Borylene Complexes

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Borylene Metathesis through [2+2] Cycloaddition**

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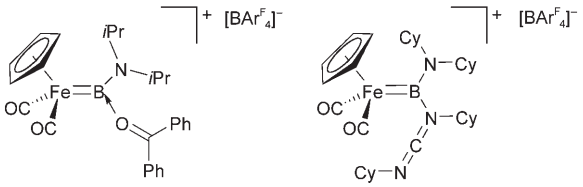
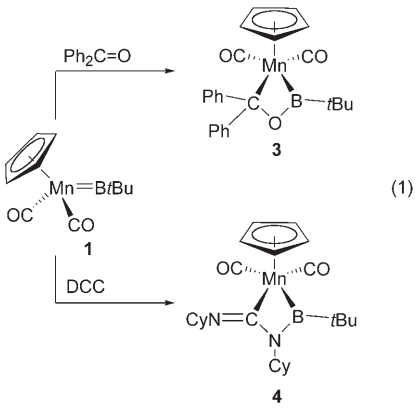
A variety of synthetic approaches to neutral terminal borylene complexes $[L_xM{=}BR]$ ($R = N(SiMe_3)$, $Si(SiMe_3)$) has been developed over the past years on the basis of salt elimination[1] or transmetalation reactions.[2] Recently, we also demonstrated that homo-[3] and heterodinuclear[4] bridged borylene species are susceptible to cleavage reactions, thus yielding in the former case the first terminal alkyl borylene species $[(\eta^5\text{-}C_5H_5)(OC)_2Mn{=}BtBu]$ (**1**). In addition, Aldridge et al. have established a versatile route to cationic iron species such as $[(\eta^5\text{-}C_5H_5)(OC)_2Fe{=}B{=}NR_2][BAr^F{}_4]$ (**2a**: $R = i$Pr; **2b**: $R =$ Cy; $Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$, Cy = cyclohexyl),[5] which was subsequently extended to a corresponding platinum borylene complex.[6] In contrast to the wide spectrum of syntheses now available, reactivity patterns, particularly for neutral complexes, are still restricted to borylene transfer reactions[7] and the addition of metal bases.[8] Given the fundamental importance of metal complexes $[L_xM{=}ER_n]$ in metathesis reactions[9] on the one hand, and the presence of a polar metal–borylene linkage with considerable multiple-bond character in species of the type $[L_xM{=}BR]$ on the other,[10] the latter species should be particularly well-suited precursors for borylene metathesis chemistry. Aldridge et al. have already reported on the reactions of **2a** and **2b** with polar substrates such as $EE'Ph_n$ ($E = O$, $E' = C$, $n = 2$; $E = S$, $E' = P$, $n = 3$) and dicyclohexylcarbodiimide (DCC),[11,12] which, however, do not proceed by concerted [2+2] cycloaddition but in a stepwise fashion with initial attack of the Lewis basic oxygen and nitrogen centers, respectively, at the cationic boron center, thus yielding adducts $[(\eta^5\text{-}C_5H_5)(OC)_2Fe{=}B(NR_2)(L)][BAr^F{}_4]$ ($L = OCPh_2$, DCC).

Moreover, substrates such as benzophenone[11] and DCC[12] lead to subsequent rearrangement of the initially formed adducts, while only in the case of $SPPh_3$ were the products of formal metathesis, $[(\eta^5\text{-}C_5H_5)(OC)_2Fe(PPh_3)][BAr^F{}_4]$ and $[(R_2N)BS]_2$, observed.[5a]

Herein, we report the first example of a concerted borylene metathesis reaction that proceeds via a structurally characterized cyclic intermediate that subsequently undergoes cycloreversion with clean formation of the metathesis products.



Treatment of $[(\eta^5\text{-}C_5H_5)(OC)_2Mn{=}BtBu]$ (**1**) with equimolar amounts of benzophenone or DCC immediately furnished the cyclic products $[(\eta^5\text{-}C_5H_5)(CO)_2Mn\{B(tBu)OC(Ph_2)\}]$ (**3**) and $[(\eta^5\text{-}C_5H_5)(CO)_2Mn\{B(tBu)N(Cy)C(NCy)\}]$ (**4**), which were isolated in about 70% yield as bright yellow (**3**) or colorless (**4**) crystals upon cooling of the reaction mixture to −35 °C [Eq. (1)]. The spectroscopic data are in agreement with the formulation of **3** and **4** as the products of a [2+2] cycloaddition. In particular, the resonances in the ^{11}B NMR spectra at $\delta = 72$ (**3**) and 62 ppm (**4**) are shifted



(1)

significantly upfield from that of **1** ($\delta = 144$ ppm), thus indicating the formation of B–O and B–N bonds, respectively.

The constitution of both products was confirmed by X-ray diffraction studies on suitable single crystals.[13] The compounds crystallize in the space groups $Pna2_1$ (**3**) and $P\bar{1}$ (**4**); both display a Mn-B-X-C (X = O, N) four-membered ring. The two planar rings (sum of the internal angles **3**:359.8°; **4**: 359.85°) are characterized by acute C3-Mn1-B1 angles (**3**: 59.70(6)°; **4**: 61.75(16)°), while the other three angles adopt values close to 100° (Figure 1). The Mn1–B1 distances of 2.1274(16) (**3**) and 2.185(5) Å (**4**) are much longer than that in **1** (1.809(9) Å) and resemble those of Mn boryl complexes.[14] These separations thus not only account for the increased coordination number of the boron centers but also indicate a significant loss of Mn–B multiple-bond character. The Mn1–

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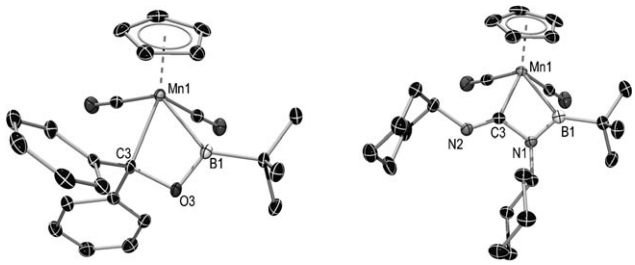
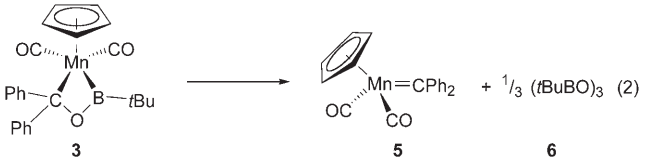


Figure 1. Molecular Structure of **3** (left) and **4** (right). Thermal ellipsoids are set at the 50% probability level; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **3**: Mn1-B1 2.1274(16), B1-O3 1.3478(19), O–C3 1.4655(15), Mn1–C3 2.1791(13); B1-Mn1-C3 59.70(6), O3-C3-Mn1 97.22(8), B1-O3-C3 99.20(10), O3-B1-Mn1 103.67(10); selected bond lengths [Å] and angles [°] for **4**: Mn1-B1 2.185(5), Mn1-C3 2.056(4); C3-Mn1-B1 61.75(16), N1-C3-Mn1 101.2(2), B1-N1-C3 101.2(3), N1-B1-Mn1 95.7(3).

C3 distance in **3** (2.1791(13) Å) is in agreement with the Mn–C bond length in $[(OC)_5Mn(\eta^1\text{-}C_{13}H_9)]$ (2.2472(15) Å),[15] while the decreased coordination number and the sp^2 hybridization of the corresponding carbon atom in **4** impose a shorter Mn1–C3 separation of only 2.056(4) Å.

Complex **3** turned out to be extremely sensitive towards air and moisture but could be stored in the solid state under argon at −35 °C for several weeks without decomposition. In solution at ambient temperature, however, the complex readily undergoes a cycloreversion within 6 h with formation of the manganese carbene complex $[(\eta^5\text{-}C_5H_5)(OC)_2Mn{=}CPh_2]$ (**5**) and tri-*tert*-butylboroxine (**6**), thus completing the overall metathesis reaction [Eq. (2)].



3 **5** **6**

Monitoring of the reaction mixture by multinuclear NMR spectroscopy revealed only the characteristic signals associated with **5** and **6** (**5**: ^{13}C NMR: $\delta = 353$ ppm (Mn = C);[16] **6**: ^{11}B NMR: $\delta = 33$ ppm); no further signals indicative of soluble side or degradation products were observed. In contrast to the facile cleavage of **3**, the corresponding complex **4** remained unaltered under similarly mild conditions.

The first example of a concerted metathesis reaction facilitated by a highly reactive alkyl borylene species reported herein adds a new facet to the reactivity patterns of terminal borylene complexes. The fact that neither the rather inert neutral nor the much more reactive cationic amino borylene complexes are susceptible to [2+2] cycloadditions under these conditions emphasizes the significant influence that boron-bound substituents, in particular alkyl groups, have on the reactivity of borylene complexes.

Experimental Section

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

3: Benzophenone (0.018 g, 0.082 mmol) was added to a solution of **1** (0.020 g, 0.082 mmol) in toluene (2 mL). The color of the solution immediately changed from pale to bright yellow. Storage at −35 °C afforded yellow crystals (0.025 g, 66% yield).

^{1}H NMR (500 MHz, $CDCl_3$, −30 °C): $\delta = 7.9$–6.8 (m, 10H, Ph), 4.29 (s, 5H, C_5H_5), 1.34 ppm (s, 9H, *t*Bu); ^{13}C NMR (126 MHz, $CDCl_3$, −30 °C): $\delta = 231.2$, 225.4 (s, CO), 162.0 (Mn-C) 151.1, 149.7 (s, *ipso*-C), 130.0, 128.4, 127.6, 127.1, 126.5, 125.7, 124.8, 124.0, 122.9, 120.6 (s, Ph), 87.5 (s, C_5H_5), 28.5 ppm (s, *t*Bu); ^{11}B NMR (160 MHz, $CDCl_3$, −30 °C): $\delta = 72$ ppm (s, broad); IR (benzene): $\tilde{\nu} = 1988$, 1906 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{24}BMnO_3$: C 67.63, H 5.67; found: C 67.12, H 5.95.

4: Dicyclohexylcarbodiimide (0.034 g, 0.164 mmol) was added to a solution of **1** (0.040 g, 0.164 mmol) in pentane (3 mL). Storage at −35 °C afforded colorless crystals (0.053 g, 72%).

^{1}H NMR (500 MHz, C_6C_6, 25 °C): $\delta = 4.29$ (s, 5H, C_5H_5), 3.48 (m, 1H, Cy), 3.20 (m, 1H, Cy), 1.26 (s, 9H, *t*Bu), 2.10–1.05 ppm (m, 20H, Cy); ^{13}C NMR (126 MHz, C_6C_6, 25 °C): $\delta = 231.1$, 224.3 (s, CO), 151.1 (s, Mn-C), 85.8 (s, C_5H_5), 63.3, 63.0 (s, CyN), 35.7, 35.2, 32.8, 32.3 (s, Cy), 30.0 (s, *t*Bu), 29.6, 27.6, 27.2, 26.6, 25.8, 25.5 ppm (s, Cy); ^{11}B NMR (160 MHz, C_6C_6, 25 °C): $\delta = 62$ ppm (broad); IR (benzene): $\tilde{\nu} = 1970$, 1890 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{36}BMnN_2O_2$: C 64.01, H 8.06, N 6.22; found: C 63.58, H 7.92, N 6.44.

Metathesis: Complex **3** (0.015 g, 0.035 mmol) was dissolved in C_6D_6 (0.4 mL). Within 15 min, the bright yellow solution darkened. After 6 h the reaction was complete, and NMR spectroscopy revealed the exclusive formation of **5** (^{1}H NMR: $\delta = 4.37$ ppm (s, 5H, C_5H_5); ^{13}C NMR: $\delta = 353$ ppm (s, Mn=C)) and **6** (^{1}H NMR: $\delta = 1.07$ ppm (s, 27H, *t*Bu); ^{11}B NMR: $\delta = 33$ ppm).

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