(SiMe₃)(tBu)] (M = Cr, Mo, W) have been synthesised by salt elimination of the corresponding dibromoborane and the dianionic metallates Na₂[M(CO)₅]. The borylene complexes have been characterised by multinuclear solution-state NMR spectroscopy and solid-state molecular structure determination. The group 6 borylene complexes can be used to effectively transfer the borylene ligand to other transition metal complexes by replacing one or two carbonyl ligands upon irradiation of the reaction mixture with UV light. This borylene transfer reaction led to the formation of new terminal and bridging borylene complexes which cannot be formed by the corresponding salt elimination reactions, including a rare example of a bis(terminal borylene) complex and only the second reported terminal borylene complex of an early transition metal (vanadium).

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Introduction

As ligands, borylenes (:BR) are isolobal with N₂ and CO, although the former differ substantially in terms of their binding with transition metals (TMs) and the reactivity of the resulting complexes.¹ We reported the first isolation and structural authentication of stable transition metal borylene complexes in 1995, namely the bridging borylene complexes of type I (Fig. 1).² Since that time, the field of TM-borylene chemistry has expanded significantly,³ while the related advent of base-stabilised (TM-free) borylenes⁴ has opened up a vast new playground of synthetic possibilities.

BR ligands, being isoelectronic to CO, can adopt similar coordination modes to TMs (terminal,⁵ doubly⁶ and triply bridging,⁷ and semi-bridging⁸) and similar bonding patterns to their CO counterparts. Theoretical studies have shown that the highest occupied molecular orbitals (HOMO) of free borylenes are much higher in energy than CO, making them much better σ -donors, whereas they show similar π -accepting pro-

erties, thus rationalising the thermodynamically stable metal borylene linkage.⁹ Several examples of terminal borylene complexes have been reported since their initial discovery in 1998 (II, Fig. 1),¹⁰ however, few reliable and generalised methods for their synthesis exist. The most common preparatory route for terminal transition metal borylene complexes from non-borylene starting materials involves halide abstraction^{3b,11} or salt metathesis reactions.^{3b,12} The former process allows for the production of a variety of cationic borylenes, most notably of iron, from transition metal haloboryl precursors.¹¹ On the other hand, group 6 terminal borylene complexes are synthesised by salt elimination reactions. Indeed, disodium metallates of the Cr, Mo, and W pentacarbonyl dianions, Na₂[M(CO)₅], are reported to react with dihaloboranes to furnish the corresponding borylene complexes in reasonable yields.^{12a} To this day, this method is limited to the preparation of [(OC)₅M=BN(SiMe₃)₂],^{10a,12a} [(OC)₅M=B{E(SiMe₃)₃}] (E = Si, Ge)^{12b} and [(OC)₅M=BAR],¹³ where Ar is a very bulky terphenyl

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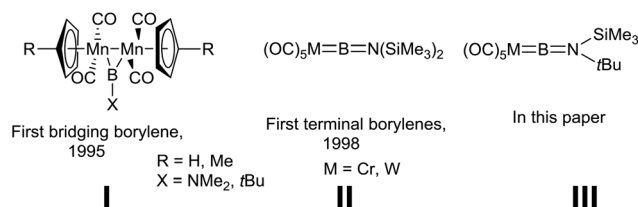


Fig. 1 Structures of relevant classes of compounds I–III.

moiety. Other more recent and less studied syntheses of borylene complexes include a direct B–H bond activation of a dihydroborane at a ruthenium center,¹⁴ as well as the use of silyliron and -ruthenium monoanions for terminal borylene synthesis through subsequent salt and halosilane eliminations.¹⁵ Among these “first-generation” borylene complexes (*i.e.* those not prepared by borylene transfer), the group 6 complexes **II** (Fig. 1) are unique in their exceptional ligand transfer reactivity, while a few other complexes have also shown limited transfer ability.^{17f} Indeed, the $[\text{:BN}(\text{SiMe}_3)_2]$ fragment can be transferred from the group 6 pentacarbonyl complexes to different metal systems through reactions that have parallels in carbene chemistry.^{16,17} This process has been invaluable in the expansion of TM borylene chemistry as it allows for the preparation of a variety of novel terminal and bridging examples for which no synthetic access exists. It should be noted that the borylene transfer concept is not limited to transition metal acceptors, borylene ligands can also be transferred to organic substrates to form heterocyclic species (*e.g.* borirenes¹⁸) and other hypovalent boron species such as doubly base-stabilised (metal-free) borylenes.^{10d} Like Fischer carbene complexes, terminal borylene complexes can also participate in metathesis chemistry.^{11d,19}

Rather surprisingly considering their rich transfer chemistry,¹⁷ aminoborylenes of the group 6 metals remain limited in scope to the $[\text{L}_n\text{M}=\text{BN}(\text{SiMe}_3)_2]$ family of complexes. One reason for this is the difficulty of obtaining suitable monomeric aminodihaloborane precursors for such borylene complexes. Furthermore, it is well established that steric shielding is an important contributing factor to the stability of terminal borylenes. In this report we present the first synthesis of a family of non- $[\text{:BN}(\text{SiMe}_3)_2]$ aminoborylene complexes of the group 6 metals. The rich transfer chemistry of these compounds was investigated, providing a number of new borylene complexes including terminal and bridging mono and bis(borylene) complexes.

Results and discussion

Synthesis of unsymmetrical group 6 borylene complexes

The terminal borylenes $[(\text{OC})_5\text{M}=\text{BN}(\text{SiMe}_3)(t\text{Bu})]$ ($\text{M} = \text{Cr}$ (**1a**), Mo (**1b**), W (**1c**)) were prepared similarly to salt elimination procedures reported for the known $[\text{L}_n\text{M}=\text{BN}(\text{SiMe}_3)_2]$ complexes (Fig. 2).¹² In such a procedure, the freshly syn-

thesised sodium salts of the $[\text{M}(\text{CO})_5]^{2-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) dianions, generated by the reduction of $[\text{M}(\text{CO})_5(\text{NMe}_3)]^{20}$ with sodium naphthalenide, were reacted with $\text{Br}_2\text{BN}(\text{SiMe}_3)(t\text{Bu})$ in toluene at low temperature (-78°C). Extraction and crystallisation of the reaction products in pentane allowed isolation of all three unsymmetrical borylene compounds as pure products. The yields were found to be moderate in the cases of the chromium, **1a** (39%) and tungsten analogues, **1c** (35%), but very low for the molybdenum complex **1b** (10%), which is an extremely sensitive species. Indeed, while melting points could be measured for **1a** and **1c** (60 and 73°C , respectively), compound **1b** decomposes above 0°C . By contrast, **1a** and **1c** only decompose above *ca.* 150°C .

All three borylene complexes were characterised by ^1H , ^{11}B , ^{13}C , and ^{29}Si NMR spectroscopy. In all cases, the $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopic signal of the unsymmetrical borylene complexes (**1a**: $\delta = 97$, **1b**: $\delta = 96$, **1c**: $\delta = 92$) is significantly downfield shifted relative to the signals of the previously reported $[(\text{OC})_5\text{M}=\text{BN}(\text{SiMe}_3)_2]$ analogues (δ : **I**: 92, **II**: 90 **III**: 87).^{12a} In the borylene complexes **1a–c**, one of the SiMe_3 groups is replaced by a *t*Bu group, leading to a more downfield signal for the CH_3 protons due to the higher electronegativity of carbon relative to silicon. In their ^1H NMR spectra, a sharp singlet is observed in the aliphatic region corresponding to the *t*Bu group (**1a**: $\delta = 1.15$, **1b**: $\delta = 1.14$, **1c**: $\delta = 1.14$), along with a singlet for the SiMe_3 protons (**1a**: $\delta = 0.16$, $^1J_{\text{H-Si}} = 6.7$ Hz; **1b**: $\delta = 0.14$, $^2J_{\text{H-Si}} = 6.6$ Hz; **1c**: $\delta = 0.15$, $^2J_{\text{H-Si}} = 6.8$ Hz). The respective signals for the SiMe_3 groups can easily be identified by their satellite signals arising from coupling to ^{29}Si nuclei, which have $^2J_{\text{Si-H}}$ values of around 6.5 Hz. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1a–c** showed the usual low-field shift for four equatorial (*cis* to borylene) and one axial (*trans* to borylene) CO ligands, (**1a**: $\delta = 218.4$ (CO_{ax}), 217.9 (CO_{eq}); **1b**: $\delta = 206.9$ (CO_{ax}), 207.5 (CO_{eq}); **1c**: $\delta = 191.2$ (CO_{ax}), 197.7 ppm (CO_{eq}). The $^{29}\text{Si}\{^1\text{H}\}$ NMR signals of all the three compounds appeared in a similar region to those of their previously reported analogues^{12a} ($\delta = 3.4$ ppm for **1a** and **1b**, $\delta = 2.5$ ppm for **1c**).

The formation of **1a–c** was further confirmed by their molecular structures (Fig. 3). Single crystals of suitable quality for X-ray diffraction were grown from saturated hexane solutions. All three complexes crystallised in monoclinic space groups, **1a** in $P2_1/n$ and **1b** and **1c** in $P2_1/c$. As the data quality of **1a** is not sufficient to discuss the bond lengths and angles, only those of **1b** and **1c** will be discussed. All of the metal–boron (**1b**: 2.1356(19); **1c**: 2.143(2) Å) and boron–nitrogen bond distances (**1b**: 1.361(2), **1c**: 1.356(3) Å) are in line with those of previously reported group 6 terminal borylene complexes.^{12a} The N–B–M moiety is almost linear with angles of $175.78(15)^\circ$ (**1b**) and $176.08(17)^\circ$ (**1c**). The $\text{C}_{\text{ax}}\text{–M–B}$ axes are also almost linear (**1b**: C1–Mo–B $173.59(7)^\circ$; **1c**: C1–W–B $173.38(8)^\circ$). The M– C_{ax} distances of **1b,c** (**1b**: 2.070 (2), **1c**: 2.056 (2) Å) are slightly longer than the M– C_{eq} distances (avg. equatorial M–C distances for **1b** and **1c**: 2.045 Å) revealing the *trans* effect of the borylene ligand, as previously observed in transition metal borylene complexes.^{3,12b,c}

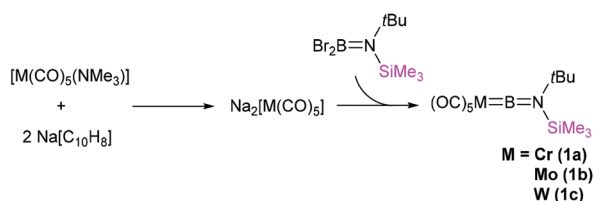


Fig. 2 Synthesis of first-generation unsymmetrical group 6 borylene complexes **1a–1c**.

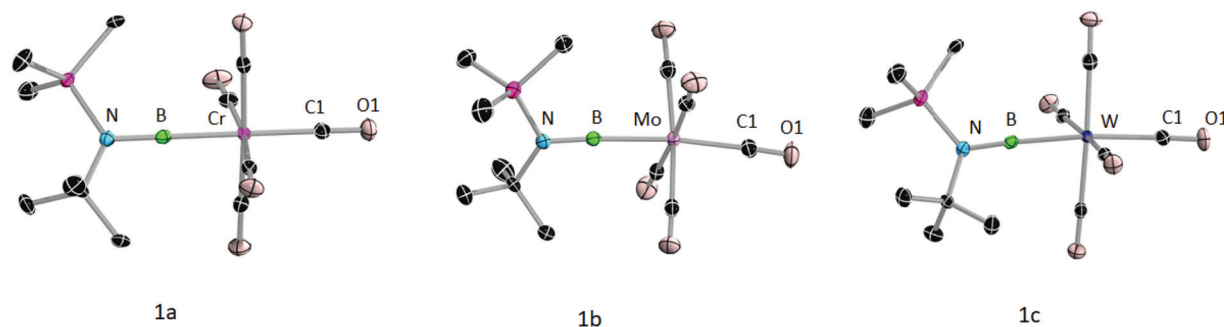


Fig. 3 Molecular structures of **1a–c** with thermal ellipsoids shown at 50% probability level, all H atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: **1b**: B–Mo 2.1356(19); B–N 1.361(2); N–B–Mo 175.78, C1–Mo–B 173.59(7)°. **1c**: B–W 1.356(3) Å, B–N 2.143(2) Å; N–B–W 176.08(17), C1–W–B 173.38(8). Due to poor diffraction quality of the crystals we refrain from discussing the selected bond lengths and angles of **1a**.

Synthesis of second-generation borylene complexes by borylene transfer

With these first-generation borylene complexes in hand, we set out to investigate their transfer chemistry, for the synthesis of novel borylene complexes. Our group has previously shown that intermetallic borylene transfer is a viable synthetic route to both terminal as well as bridging borylene complexes.¹⁷ In this study, we concentrated on the photolytic transfer of borylene moieties from the chromium and tungsten precursors **1a** and **1c**, as the molybdenum derivative is highly sensitive and can only be isolated in very low yields. Furthermore, preliminary experiments suggested that **1b** decomposes under the applied reaction conditions at a faster rate than any of the transfer processes. It should be noted that the following transfer experiments were first attempted on small scales in NMR tubes, and in each case proceeded regardless of whether **1a** or **1c** was used. The experiments described below were subsequent reactions performed on larger scales using the precursor that showed the most selective reaction on the NMR scale. Unsymmetrical tungsten borylene **1c** reacts readily with vanadium cyclopentadienyl tetracarbonyl complex $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4]$ in benzene under UV irradiation. The progress of the reaction can be followed by $^{11}\text{B}\{^1\text{H}\}$ NMR, wherein the signal intensity of the starting borylene progressively decreases over 6 h, giving way to a slightly more deshielded resonance (100 ppm) relative to that of its precursor **1c**, but in line with that of a previously reported similar half sandwich terminal vanadium borylene complex ($\delta = 98$ ppm).^{17b} After the reaction, removal of the volatiles under vacuum followed by recrystallisation of a silica-filtered hexane solution of the mixture afforded $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{V}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$ (**2**) in 84% yield. In a similar manner, two molar equivalents of **1a** reacted with $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2]$ under UV irradiation, replacing both carbonyl ligands with borylene moieties and providing **5** (Fig. 4) in a 58% yield after fractional crystallisation. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5** showed a signal ($\delta = 70.8$ ppm) at high field relative to that of its starting material but essentially identical to that of a reported half sandwich bis(borylene) complex of iridium ($\delta = 69$ ppm).^{17e} The solid-state structures of **2** and **5** were ascertained by single-crystal X-ray diffraction (Fig. 5).

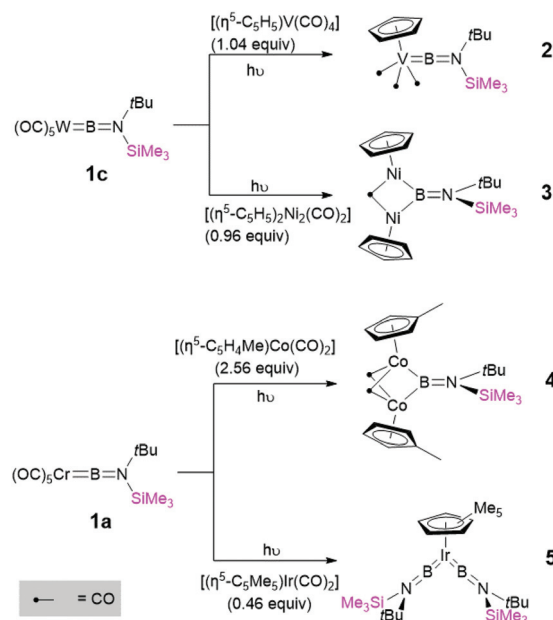


Fig. 4 Synthesis of second-generation unsymmetrical borylene complexes **2–5** by borylene transfer.

The vanadium half sandwich complex **2** crystallised in the orthorhombic *Pbca* space group. Its B–V bond distance was found to be 1.964(2) Å, which is similar to that of the previously reported vanadium borylene complex (1.959(6) Å)^{17b} and within the typical range of known terminal M–B distances.³ The V–B–N moiety is almost linear (V–B–N 177.5 (1)°), while the B–N distance 1.3714(17) matches those of related complexes.^{17b} The half-sandwich bis(borylene) complex **5** crystallises in the monoclinic space group *P21/n*. The primary structure showed the expected “two-legged piano stool” geometry in the solid-state like its published analogues.^{17e} However, due to the poor quality of the crystal data we cannot elaborate further on its structural parameters.

In addition to replacing terminal CO ligands on TM centres through borylene transfer, the borylene moieties of **1a** and **1c** can also replace bridging CO ligands, providing a complex



Fig. 5 Molecular structure of 2–5 with the thermal ellipsoids shown at 50% probability level, all H atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: 2: B–V 1.964 (2), B–N 1.3714(17); (V–B–N 177.5 (1)). 3: B1–Ni1 1.933 (3), B1–Ni2 1.936(3), Ni1–Ni2 2.370 (8); Ni–B–Ni 75.56(11)°. Due to poor diffraction quality of crystal we refrain from discussing the selected bond lengths and angles of 4, 5.

with a bridging borylene ligand. Thereby, irradiation of a hexane solution of **1c** and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2]$ for 7 h afforded dinickel bridging borylene complex **3** (Fig. 4). After the completion of the reaction, **3** was extracted with hexamethyldisiloxane and crystallised from the same solution as dark red crystals in a 74% yield. In a similar reaction, **1a** was irradiated in the presence of 2.5 equivalents of $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Co}(\text{CO})_2]$ in hexane solution at room temperature. Monitoring the reaction mixture by ^{11}B NMR spectroscopy showed the consumption of precursor **1a** and appearance of two new peaks at $\delta = 81$ ppm and $\delta = 104$ ppm. These signals likely correspond to the expected terminal and bridging borylene complexes, *i.e.* $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{OC})\text{Co}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Co}]_2\{\mu\text{-}(\text{CO})_2\}\{\mu\text{-BN}(\text{SiMe}_3)(t\text{Bu})\}$ (**4**), respectively, although we were unable to isolate the intermediate mononuclear complex due to thermal lability. After complete consumption of **1a** (*ca.* 8 h reaction time) the reaction mixture was evaporated and extracted with hexane and filtered through silica gel, and subsequent crystallisation of the filtrate at -30 °C allowed isolation of **4** in a 65% yield (Fig. 4).

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopic signals of bridging borylene complexes **3** and **4** were both significantly broadened, indicating their bridging binding mode, and were found slightly downfield (**3**: $\delta = 94.1$, **4**: $\delta = 103.6$) of those of their starting material. The ^1H NMR spectrum of **3** showed a downfield shift of the proton signal of the cyclopentadienyl ring ($\delta = 5.32$ ppm) relative to that of its starting material ($\delta = 5.15$ ppm), suggesting that the σ -donor properties of cyclopentadienyl ring increase in the presence of the borylene ligand.²¹ The signals for the *t*Bu and TMS protons show a downfield shift with respect to those of the starting materials ($\delta = 1.18$ and 0.24 ppm, respectively). The corresponding spectrum of the dicobalt bridging borylene complex **4** also shows similar phenomena relative to its precursor. The ^1H NMR spectrum of **4** showed signals at $\delta = 4.75$, 4.49 and 1.94 ppm for the protons of the methylcyclopentadienyl ligand ($\eta^5\text{-C}_5\text{H}_4\text{CH}_3$), all significantly deshielded with respect to the corresponding signals of the precursor ($\delta = 4.53$, 4.33, 1.47 ppm).²² The signals for the *t*Bu and SiMe_3 protons are also downfield ($\delta = 1.40$ and 0.34 ppm.) of those of **1a**.

The solid-state molecular structures of both **3** and **4** (Fig. 5) confirm the presence of a single bridging borylene ligand. However, due to poor quality of the crystal data we refrain from discussing the structural parameters of compound **4**. The M–B distances of **3** (B1–Ni1 1.933 (3) Å, B1–Ni2 1.936(3) Å) are comparable to previously reported M–B distances of bridging borylene complexes (avg. Ni–B 1.93(14) Å).²³ The Ni–Ni distance (2.370(8) Å) is slightly longer than that of a similar compound (Ni–Ni: 2.341(2) Å)²³ and that of the starting material (2.348(2) Å),²¹ which rules out the possibility of a metal–metal bond. The Ni–B1–Ni angle (75.56(11)°) is furthermore significantly smaller than the Ni–C–Ni angle (80.38(12)°).

Conclusions

Our results herein show that the family of group 6 aminoborylene complexes is amenable to further variation, including complexes with unsymmetrical aminoborylene ligands. These terminal borylene complexes have proven to be excellent precursors for both terminal and bridging mono- and diborylene species through facile borylene transfer reactions with other TM carbonyl complexes, leading to rare examples of nickel borylene complexes, bis(terminal borylene) complexes, and only the second reported terminal borylene complex of an early transition metal (vanadium).

Conflicts of interest

There are no conflicts to declare.

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