Reactions of $H_2Os_3(CO)_{10}$ with triallylboranes: formation of novel triosmium boron-containing olefin clusters†

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$H_2Os_3(CO)_{10}$ (**1**) reacts with triallylborane $B(CH_2CH{=}CH_2)_3$ at 25 °C to form the cluster $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\textit{trans}\text{-}MeHC{=}CH)_2BC_3H_7]$ (**2**). Reaction of **1** with a mixture of triallylborane–trimethallylborane (1 : 3) gives a mixture of clusters **2**, $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_2C{=}CH)_2BC_3H_7]$ (**3**) and $\{Os_3(CO)_{10}[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(\textit{trans}\text{-}MeCH{=}CH)(Me_2C{=}CH)]BC_3H_7\}$ (**4**). The reaction results in the B–C bond cleavage and the isomerization of two allyl fragments into substituted vinyl groups coordinated to the osmium atoms in an η^2-fashion, and reduction of the third fragment to a propyl group. The mechanism of the reaction is discussed based on isotope labelling and influence of the boron substituent ligand on the reaction path and product identity. Clusters **2**, **3**, **4** are characterized by spectroscopic means as well as by X-ray studies.

Introduction

The high interest in the chemistry of boron-containing transition-metal complexes can be attributed to the fact that they are intermediates in catalytic hydro-, halo- and diboration processes.[1–3] Boron halides and hydrides were typically used for the synthesis of transition metal boryls $[M]BR_2$ and borylenes $[M]{=}BR$.[4] A number of the publications (some of which are cited here) also deal with the reactions of triorganoboranes[3,5a–l] (including those containing one allyl group[5m,n]) with transition metal (in particular Os[5o,p]) complexes. At the same time, to the best of our knowledge, the reactivity of triallylboranes toward transition metal complexes still remains unexplored. Allylboranes are very reactive compounds able to transfer allyl groups to organic molecules and their reactions with the main group organometallics have been studied since the late 1990s.[6,7] Therefore reactions of triallylboranes with transition metal clusters seemed to us a very promising area for investigation. We report here on our studies on reactions of triallylboranes with the neutral triosmium cluster $H_2Os_3(CO)_{10}$ bearing bridging acidic hydride ligands.[8] These reactions lead to the novel triosmium boron-containing olefin clusters $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\textit{trans}\text{-}MeCH{=}CH)_2BC_3H_7]$ (**2**), $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_2C{=}CH)_2BC_3H_7]$ (**3**),[9] and $\{Os_3(CO)_{10}[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(\textit{trans}\text{-}MeCH{=}CH)(Me_2C{=}CH)]BC_3H_7\}$ (**4**) under mild conditions in high yields. Formally, the reaction involves the transformation of two allyl fragments of the borane into η^2-coordinated substituted vinyl fragments, and hydrogenation of the third allyl fragment into a propyl group. However, as will be shown below, the reaction appears to be more complex and the participation of the second allylborane molecule is required to achieve a high yield of clusters **2–4**.

Results and discussion

Reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ (1) with $B(CH_2CH{=}CH_2)_3$

The interaction of **1** with two equivalents of triallylborane (All_3B) was carried out in benzene-d_6 (or methylene chloride-d_2) solution at room temperature. After 10 h, the ^1H NMR spectrum indicated the absence of **1** in the reaction mixture and the formation of a new complex. The ^1H, ^{11}B, and ^{13}C NMR spectra indicated the formation of the symmetrical decacarbonyl triosmium cluster with an η^2:η^2-coordinated boron-containing olefin ligand. The complex was air- and moisture-stable and was isolated by column chromatography. Its structure was determined by X-ray diffraction as $[Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}\textit{trans}\text{-}MeCH{=}CH)_2BC_3H_7]$ (**2**) (Scheme 1). In a full accordance with the symmetrical structure of **2** the coordinated methylvinyl fragments are equivalent in the ^1H, ^{13}C NMR spectra; there are six ^{13}C resonances in the carbonyl region of the ^{13}C NMR spectrum with relative intensities of 1 : 1 : 2 : 2 : 2 : 2 due to pairwise averaging of eight of ten carbonyl groups.[10] The NMR characteristics of **2** seemed to indicate the importance of a $B\ 2p_z/\pi(C{=}C)$ orbital interaction,[11] *i.e.* a high-field shifted ^{11}B resonance (δ 7.3 ppm) and ^1H resonance of the boron-bonded methylene group of the propyl ligand $B\text{–}CH_2C_2H_5$. The chemical shift of the boron atom in **2** is typical of a four-coordinate boron[12] rather than a three-coordinated boron as exists in **2**. The resonance of the methylene group is shifted upfield δ 0.16 ppm in comparison to that for *trans*-cinnamyl(dipropyl)borane $PhCH{=}CHCH_2B(C_3H_7)_2$ (δ 1.32 ppm)[13a] and even for the

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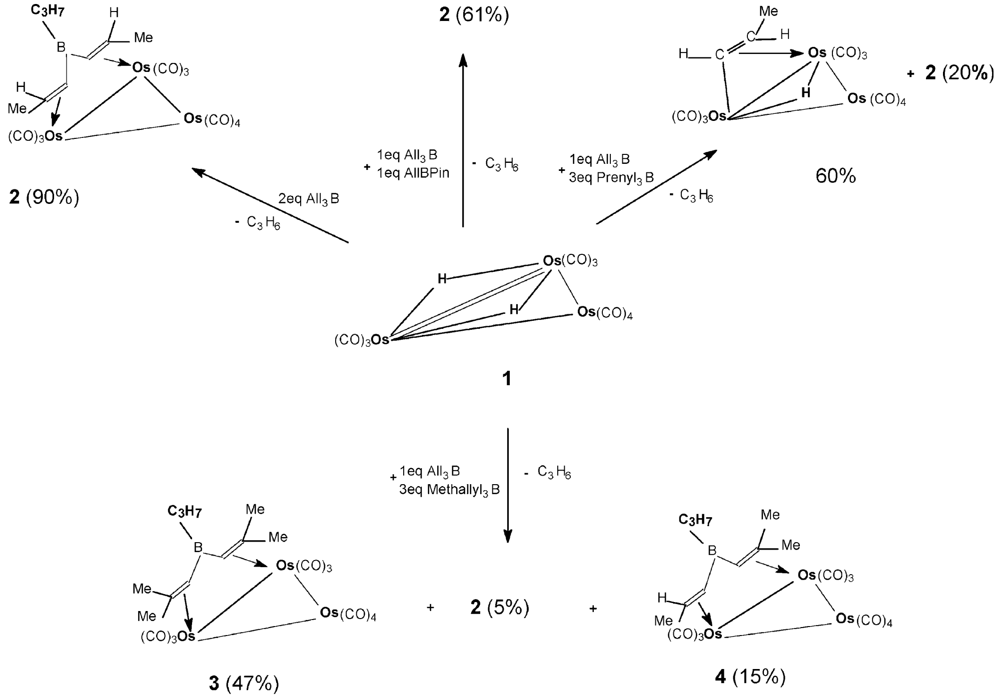


Scheme 1

tripropylborane ammonia adduct $H_3N{\cdot}B(C_3H_7)_3$ (0.25 ppm).[13b] Coordinated methylvinyl fragments are equivalent in the ^1H NMR spectra due to the symmetrical structure of the cluster; the comparison of the chemical shifts with those for clusters containing the $\eta^2{:}\eta^2$-diene ligand shows that they are in accordance with the literature data.[14a] However, in the ^{13}C NMR spectra, the resonance of C_β atom of the osmium-coordinated methylvinyl group (69.8 ppm) is shifted to low field in comparison with the chemical shifts of the $=CH_2$ groups of the clusters $[Fe_2(CO)_5\{\mu\text{-}\eta^2,\eta^3\text{-}H_2C{=}C(Bu^t)C{=}CH_2\}(\mu\text{-}PPh_2)]$ (δ 45.0 and 39.1 ppm) and $[Fe_2(CO)_5\{\mu\text{-}\eta^2,\eta^3\text{-}H_2C{=}C(Me)C{=}CH_2\}(\mu\text{-}PPh_2)]$ (δ 51.9 and 38.6 ppm).[14b] This shift is probably caused by a combination of B $2p_z/\pi(C{=}C)$ orbital interaction and osmium–olefin back bonding.

Importantly for elucidating the reaction pathway, a high yield of **2** (87%) can be achieved only upon using two equivalents of allylborane. If the reaction is run at **1** : allylborane in a 1 : 1 ratio, the yield of **2** decreases to 32%, and 56% of **1** remains. This finding contradicts with the proposal that only one equivalent of both **1** and allyl$_3$B enter into reaction and the hydridic hydrogens of the former add to one of boron-bonded allyls converting it into a propyl moiety. To better understand how this reaction can be explained we studied the reactions of **1** with "substituted" triallylboranes: trimethallylborane (Methallyl$_3$B) or allylboronic acide pinacolate (AllBPin) as well as the reaction of $D_2Os_3(CO)_{10}$ ($\mathbf{1^d}$) with All$_3$B. The results obtained are described below.

Crystal structure of $[Os_3(CO)_{10}(\mu\text{-}\eta^2{:}\eta^2\text{-}\textit{trans}\text{-}MeCH{=}CH)_2BC_3H_7]$ (2)

The molecular structure of complex **2** is shown on Fig. 1; selected bond distances and angles are given in Table 1.

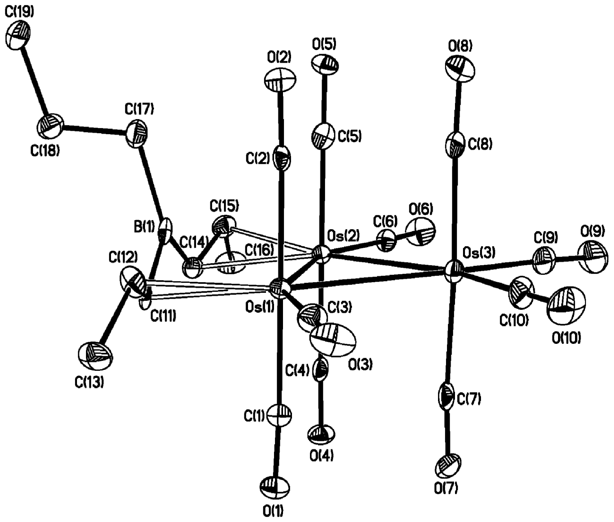


Fig. 1 ORTEP presentation of the molecular structure with numbering scheme for complex **2**, with thermal ellipsoids drawn at the 30% probability level (the hydrogen atoms are omitted for clarity).

The cluster contains a triangular array of osmium atoms and a bridging $\eta^2{:}\eta^2$ boron-containing olefin ligand, which is π-bonded to Os(1) and Os(2). The positions of the carbonyl groups relative to the equatorial plane of the osmium triangle do not deviate from the planes thus indicating the absence of bridging hydride ligands. Some elongation of Os(1)–Os(2) distance (2.9410(5) Å) *vs.* 2.87 Å for $Os_3(CO)_{12}$[15]) is probably caused by the μ-diene ligand just as in the case of $[Os_3(CO)_{10}(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_2{=}CHCH{=}CH_2)]$.[16] The lengths of the $\mu\text{-}\eta^2{:}\eta^2$-coordinated C=C bonds in complex **2** (1.407(14) and 1.390(13) Å) correspond to those found for a

Table 1 Selected bond lengths (Å) and angles (°) for complexes **2–4**

Complex	**2**	**3**	**4A**[a]	**4B**[a]
Os(1)–Os(2)	2.9410(5)	2.9503(8)	2.9481(4)	2.9319(4)
Os(1)–Os(3)	2.8797(5)	2.8727(10)	2.8695(4)	2.8776(4)
Os(2)–Os(3)	2.8763(5)	2.8706(8)	2.8629(4)	2.8759(4)
Os(1)–C(11)	2.236(9)	2.261(11)	2.239(6)	2.247(6)
Os(1)–C(12)	2.311(10)	2.359(13)	2.365(8)	2.382(7)
Os(2)–C(14)	2.242(9)	2.247(11)	2.257(6)	2.239(6)
Os(2)–C(15)	2.308(10)	2.379(13)	2.304(7)	2.296(7)
Os(3)–C(10)	1.921(11)	1.898(14)	1.904(8)	1.918(8)
B(1)–C(11)	1.571(14)	1.609(17)	1.497(10)	1.537(9)
B(1)–C(14)	1.520(14)	1.537(17)	1.568(10)	1.542(9)
B(1)–C(17)	1.598(14)	1.557(16)	1.639(10)	1.648(10)
C(11)–C(12)	1.407(14)	1.397(15)	1.404(10)	1.408(9)
C(12)–C(13)	1.513(13)	1.525(16)	1.540(11)	1.497(10)
C(12)–C(131)		1.506(16)	1.487(11)	1.491(10)
C(14)–C(15)	1.390(13)	1.386(16)	1.398(10)	1.402(9)
C(15)–C(16)	1.500(14)	1.540(18)	1.486(10)	1.518(9)
C(15)–C(161)		1.497(17)		
C(17)–C(18)	1.530(14)	1.546(16)	1.540(9)	1.538(9)
C(18)–C(19)	1.522(14)	1.501(16)	1.499(10)	1.499(9)
Os(2)–Os(1)–Os(3)	59.22(1)	59.05(2)	58.939(9)	59.336(9)
Os(1)–Os(2)–Os(3)	59.33(1)	59.13(2)	59.161(9)	59.391(9)
Os(1)–Os(3)–Os(2)	61.45(1)	61.82(2)	61.900(9)	61.272(9)
C(3)–Os(1)–Os(3)	93.2(3)	93.5(4)	95.8(2)	93.5(2)
C(6)–Os(2)–Os(3)	95.4(3)	97.4(4)	93.2(2)	93.2(2)
C(10)–Os(3)–Os(1)	98.8(4)	102.0(4)	96.2(2)	99.7(2)
C(9)–Os(3)–Os(2)	101.0(3)	92.3(4)	98.6(2)	97.6(2)
C(11)–B(1)–C(14)	116.6(8)	110.4(10)	116.1(6)	118.3(6)
C(11)–B(1)–C(17)	119.2(8)	121.4(10)	126.7(6)	123.0(6)
C(14)–B(1)–C(17)	123.1(9)	126.5(11)	115.5(6)	117.2(6)
C(12)–C(11)–B(1)	128.2(9)	133.2(9)	134.9(7)	133.4(6)
C(11)–C(12)–C(13)	124.3(9)	118.2(10)	119.6(7)	118.9(6)
C(11)–C(12)–C(131)		123.4(10)	124.6(8)	124.1(6)
C(131)–C(12)–C(13)		111.9(10)	110.5(8)	111.4(6)
C(15)–C(14)–B(1)	126.7(9)	133.8(11)	128.0(6)	128.7(6)
C(14)–C(15)–C(16)	121.8(9)	118.8(11)	121.7(7)	123.2(7)
C(14)–C(15)–C(161)		127.0(12)		
C(161)–C(15)–C(16)		109.6(11)		
C(18)–C(17)–B(1)	108.9(8)	109.7(9)	108.8(5)	105.9(5)
C(19)–C(18)–C(17)	111.9(9)	114.9(10)	113.5(6)	113.5(6)

[a] Data for two crystallographically independent molecules are presented.

number of known diene complexes;[17] at the same time they are longer than corresponding distances in non-coordinated vinylborane (gas electron diffraction, GED 1.370(6) Å).[18] The B–C(sp^2) distances 1.571(14) and 1.520(14) Å) in **2** are comparable with those in vinylborane (GED 1.558(3) Å).[18]

Unlike planar three-coordinated boron, the boron atom in **2** deviates from the plane of the three adjacent carbon atoms, C(11), C(14) and C(17), bending toward the metal triangle by 0.096(11) Å, which is presumably caused by an additional interaction of the vacant boron 2p$_z$-orbital with the triosmium cluster;[19] rather short distances from the boron atom to the nearest osmium atoms (B(1)–Os(1) and B(1)–Os(2): 2.793(11) and 2.776(10) Å, respectively), and especially to the median of the Os(1)–Os(2) bond (Table 2), are in agreement with this proposal.

Analogous deviation of the boron atom from the substituent plane by 0.092(1) Å caused by 2p$_z$/π-(Ph) dative interaction was shown to occur in 3-chloro-7α-phenyl-3-borabicyclo[3.3.1]-nonane.[20]

Reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ (1) with $B(CH_2C(Me){=}CH_2)_3$ and $B(CH_2CH{=}CH_2)_3$

In contrast to triallylborane, trimethallylborane (Methallyl$_3$B, three equivalents) does not react with **1** at room temperature for at least 10–15 days, but the reaction can be induced by addition of one equivalent of triallylborane. The absence of

Table 2 Selected geometrical parameters (Å) for complexes **2–4**

Deviation of B(1) from C(11)C(14)C(17) plane/Å	0.096(11)	0.117(14)	0.117(8)	0.113(8)
B(1)···Os(1)	2.793(10)	2.817(13)	2.773(7)	2.774(7)
B(1)···Os(2)	2.776(10)	2.805(13)	2.796(7)	2.768(7)
B(1)···centroid Os(1)–Os(2)	2.365(10)	2.393(13)	2.362(7)	2.351(7)

initial **1** and formation of a mixture of complexes was detected by ^{1}H NMR spectroscopy after 20 h at room temperature. Using column chromatography on silica we obtained the fraction containing complex **2** as a minor component ($\leq$5%, ^{1}H NMR) along with the analogous symmetrical $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_2C{=}CH)_2BC_3H_7]$ (**3**), and unsymmetrical $\{Os_3(CO)_{10}[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(\textit{trans}\text{-}MeCH{=}CH)(Me_2C{=}CH)]BC_3H_7\}$ (**4**) clusters (Scheme 1). Compounds **3** and **4** were isolated in pure form by fractional crystallization and were characterized by ^{1}H, ^{11}B (of **3**), and ^{13}C NMR spectra as well as by X-ray diffraction. Regrettably, **4** was not obtained in adequate amounts to get its ^{11}B NMR spectrum and only a wide ^{11}B resonance characteristic of a mixture of clusters **2–4** is observed. Notably, cluster **3** is formed in this reaction only with a large excess of trimethallylborane. With $Methallyl_3B : All_3B$ in a 2 : 1 ratio the ^{1}H NMR spectrum of the reaction mixture showed only resonances of **2** and **4** in ~1 : 2 ratio but not signals of **3**. Further decrease of excess trimethallylborane increased the proportion of **2**. Clusters **2**, **3** and **4** have similar structures. Both the signal of the boron atom of **3** in its ^{11}B NMR spectrum and the resonances of boron-bonded methylene protons for **3** and **4** in their ^{1}H NMR spectrum are shifted to high field just as was found for **2**. In a full accordance with symmetrical structure of **3** the ^{13}C NMR spectrum in the carbonyl region is analogous to that of **2.** The methyl groups of the coordinated olefin ligand [Fig. 2, C(13) and C(16), C(131) and C(161)] in **3** are pairwise equivalent and appear in the ^{1}H and ^{13}C NMR spectra as two signals of double intensity due to symmetrical structure of the cluster.[10] It is noteworthy that ^{13}C signals of the coordinated terminal $=CMe_2$ groups in **3** and **4** are even more downfield-shifted as compared to the $=CHMe$ resonance in **2**. Cluster **4**, in contrast to **2** and **3**, is unsymmetrical; therefore, the signals of the propyl group appear in the ^{1}H NMR spectrum as complex multiplets, and the ^{13}C NMR spectrum reveals 10 separate signals of the carbonyl groups.

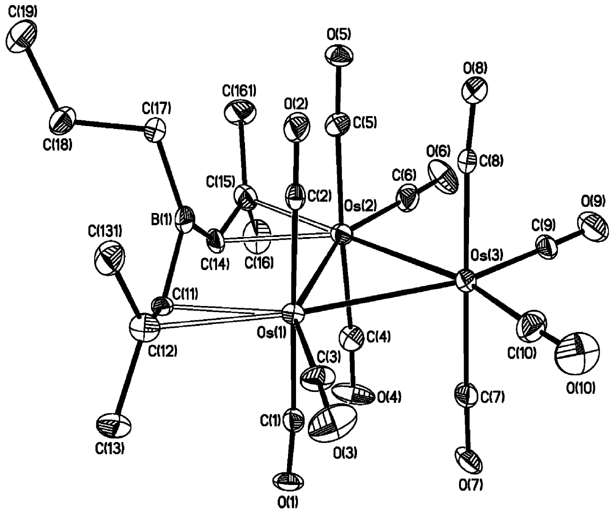


Fig. 2 ORTEP presentation of the molecular structure with numbering scheme for complex **3**, with thermal ellipsoids drawn at the 30% probability level (the hydrogen atoms are omitted for clarity).

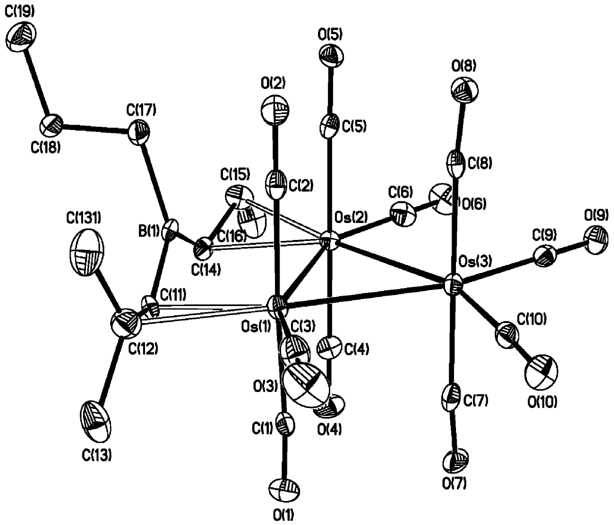


Fig. 3 ORTEP presentation of the one of two independent molecules with numbering scheme for complex **4**, with thermal ellipsoids drawn at the 30% probability level (the hydrogen atoms are omitted for clarity).

Crystal structure of clusters $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_2C{=}CH)_2BC_3H_7]$ (3) and $\{Os_3(CO)_{10}[\mu\text{-}\eta^2\text{:}\eta^2\text{-}(\textit{trans}\text{-}MeCH{=}CH)(Me_2C{=}CH)]BC_3H_7\}$ (4)

The molecular structures of **3** and **4** are shown on Fig. 2 and 3 with selected bond distances and angles given in Table 1. Two crystallographically independent molecules of nearly the same structure are present in the crystal of **4**. The structures of complexes **3** and **4** are similar to that of complex **2** (Tables 1 and 2). The difference in the structure of the $\mu\text{-}\eta^2\text{:}\eta^2$ coordinated ligands does not influence the geometric parameters of the core of the clusters.

Reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ (1) with a mixture of $B(CH_2CH{=}CMe_2)_3$ and $B(CH_2CH{=}CH_2)_3$

Like trimethallylborane, triprenylborane ($Prenyl_3B$) does not react with cluster **1** at room temperature and again addition of triallylborane induces the reaction. After stirring of the reaction mixture in benzene-d_6 for 20 h at room temperature it was separated by column chromatography to afford **2** (20%) and the known methylvinyl cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu,\eta^2\text{-}\textit{trans}\text{-}HC{=}CHMe)$[21] (60%) (Scheme 1). No products containing prenyl groups were found.

Reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ (1) with a mixture of $(CH_2{=}CHCH_2)BPin$ and $B(CH_2CH{=}CH_2)_3$

Allylboronic acid pinacolate (AllBPin) does not react with **1** under the above-mentioned conditions. Nevertheless, the reaction of **1** with a $(CH_2{=}CHCH_2)BPin : B(CH_2CH{=}CH_2)_3$ 1 : 1 mixture leads to **2** as the sole boron-containing product in a high yield (61%).

Reaction of $Os_3(\mu\text{-}D)_2(CO)_{10}$ (1^d) with $B(CH_2CH{=}CH_2)_3$

The reaction of $D_2Os_3(CO)_{10}$ (1^d) with triallylborane was carried out analogously to the reaction of non-deuterated **1** and gave a mixture of clusters containing deuterium distributed exclusively over the propyl group carbons

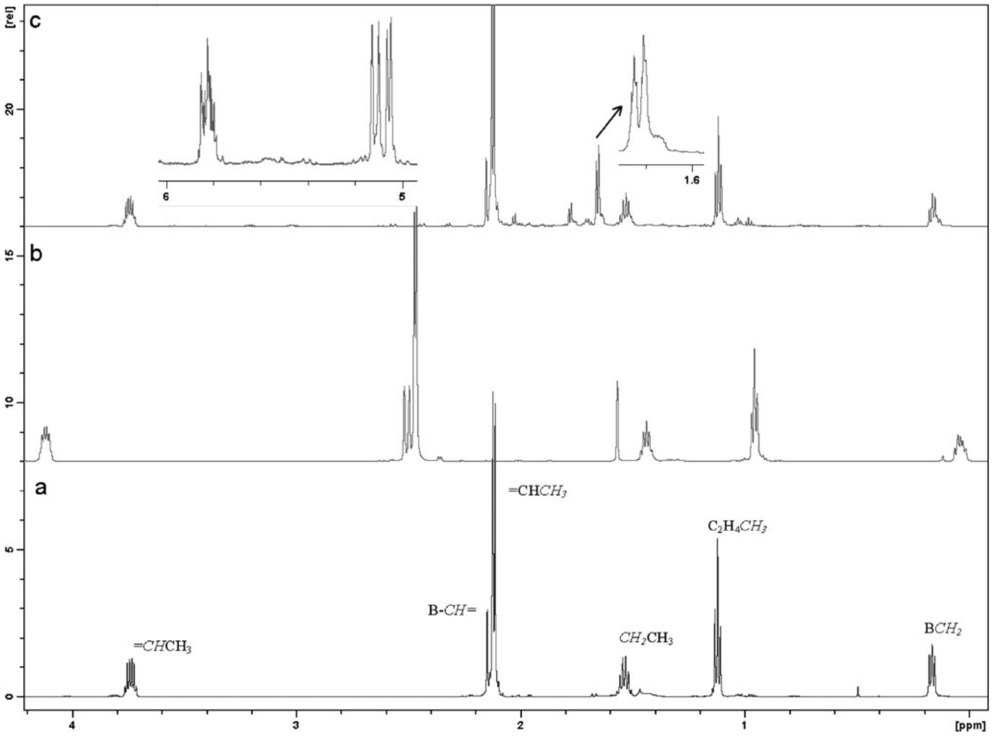


Fig. 4 ^{1}H NMR spectra for (a) **2** in C_6D_6, (b) $\mathbf{2^d}$ in CD_2Cl_2 and (c) reaction mixture of $\mathbf{1^d}$ with triallylborane in C_6D_6.

$[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}trans\text{-}MeCH{=}CH)_2BCHDCH_2CH_3]$ ($\mathbf{2^{d1}}$), $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}trans\text{-}MeCH{=}CH)_2BCH_2CHDCH_3]$ ($\mathbf{2^{d2}}$), and $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}trans\text{-}MeCH{=}CH)_2BCHDCHDCH_3]$ ($\mathbf{2^{d1,2}}$) as evidenced by ^{1}H and ^{13}C NMR (Fig. 4 and 5) spectra. The ^{13}C NMR spectrum of the deuterated sample (Fig. 5(b) and (c)) contained four methyl singlet resonances for three deuterated clusters $\mathbf{2^d}$ ($\mathbf{2^{d1}}$ + $\mathbf{2^{d2}}$ + $\mathbf{2^{d1,2}}$) and one for non-deuterated complex **2**. On the basis of the signal shape of the central methylene group of the propyl ligand the signals of clusters ($\mathbf{2^{d2}}$) and ($\mathbf{2^{d1,2}}$) are practically coincident triplets. According to methylene group signal intensities the cluster ($\mathbf{2^{d1}}$) is the predominant product. In the ^{1}H NMR spectrum (Fig. 4(b)) integral intensity and multiplicity distortion are observed only for the proton resonances of the boron-bonded methylene group of the propyl fragment.

When the analogous reaction of $\mathbf{1^d}$ with All_3B was run in a sealed NMR tube without traces of moisture, a low-intensity hydride signal of non-deuterated cluster **1** was found in the ^{1}H NMR spectrum of the reaction mixture, though this signal was absent in the spectrum of initial $\mathbf{1^d}$ recorded with strictly the same parameters. The presence of propylene in the reaction mixture was detected in the ^{1}H NMR spectrum (Fig. 4(c)) (see ESI,† Part I). It is propylene that can isomerize[22] on $\mathbf{1^d}$ exchanging deuterium for hydrogen and causing some loss of the D-marker in $\mathbf{1^d}$. A comparison of the ^{13}C NMR spectra of the deuterated products of the reaction $\mathbf{1^d}$ with triallylborane in a Schlenk flask with those of the same reaction in a sealed tube (Fig. 4(c) and 5(c)), in which propylene from the solution evolution is reduced, shows that the intensity ratio for the signals of the boron-bonded methylene groups and of the terminal methyl groups of the propyl fragment in **2** and $\mathbf{2^{d1}}$ changes. The intensity of the signal of **2** markedly increases in the latter case indicating an increase of the yield of non-deuterated cluster **2**.

The shapes of the propylene resonances (Fig. 4(c)) indicate that the deuterium is located mainly in the methyl and methyne groups. The presence of only a signal for a terminal methylene group at δ 115.7 ppm and the absence of the signals of methyne and methyl groups in the 2D HC HSQC spectrum provide additional support for this proposal, though the ^{1}H NMR spectrum (Fig. 4(c)) of this mixture shows that propylene content is rather high. This deuterium distribution indicates that propylene forms by protolysis of the boron–allyl bond.[23]

The reaction of $\mathbf{1^d}$ with a mixture of allyl- and methallylboranes under the above conditions gives a mixture of deuterated clusters $\mathbf{2^d}$, $\mathbf{3^d}$ and $\mathbf{4^d}$ as determined from the ^{1}H NMR spectrum of the reaction mixture. For all clusters studied we also observe a distortion of the multiplicity for the signals of the boron-bonded methylene protons. Notably, in the reactions of **1** with All_3B–$Methallyl_3B$ or All_3B–AllBPin (1 : 3) mixtures carried out in an NMR tube the propylene signals were always observed in the ^{1}H NMR spectrum. A summary of the reactivity of **1** toward triallylboranes is given in Scheme 1.

The following conclusions can be drawn from this study: (1) cluster **1** reacts directly only with triallylborane. The high yield of boron-containing olefin cluster **2** can be achieved by using two equivalents of boron (2 equivalents All_3B or 1 equivalent of $(All)_3B$–AllBPin 1 : 1 mixture) per equivalent of osmium cluster **1**. During the reaction propylene is evolved as was shown for the "sealed tube reaction" of $\mathbf{1^d}$ with All_3B. (2) When a mixture of boranes is used, the reaction products contain only propyl as the reduced ligand indicating that only

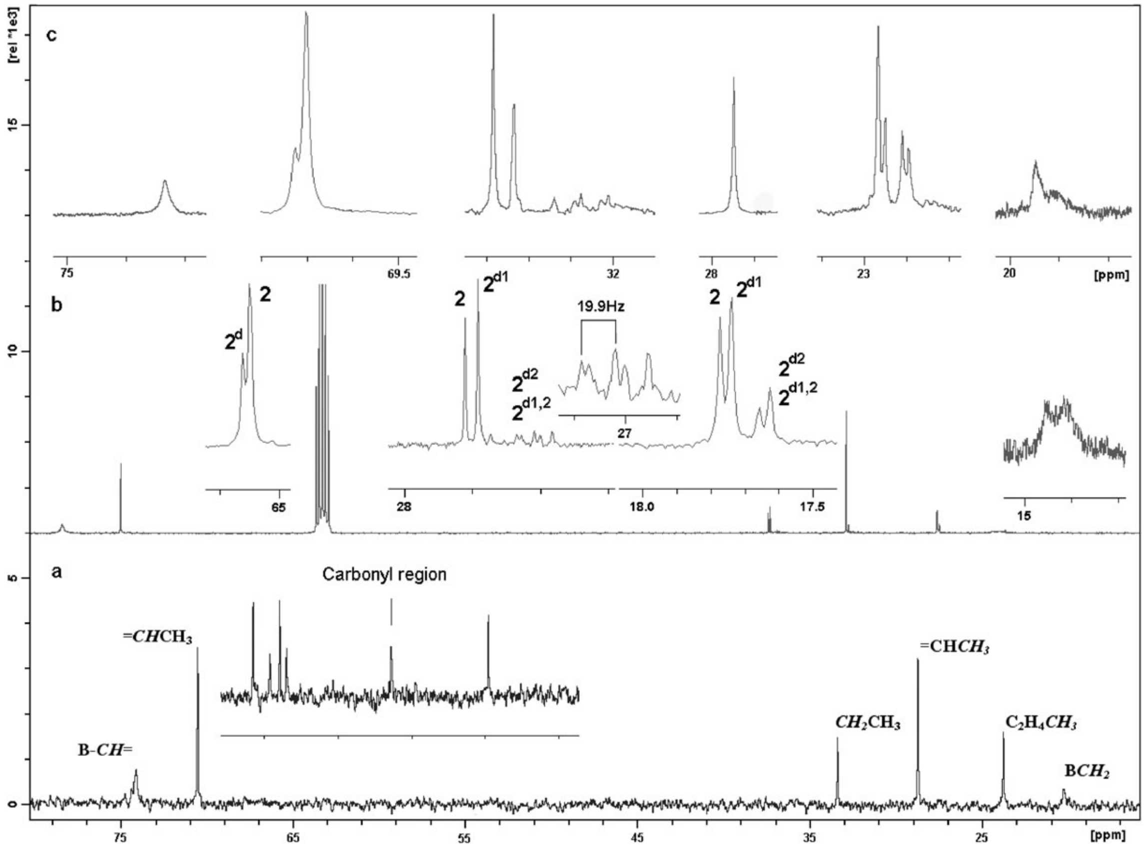


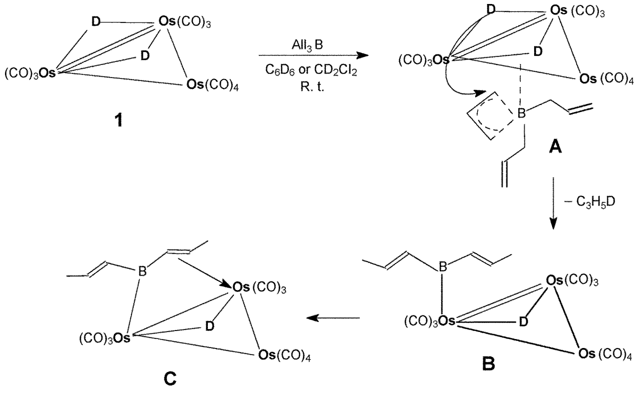
Fig. 5 ^{13}C NMR spectra for (a) **2** in C_6D_6, (b) mixture of the clusters $\mathbf{2^d}$: [$Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}trans\text{-}MeCH{=}CH)_2BCHDCH_2CH_3$] ($\mathbf{2^{d1}}$), [$Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}trans\text{-}MeCH{=}CH)_2BCH_2CHDCH_3$] ($\mathbf{2^{d2}}$), [$Os_3(CO)_{10}(\mu\text{-}\eta^2\text{:}\eta^2\text{-}trans\text{-}MeCH{=}CH)_2BCHDCHDCH_3$] ($\mathbf{2^{d1,2}}$) in CD_2Cl_2, and (c) reaction mixture of $\mathbf{1^d}$ with triallylborane in C_6D_6.

non-substituted allyl fragments are hydrogenated as evidenced by the deuterium distribution in the products of reactions of $\mathbf{1^d}$ with All_3B. (3) Cluster **4** is always formed in the reaction of **1** with triallylborane–trimethallylborane mixtures, whereas cluster **3** is formed only with a three-fold excess of trimethallylborane. (4) Triprenylborane does not react with **1** even in the presence of triallylborane and the known methylvinyl cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu,\eta^2\text{-}trans\text{-}HC{=}CHMe)$[26] is isolated as a major product. It is noteworthy, that trace amounts of the latter are always formed in reactions of cluster **1** with a mixture of allylboranes without an excess of triallylborane.

These findings show the reaction route to be rather complex. The initial stage, the interaction of **1** with $B(All)_3$, can proceed in two ways. The first one is known and consists of the coordination of the double bond of triallylborane to the osmium atom followed by the olefin isomerisation *via* a hydrogen shift.[22,24–26] The results obtained earlier for the interaction of **1** with diallyl sulfide are in agreement with this pathway.[27] This mechanism applied to the interaction of **1** with All_3B should involve 1,3-sigmatropic shift of the hydrogen atom[22,24–26] followed by the protolysis of the boron–carbon bond. Despite the fact that this mechanism is generally accepted, we have to discard it on the basis of the deuterium distribution in the products of the reaction of $D_2Os_3(CO)_{10}$ ($\mathbf{1^d}$) with triallylborane (see ESI,† Part II).

We therefore suggest a second reaction pathway involving in the initial step a coordination of triallylborane to cluster **1** through the boron atom (Scheme 2, presented for $\mathbf{1^d}$). The formation of intermediates **B** and **C** is suggested by analogy with the formation of known olefin osmium clusters.[22,24–26]

The ability of only triallylborane rather than other allylboranes studied here to coordinate to **1** is presumably attributable to the greater Lewis acidity of the former. It cannot be excluded that the selectivity of the reaction is caused by steric factors. At the same time the electrophilicity of the bridging hydride atoms in intermediate **A** should increase upon this coordination thus making possible the protolysis of the B–allyl bond[23] by the acidic hydridic hydrogens in **A** to give σ-boryl intermediate



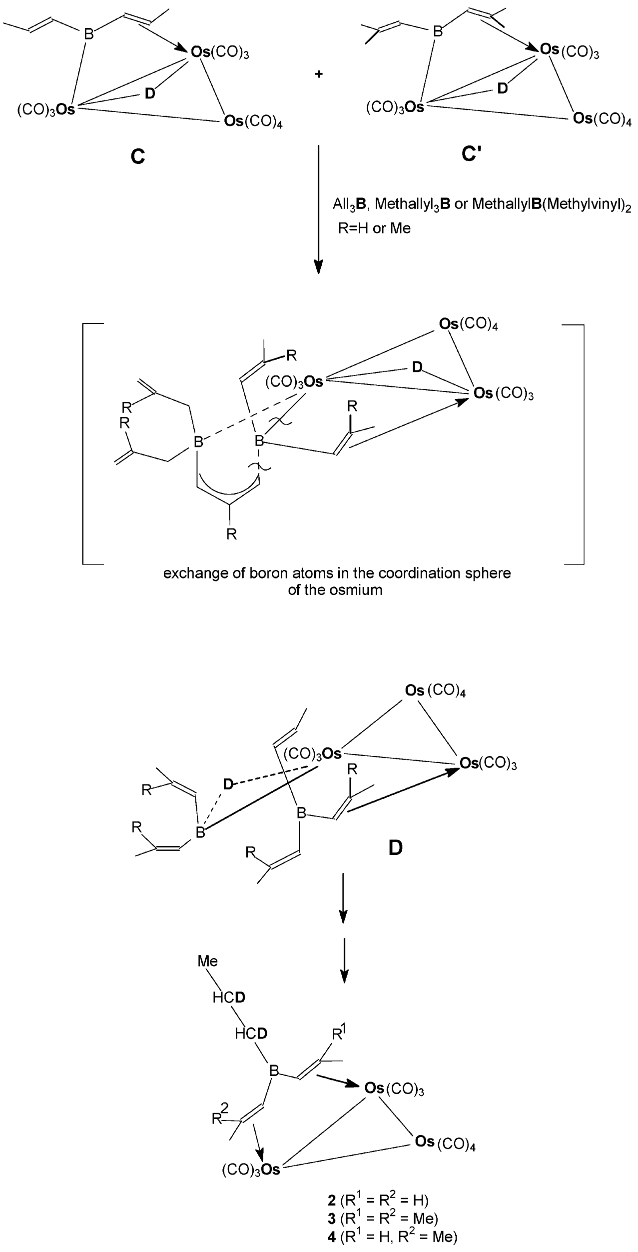
Scheme 2

B, loss of propylene preceeding the isomerization of the carbon–carbon double bond. The formation of methylvinyl ligands non-coordinated to the osmium atoms is confirmed by NMR ^{1}H data (see ESI,† Part III). These methylvinyl groups are formed due to metal-induced hydrogen atom shifts, the necessary condition for this shift being the formation of the boron–osmium bond. The latter process is necessary for stabilization of **B** by electron density transfer from the carbon–carbon double bond to the boron atom. Presumably, intermediate **B** transforms further into σ,π-boryl intermediate **C** and this is in accordance with literature data.[22,24,25] Indirect evidence for the formation of **C** arises from the fact that hydrolysis of the reaction mixture of **1** with All$_3$B produced two complexes only, namely **2** and the known propenyl cluster $Os_3(\mu\text{-H})(CO)_{10}(\mu,\eta^2\text{-}trans\text{-HC=CHMe})$.[21]

Notably, further interaction of **C** with the "second boron equivalent" is faster than its formation as follows from the requirement of excess allylborane to achieve a high yield of olefin clusters, otherwise substantial amounts of cluster **1** is recovered.

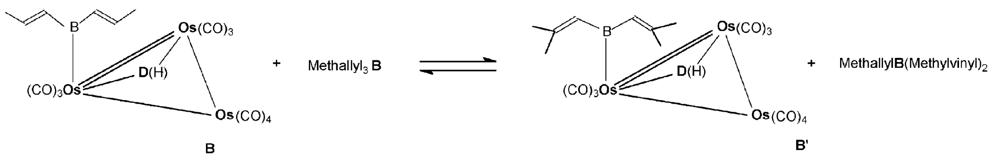
The next stage of the process involves the interaction of **C** with the second equivalent of allylboranes (All$_3$B or Methallyl$_3$B). The structure of complexes **3** and **4** provides unambiguous evidence for the occurrence of this process. The former process is known to proceed as allylic rearrangement for All$_3$B/All$_2$BSR as well as Crotyl$_3$B/BX$_3$ (X = CI, OR or SR) couples *via* a six-membered transition state[28,29] (see ESI,† Part IV). We assume that an analogous rearrangement can also occur during interaction of **B** with the additional equivalent of trimethallylborane because the boron atom B is sufficiently electrophilic in the former due to polarization of Os–B bond. It is noteworthy that isomerization of allyl groups into methylvinyl groups proceeds necessarily within intermediate **B**. So the interaction of **B** with Methallyl$_3$B (Scheme 3) should result in a mixture of Methallyl$_3$B, with di(methylvinyl)methallylborane [MethallylB(Methylvinyl$_2$)].

Obviously, only an excess of Methallyl$_3$B ensures the methylvinyl–methallyl exchange in **B** providing an opportunity for the formation of **3** under these conditions. According to the formation of intermediates **B** and **B′**, the intermediate **C** should also consist of a mixture of **C** and **C′** (Scheme 4). Further transformations proposed to lead to the final products are depicted in Scheme 4 for the reaction of **1**^{d} with All$_3$B/Methallyl$_3$B mixture.



Scheme 4

We suppose that both **C** and **C′** are able to undergo intermolecular exchange that in turn could lead to exchange of the boron atoms in the osmium coordination sphere. The above exchange processes seem to promote further transformations of intermediate **C**. Similar processes occur *via* allylic rearrangement, accompanied by allyl-to-methylvinyl (or methallyl to α,α-dimethylvinyl) isomerization, to afford intermediate **D**. The boron atom of the σ,η^2-boryl ligand in **C** (**C′**) adds an allyl(metallyl) group from the "external" triallyl(metallyl)borane and converts in to an η^2-borane ligand while the entering borane coordinates to one of the osmium atoms as a σ-boryl ligand. The barriers for an intramolecular allyl exchange in triallyl- and trimethallylboranes[29] are very similar (61.9 and 62.3 kJ mol^{-1}), whereas that for



Scheme 3

triprenylborane the barrier is much higher (77.5 kJ mol^{-1}) and provides an explanation for why triprenylborane does not enter the reaction.

The intimate character of this isomerization remains uncertain (unclear). We suppose that it is a metal-induced allyl/methylvinyl rearrangement since there is the possibility of interaction of the vacant boron $2p_z$ orbital with the orbitals of the metal coordinated olefin, and a 1,3-shift of a hydrogen atom becomes allowed.

The proposal shown in Scheme 4 corresponds fully to the experimental results for the formation of clusters **2–4**. The formation of cluster **3** is regulated by an excess of $Methallyl_3B$ which is necessary for intermediate **C′** regeneration (Scheme 3) whereas the presence of $Methallyl_3B$ in the reaction mixture is enough for the formation of **4**.

A further reaction path is concerned with reduction of the vinylborane moiety to the alkyl group. It cannot proceed by insertion of olefin across the osmium–boron bond[30] in intermediate **D**, since this path does not exclude the formation of complexes **3**, **4** containing isobutyl ligands that would result from oxidative addition of a dimethylvinyl ligand at the Os–B bond, which contradicts our experimental data.

We assume that the olefin ligand hydrogenation at room temperature is caused by a number of fast processes, *i.e.* protolysis of boron–carbon bond, allyl ligands exchange at the boron atom and hydroboration of methylvinyl ligand (see ESI,† Part V).

The deuterium distribution during rhodium-catalyzed hydroboration of terminal olefins by D-catecholborane[31] was interpreted in terms of reversible hydrogen atom migrations between the coordinated olefin and the metal atom. The deuterium distribution in this case can be caused by non-regiospecific hydroboration (leading to formation of $\mathbf{2^{d1}}$ and $\mathbf{2^{d2}}$) as well as by hydrogen atom exchange (leading to $\mathbf{2^{d1,2}}$) through a σ-bond metathesis mechanism.[32]

The proposed reaction pathway is in agreement with the experimental data. With the aid of NMR monitoring of the reaction mixture of **1** with All_3B, we observed three sets of resonances which could be tentatively assigned to intermediates **B**, **C** and **D** (see ESI,† Part VI).

Schemes 2–4 are also applicable to the reaction of **1** with an All_3B–AllBPin mixture. In correspondence with Scheme 3, in this case an intermolecular allyl moiety exchange leads to the mixture of intermediates **B** and $HOs_3(CO)_{10}$-BPin (**B″**), and to AllBPin and All_3B as well. Evidently, the decreased yield of cluster **2** is caused by the fact that intermediate **B″** is not able to convert into cluster **2**.

Conclusion

In this work the reactions of triallylboranes with dihydridotriosmium decacarbonyl cluster **1** were studied. The formal outcome of the reactions is quite compatible with the **1** : All_3B stoichiometry of 1 : 1 but the proposed reaction pathway implies the participation of the second equivalent of allylborane and involves the following steps:

(i) coordination of triallylborane to **1** through the boron atom (Scheme 2, intermediate **A**);

(ii) B–C bond cleavage as the result of protolysis of the boron–allyl bond and novel metal-induced isomerization of the carbon–carbon double bond to give boryl intermediates **B** and **C** (Scheme 2), one of the hydridic hydrogens being lost at this step;

(iii) intermolecular transfer of an allyl group from "the second boron equivalent" to the boryl boron atom in **C**, accompanied by an exchange of the boron atoms in the osmium coordination sphere (Scheme 4, intermediate **D**).

Experimental

General

The reactions were carried out under an argon atmosphere. All solvents were distilled under dry argon from the appropriate drying agent. Silica gel 230–400 mesh ASTM Merck was used for chromatography. $H_2Os_3(CO)_{10}$, $D_2Os_3(CO)_{10}$ (99.97% D_2),[33] triallylborane (All_3B),[34a] trimethallylborane ($Methallyl_3B$),[34b] triprenylborane ($Prenyl_3B$),[34c] allylboronic acid pinacolate (AllylBPin)[34d] were prepared by known methods. NMR spectra were registered on a Bruker AMX-400 spectrometer at 400.13 MHz for ^1H (relative to Me_4Si), at 128.38 MHz for ^{11}B (relative to $BF_3{\cdot}Et_20$), at 100.13 MHz for ^{13}C in C_6D_6, CD_2Cl_2 (relative to Me_4Si), on a Bruker Avance-600 spectrometer at 150.92 MHz for ^{13}C in C_6D_6 (relative to Me_4Si). IR-spectra of hexane and cyclohexane solutions were recorded on a IR Fourier-spectrometer Nicolet Magna 75 IR. Atmospheric pressure chemical ionization (APCI) mass-spectra were recorded on a Shimadzu LCMS 2010A system; positive ion registration mode; a full scan, 300–2000 m/z range; acetonitrile as a moving phase modifier.

Syntheses

[Os₃(CO)₁₀(μ-η²:η²-*trans*-MeCH=CH)₂BC₃H₇] (2). $B(CH_2CH{=}CH_2)_3$ (0.08 ml, 0.468 mmol) was added to a solution of **1** (200 mg, 0.234 mmol) in 3 ml C_6D_6 at 22 °C. After completion of the reaction (∼3 days) the reaction mixture changed from purple to bright yellow. It was then poured onto SiO_2 and the solvent was removed *in vacuo*. The dry residue was placed at the top of an SiO_2 column and eluted with hexane. Bright yellow crystals of cluster **2** were isolated (201 mg, 87%, crystallized from hexane). ^1H NMR (600.13 MHz, C_6D_6, 25 °C): δ 3.74 (dq, 2H, $^3J_{(H-H)}$ = 12.8, 5.8 Hz, =C*H*Me), 2.14 (d, 2H, $^3J_{(H-H)}$ = 12.8 Hz, BC*H*=), 2.12 (d, 6H, $^3J_{(H-H)}$ = 5.8 Hz, =CH*Me*), 1.54 (m, 2H, C*H*₂Me), 1.12 (t, 3H, $^3J_{(H-H)}$ = 7.6 Hz, CH₂*Me*), 0.16 (pseudo-t, 2H, $^3J_{(H-H)}$ = 8, 1.8 Hz, BC*H*₂); ^{11}B (128.38 MHz, C_6D_6, 25 °C): δ 7.3; ^{13}C (400.13 MHz, C_6D_6, 25 °C): δ 189.0 (2C≡O), 188.7 (C≡O), 188.1 (2C≡O), 187.6 (C≡O), 180.5 (2C≡O), 178.8 (2C≡O), 73.4 (br, 2BC=), 69.8 (2 =*C*HMe), 32.7 (*C*H₂Me), 28.0 (2 =CH*Me*), 23.1 (CH₂CH₂*Me*), 19.6 (br, BCH₂) ppm. IR ($\nu_{C\equiv O}/cm^{-1}$, hexane): 2111m, 2053m, 2047s, 2026vs, 2002s, 1982m br. CI-MS: m/z 988 (**2** + H)$^+$. $C_{19}H_{17}O_{10}BOs_3$ (986.75): calc. C 23.13, H 1.74, B 1.10, Os 57.83; found C 23.45, H 1.92, B 0.84, Os 58.25%.

Table 3 Crystal data, data collection and structure refinement parameters for complexes **2–4**

Complex	**2**	**3**	**4**
Molecular formula	$C_{19}H_{17}BO_{10}Os_3$	$C_{21}H_{21}BO_{10}Os_3$	$C_{20}H_{19}BO_{10}Os_3 \cdot 0.25C_5H_{12}$
M_r	986.74	1014.79	1018.80
Dimensions/mm	0.18 × 0.16 × 0.10	0.52 × 0.16 × 0.15	0.15 × 0.12 × 0.10
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	9.5816(7)	9.707(3)	9.6191(5)
b/Å	28.057(2)	16.418(5)	14.8240(7)
c/Å	9.7448(7)	16.152(5)	19.270(1)
α/°			93.924(1)
β/°	114.831(1)	97.054(7)	98.035(1)
γ/°			102.923(1)
V/Å^3	2377.5(3)	2555(1)	2637.7(2)
Z	4	4	4
D_c/g cm^{-3}	2.757	2.639	2.566
Temperature/K	115	110	120
$2\theta_{max}$/°	60.0	60.0	58.0
μ/cm^{-1}	160.44	149.36	144.66
T_{min}/T_{max}	0.127/0.265	0.021/0.099	0.081/0.199
Refl. collected	18626	28722	29025
Indep, refl. (R_{int})	6820 (0.0487)	7365 (0.0742)	13834 (0.0357)
Obs. refl. ($I > 2\sigma(I)$)	5033	5013	9729
Parameters	301	321	654
wR_2 (on F^2 all refl.)[a]	0.1018	0.1239	0.0677
R_1 (on F obs. refl.)[b]	0.0461	0.0541	0.0331

[a] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

Preparation of [$Os_3(CO)_{10}$(μ-η^2:η^2-$Me_2C{=}CH)_2BC_3H_7$] (3) and [$Os_3(CO)_{10}$[μ-η^2:η^2(*trans*-MeCH=CH)(-$Me_2C{=}CH$)]BC_3H_7} (4). $B(CH_2C(Me){=}CH_2)_3$ (0.158 ml, 0.752 mmol) was added to a solution of **1** (200 mg, 0.234 mmol) in 3 ml C_6D_6 at 22 °C and the mixture was stirred at room temperature for 12 h. No signs of reaction were observed. Then $B(CH_2CH{=}CH_2)_3$ (0.041 ml, 0.234 mmol) was added and stirring continued for 5 days until the reaction mixture became bright yellow. The reaction mixture was then poured onto SiO_2, the solvent was removed *in vacuo* and the dry residue was chromatographed on an SiO_2 column using hexane as eluent. A bright yellow fraction (150 mg) containing a mixture of clusters **3** and **4** in a ratio of 3 : 1 was isolated. The yields of clusters **3** and **4** were determined from the ^{1}H NMR spectrum (47 and 15%, respectively). Pure samples were isolated as yellow crystals by fractional crystallization from hexane.

Cluster **3**; ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ 2.35, 2.24 (s, 6H, $=CMe_2$), 1.75 (s, 2H, $BCH{=}$), 1.6 (m, 2H, CH_2Me), 1.09 (t, 3H, $^3J_{(H-H)}$ = 7.4 Hz, CH_2Me), 0.89 (t, 2H, $^3J_{(H-H)}$ = 7.6 Hz, BCH_2); ^{11}B NMR (128.38 MHz, C_6D_6, 25 °C): δ 10; ^{13}C NMR (400.13 MHz, C_6D_6, 25 °C): δ 186.7 (2C≡O), 185.8 (2C≡O), 183.6 (C≡O), 183.5 (C≡O), 177.9 (2C≡O), 169.7 (2C≡O), 90.2 (2CMe_2), 68.1 (br, 2BCH=), 34.8, 26.8 (2CMe_2), 27.5 (CH_2Me), 18.3 (CH_2Me), 17.6 (br, BCH_2) ppm. IR ($\nu_{C\equiv O}$/cm^{-1}, hexane): 2109m, 2050m, 2042s, 2024vs, 1998s br, 1977m br. CI-MS: *m*/*z* 1016 (**3** + H)$^+$. $C_{21}H_{21}O_{10}B_1Os_3$ (1014.8): calc. C 24.86, H 2.09, B 1.07, Os 56.23; found C 25.10, H 2.28, B 0.76, Os 56.06%.

Cluster **4**: ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ 3.75 (dq, 1H, $^3J_{(H-H)}$, = 12.5, 6.0 Hz, =CHMe), 2.34, 2.25 (s, 6H, $=CMe_2$), 2.08 (s, 3H, =CH*Me*), 1.97 (d, 1H, $^3J_{(H-H)}$ = 12.5 Hz, BC*H*=CHMe), 1.89 (s, 1H, BC*H*=CMe_2), 1.90 (t, 3H, $^3J_{(H-H)}$ = 7.5 Hz, CH_2Me), 0.83–0.75 (m, 2H, CH_2Me), 0.06–0.01 (m, 2H, BCH_2); ^{11}B NMR (128.38 MHz, C_6D_6, 25 °C): δ 7–12 (br); ^{13}C NMR (400.13 MHz, C_6D_6, 25 °C): δ 186.4, 186.1, 185.4, 183.9, 183.4, 183.2, 177.8, 176.2, 169.7, 169.4 (C≡O), 91.8 (=CMe_2), 71.1 (br, BCH=CHMe), 67.2 (br, BCH=CMe_2), 63.7 (=CHMe), 34.2, 27.9 (=CMe_2), 26.9 (CH_2Me), 23.5 (=CH*Me*), 18.6 (CH_2Me), 17.0 (br, BCH_2) ppm. CI-MS: *m*/*z* 1002 (**4** + H)$^+$.

Reaction of $H_2Os_3(CO)_{10}$ with a mixture of triallylborane and allylboronic acid pinacolate. $B(CH_2CH{=}CH_2)_3$ (0.02 ml, 0.117 mmol) and ($CH_2{=}CHCH_2$)BPin (19 mg, 0.117 mmol) were added to a solution of **1** (100 mg, 0.117 mmol) in 3 ml C_6D_6 at 22 °C. After 36 h (the color of the reaction mixture changed from pink to bright yellow) the reaction was complete and the reaction mixture was poured onto SiO_2. The solvent was removed *in vacuo* and the dry residue was chromatographed on a SiO_2 column with hexane as eluent to give cluster **2** (71 mg, 61%).

X-Ray diffraction study. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, ω-scans). The collected frames were integrated by SAINT software[35] and corrected for absorption using the SADABS program.[36a] The structures were solved by direct methods and refined by full-matrix least-squares technique against F^2 with anisotropic displacement parameters for non-hydrogen atoms using the SHELXTL program package.[36b] The positions of hydrogen atoms were calculated and included in the refinement in the rigid body approximation. In the crystal structure of **4**, an *n*-pentane solvate molecule is disordered around an inversion center. The principal experimental and crystallographic parameters are presented in Table 3.

Acknowledgements

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