Formation, Structure and Reactivity of Boryloxycarbyne Complexes of Group 6 Metals

Holger Braunschweig,*[a, d] Karl W. Klinkhammer,[b, e] Margot Koster,[c] and Krzysztof Radacki[a]

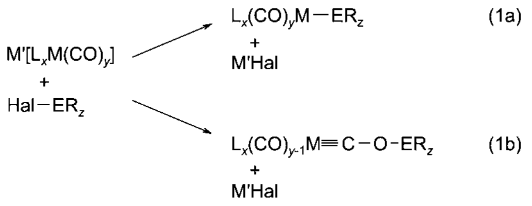
Dedicated to Professor Wolfgang Malisch on the occasion of his 60th birthday

Abstract: Reaction of the diborane(4) $B_2(NMe_2)_2I_2$ with two equivalents of $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Cr, Mo, W) yielded the dinuclear boryloxycarbyne complexes $[\{(\eta^5\text{-}C_5H_5)(OC)_2M{\equiv}CO\}_2\text{-}B_2(NMe_2)_2]$ (**4a**, M = Mo; **b**, M = W; **c**, M = Cr), which were fully characterised in solution by multinuclear NMR methods. The Mo and W complexes **4a**, **b** proved to be kinetically favoured products of this reaction and underwent quantitative rearrangement in solution to afford the complexes $[\{(\eta^5\text{-}C_5H_5)(OC)_2M{\equiv}CO\}B(NMe_2)B(NMe_2)\text{-}\{M(CO)_3(\eta^5\text{-}C_5H_5)\}]$ (**5a**, M = Mo; **b**, M = W); **5a** was characterised by X-ray crystallography in the solid state. Corresponding reactions of $B_2(NMe_2)_2I_2$ with only one equivalent of $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) initially afforded 1:1 mixtures of the boryloxycarbyne complexes **4a**,**b** and unconsumed $B_2(NMe_2)_2I_2$. This mixture, however, yielded finally the diborane(4)yl complexes $[(\eta^5\text{-}C_5H_5)(OC)_3M\{B(NMe_2)\text{-}B(NMe_2)I\}]$ (**6a**, M = Mo; **b**, M = W) by $[(\eta^5\text{-}C_5H_5)(OC)_3M]$ transfer and rearrangement. Density functional calculations were carried out for **4c** and **5a**,**b**.

Keywords: boranes · boron · boryl complexes · carbyne ligands · transition metals

Introduction

Over the past decade transition-metal complexes of boron have become established as a novel class of compounds involving direct metal–boron interactions. In contrast to the other three major groups in this area, that is, borides, metallaboranes, and π complexes with boron-containing ligands, transition-metal complexes of boron are characterised by electron-precise two-centre, two-electron bonds between boron and the metal centre. A variety of different coordination modes for boron-centred ligands has been realised, and allows systematic classification of these compounds into borane, boryl and borylene complexes.[1a–e] Boryl complexes of general formula $[L_xMBR_2]$ have attracted considerable interest as key intermediates in transition-metal-catalysed hydroboration[2a–d)] and for the α-borylation of alkenes by C–H activation.[3a–c] Oxidative additions of boron–element bonds to low-valent metal centres and salt-elimination reactions between haloboranes $HalBR_2$ and anionic transition-metal complexes, most commonly carbonylate derivatives $M'[L_xM(CO)_y]$, were successfully applied to the synthesis of boryl complexes over the past decade.[1a–e] Salt-elimination reactions have a pivotal role not only for the synthesis of boryl complexes, but also for obtaining complexes of the type $[L_x(CO)_yMER_z]$ with bonds between transition metals M and main group elements E in general [Eq. (1 a)].[4a,b]



The formation of M–E bonds suggests that the transition metal acts as the nucleophilic centre in these reactions.[4b] There is, however, both spectroscopic and experimental evidence that the carbonyl oxygen atom also displays some

---

[a] Prof. Dr. H. Braunschweig, K. Radacki
Department of Chemistry, Imperial College
London SW72AY (UK)

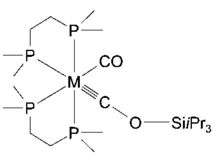
[b] Prof. Dr. K. W. Klinkhammer
Institut für Anorganische Chemie, Universität Stuttgart
Pfaffenwaldring 55, 70569 Stuttgart (Germany)

[c] M. Koster
Institut für Anorganische Chemie, Technischen Hochschule
Templergraben 55, 52056 Aachen (Germany)

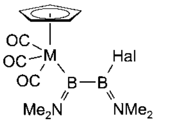
[d] Prof. Dr. H. Braunschweig
New address: Institut für Anorganische Chemie Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de

[e] Prof. Dr. K. W. Klinkhammer
New address: Institut für Anorganische Chemie
Universität Mainz (Germany)

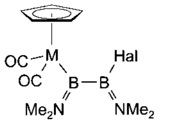
nucleophilic character in anionic complexes $M'[L_xM(CO)_y]$, especially towards hard and bulky lewis acids.[5a–d)] In the case of addition of the carbonyl oxygen atom to the element E with salt elimination according to Equation (1b), formation of transition-metal oxycarbyne complexes of the type $[L_x(CO)_{y-1}M{\equiv}C{-}O{-}ER_z]$ can be expected. This alternative pathway to the common formation of $[L_x(CO)_yM{-}ER_z]$, however, is very rare and was observed only in the case of $[(dmpe)_2(OC)M{\equiv}C{-}O{-}Si\textit{i}Pr_3]$ (**1a**, M = Nb; **b**, M = Ta; dmpe = 1,2-bis(dimethylphosphanyl)ethane), obtained from the reaction of $Na[(dmpe)_2M(CO)_2]$ with $\textit{i}Pr_3SiCl$.[6]



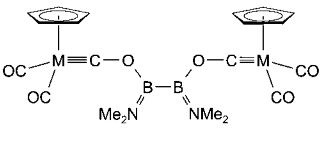
1a; M = Nb
1b; M = Ta



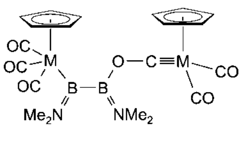
2a; M = Mo, Hal = Br
2b; M = W, Hal = Cl



3a; M = Fe, Hal = Cl
3b; M = Ru, Hal = Br



4a; M = Mo
4b; M = W



5a; M = Mo
5b; M = W

In the course of our investigations on diborane(4)yl complexes[7a–d)] we obtained a series of compounds such as $[(\eta^5\text{-}C_5H_5)(OC)_nM\{B(NMe_2)B(NMe_2)Hal\}]$ (**2a**, M = Mo; **b**, M = W; n = 3; **3a**, M = Fe; **b**, M = Ru, $n = 2$; Hal = Cl, Br)[7a,b] from salt elimination reactions of $B_2(NMe_2)_2Hal_2$ and corresponding anionic transition-metal complexes. All these reactions with 1,2-dichloro- and 1,2-dibromodiboranes(4) proceed according to Equation (1a) with nucleophilic addition of the metal centre to one boron atom and formation of a metal–boron bond.

Recently, however, we communicated the unprecedented formation of the boryloxycarbyne complexes **4a**, **b**, which were obtained from corresponding 1,2-diiododiboranes(4) with nucleophilic addition of carbonyl oxygen atoms to both boron centres, thus following the pathway outlined in Equation (1b). These complexes undergo a unique rearrangement to yield the novel diborane(4)yl complexes **5a**, **b**.[8]

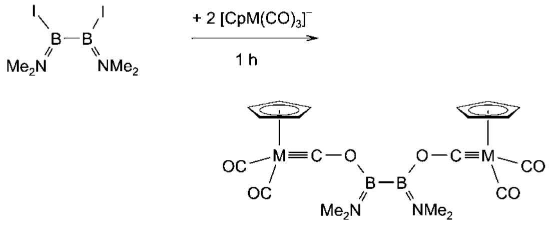
Here we report full details on the synthesis, structural characterisation, novel reactivity and computational studies of these compounds.

Results and Discussion

Treatment of $B_2(NMe_2)_2I_2$ with two equivalents of $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ for one hour at ambient temperature afforded the dinuclear boryloxycarbyne complexes $[\{(\eta^5\text{-}C_5H_5)(OC)_2M{\equiv}CO\}_2B_2(NMe_2)_2]$ (**4a**, M = Mo; **b**, M = W; **c**, M = Cr) according to Equation (2).

The molybdenum and tungsten complexes **4a** and **4b**, respectively, were obtained in yields of about 33 % as yellow, crystalline materials, while the chromium anologue **4c** could be isolated in a significantly higher yield of 62 % in the form of green crystals. All three compounds are extremely sensitive to air and moisture and dissolve readily in common aliphatic and aromatic solvents.

Their molecular structure in solution was derived from multinuclear NMR data (Table 1). Single sets of signals in all NMR spectra for the cyclopentadienyl, carbonyl and amino groups indicates C_{2v} symmetry of the molecules in solution. The presence of two CH_3 resonances in the ^1H and ^{13}C NMR spectra is due to restricted rotation about the boron–nitrogen double bonds. The signals of the carbyne carbon atoms in the ^{13}C NMR spectra were at about $\delta = 245$ ppm, and thus display the expected characteristic low-field shifts.[6] The ^{11}B NMR signals at $\delta = 31.1$ (**4a**), 30.8 (**4b**) and 31.3 ppm (**4c**) are shielded with respect to those of the borane precursors and of diborane(4)yl complexes, and hence indicate the presence of boron–oxygen bonds.[7a,b]



4a; M = Mo

(2)

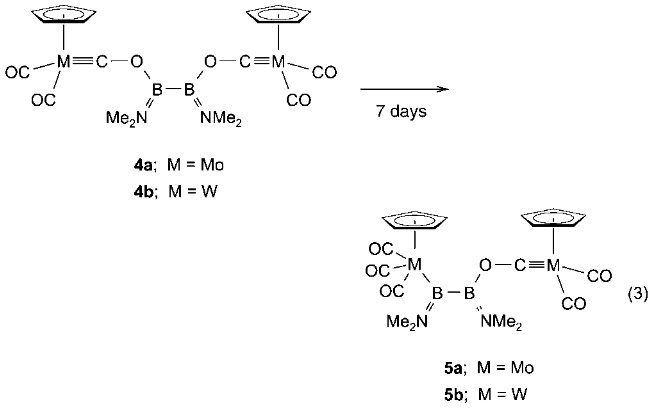
Table 1. Selected experimental and calculated data.

		4a	4b	4c	5a	5b	6a	6b
$\delta(^1H)$	Cp_{obsd}	5.22	5.15	4.72	5.03; 5.20	5.04, 5.12	5.00	4.97
	Cp_{calcd}	–	–	4.73	5.29; 5.33	5.41; 5.44	5.30	5.42
$\delta(^{11}B)$	BM_{obsd}	–	–	–	65.2	62.7	66.0	63.3
	BM_{calcd}	–	–	–	63.6	61.4	63.0	60.8
		31.1	30.8	31.3	31.5	32.6	–	–
	BO_{calcd}	–	–	29.9	29.5	30.0	–	–
	BI_{obsd}	–	–	–	–	–	35.5	37.4
	BI_{calcd}	–	–	–	–	–	44.0	44.7
$\delta(^{13}C)$	$M{\equiv}C_{obsd}$	245.2	242.7	250.4	241.2	239.0	–	–
	$M{\equiv}C_{calc}$	–	–	248.5	235.3	226.4	–	–
d/pm	BM_{obs}	–	–	–	234.8(4)	–	–	–
	BM_{calcd}	–	–	–	240.0	240.2	240.3	240.4
	BO_{obs}	–	–	–	146.0(5)	–	–	–
	BN_{obs}	–	–	–	139.8(5); 137.4(5)	–	–	–
	BN_{calcd}	–	–	139.3	140.5; 140.0	140.6; 140.2	140.4; 139.8	140.6; 139.9
	BO_{calcd}	–	–	144.7	144.7	144.5	–	–
	BB_{obsd}	–	–	–	170.4(6)	–	–	–
	BB_{calcd}	–	–	171.2	170.7	170.9	169.6	169.8
	$M{\equiv}C_{obsd}$	–	–	182.5(4)	–	–	–	–
	$M{\equiv}C_{calcd}$	–	–	170.9	184.6	185.0	–	–

Interestingly, the complexes **4a** and **4b** represent only kinetically favoured products of the reaction. These compounds undergo an unprecedented rearrangement according to Equation (3) to give the thermodynamically more stable products $[\{(\eta^5\text{-}C_5H_5)(OC)_2M{\equiv}CO\}B(NMe_2)B(NMe_2)\{M(CO)_3(\eta^5\text{-}C_5H_5)\}]$ (**5a**, M = Mo; **b**, M = W), which were isolated in quantitative yield from solutions of **4a** and **4b**, repsectively, in benzene after seven days at ambient temperature as yellow, crystalline materials. Complexes **5a**, **b** are readily soluble in all common hydrocarbons, and in contrast to their precursors, only moderately sensitive towards air and moisture. Although the conversion requires a considerable time for completion, ^{11}B NMR spectra of the reaction mixture show that traces of **5a**, **b** are already present after two hours.

To avoid contamination with the rearranged products, short reaction times of only one hour are crucial for the synthesis of the boryloxycarbyne complexes **4a**, **b**, and thus the yields of these compounds are limited. The conversion of **4a** and **4b** to **5a** and **5b**, respectively, occurs with a 1,3-shift of one boryl group from the carbyne oxygen atom to the metal centre and restoration of the former carbonyl ligand. A corresponding rearrangement of the second M≡C–O–B moiety, which would lead to compounds of the type $[\{(\eta^5\text{-}C_5H_5)(OC)_3M\}B(NMe_2)B(NMe_2)\{M(CO)_3(\eta^5\text{-}C_5H_5)\}]$ with two metal–boron bonds is not observed, even at slightly elevated temperatures. This is believed to be due to the increased steric requirements of the $(\eta^5\text{-}C_5H_5)(OC)_3M$ moiety with respect to the $(\eta^5\text{-}C_5H_5)(OC)_2M{\equiv}C{-}O$ fragment. This observation corresponds with the finding that in complexes $[(\eta^5\text{-}C_5H_5)(OC)_nMB(NMe_2)B(NMe_2)Hal]$ (**2a**, M = Mo; **b**, M = W, $n = 3$; **3a**, M = Fe; **b**, M = Ru, $n = 2$; Hal = Cl, Br) all attempts to substitute the remaining boron-bound halide by a second $(\eta^5\text{-}C_5H_5)(OC)_nM$ moiety failed.[7a,b] Although 1,3-silatropic shifts from transition-metal centres to acyl oxygen atoms are well known,[9] reverse intramolecular migration of a main group element from oxygen to a transition-metal centre was not observed before.

In contrast to the facile rearrangement of the molybdenum and tungsten complexes **4a** and **4b**, their chromium counterpart **4c** displays no such reactivity. It remains unaltered in benzene solutions at ambient or slightly elevated temperatures for weeks, as proven by ^{11}B NMR spectroscopy; heating the solution to reflux finally leads to complete degradation of the complex.



(3)

The structure of **5a** and **5b** in solution was revealed by multinuclear NMR spectroscopy (Table 1). Owing to their C_1 symmetry the complexes show two sets of signals for the cyclopentadienyl and amino ligands, the latter again doubled due to hindered rotation about the boron–nitrogen double bond. The presence of the carbyne carbon atom is proven by signals in the ^{13}C NMR spectra at $\delta = 241.2$ (**5a**) and 239.0 ppm (**5b**). The most significant spectroscopic difference between compounds **4** and **5** is found in the ^{11}B NMR spectra. The rearranged complexes display two signals: the shielded resonance signals at $\delta = 31.5$ (**5a**) and 32.6 ppm (**5b**) match those of the precursor compounds **4a** and **4b** and indicate the oxygen-bound boron atoms. The signals at $\delta = 65.2$ (**5a**) and 62.7 ppm (**5b**) are significantly deshielded and thus closely resemble the characteristic shifts of the transition-metal-bound boron atoms in diborane(4)yl complexes.[7a,b]

Single crystals of **5a** suitable for X-ray structure analysis (Figure 1) were obtained from hexane at –30 °C after several days. The compound crystallises in the space group $P2_1/c$ and has C_1 symmetry in the solid state. The geometry of the central $B_2(NMe)_2$ moiety closely resembles that of related diborane(4)yl complexes.[7a,b]

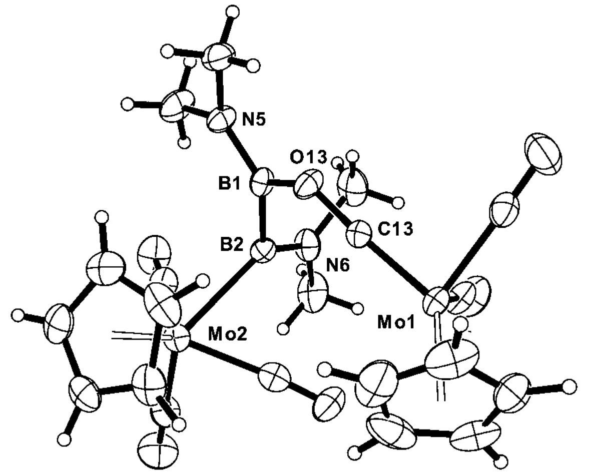
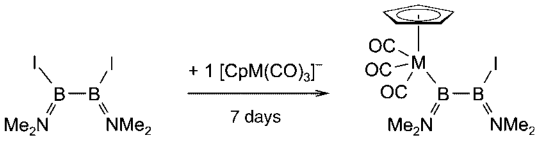


Figure 1. Structure of **5a** in the crystal. Selected distances [pm] and angles [°]: Mo2–B2 234.8(4), B1–N5 137.4(5), B2–N6 139.8(5), B1–B2 170.4(6), Mo1–C13 182.5(4); O13-C13-Mo1 174.9(3).

Both boron atoms have trigonal-planar coordination environments with boron–boron distances of 170.4(6) pm and boron–nitrogen distances of 137.4(5) pm (B1–N5) and 139.8(5) pm (B2–N6). The latter are in the expected range for boron–nitrogen double bonds. The molybdenum–boron distance of 234.8(4) pm is similar to that of 236.5(5) pm in $[(\eta^5\text{-}C_5H_5)(OC)_3Mo\{B(NMe_2)B(NMe_2)Br\}]$ (**2a**),[7b] but significantly shorter than that of 249.7(5) in $[(\eta^5\text{-}C_5Me_5)_2Mo(BH_2PMe_3)]$, in which the boron atom has a higher coordination number of four.[10] The Mo≡C–O moiety in **5a** displays the expected linear arrangement with an Mo1-C1-O1 angle of 174.9(3)° and a molybdenum–carbon distance of 182.5(4) pm, which is characteristic of a triple bond.[11] The boron–oxygen distance of 146.0(5) pm, the C1-O1-B1 angle of 127.4(3)° and the aforementioned boron–nitrogen distance suggest that the bonding situation at the boron centre should be described in terms of a boron–oxygen single and a boron–nitrogen double bond.[12]

We also investigated 1:1 reactions of $B_2(NMe_2)_2I_2$ with $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W). The diborane(4)yl complexes $[(\eta^5\text{-}C_5H_5)(OC)_3M\{B(NMe_2)B(NMe_2)I\}]$ (**6a**, M = Mo; **b**, M = W) were obtained according to Equation (4) after stirring 1:1 mixtures of the starting materials in benzene at ambient temperature for seven days.

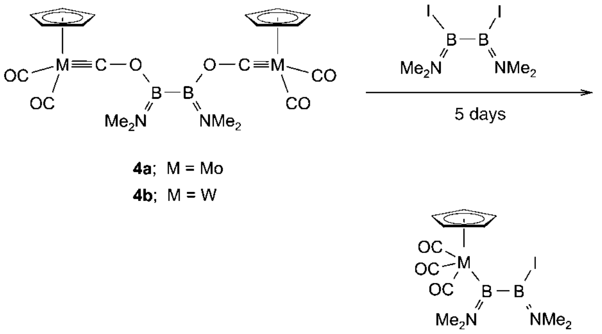


(4)

6a; M = Mo
6b; M = W

The new complexes were isolated in yields of about 28 % as red (**6a**) or maroon (**6b**) crystalline solids, which are readily soluble in aliphatic and aromatic hydrocarbons and extremely sensitive towards air and moisture. The IR and multinuclear NMR data for **6a**, **b** are unobtrusive and match corresponding findings for related diborane(4)yl complexes. The ^{11}B NMR spectra show two widely separated signals at $\delta = 35.5$ (**6a**) and 37.4 ppm (**6b**) for the iodo-substituted boron atom and at $\delta = 66.0$ (**6a**) and 63.3 ppm (**6b**) for the metal-coordinated boron centre. Both compounds display three carbonyl stretching frequencies in the IR spectra in the range from 1992 to 1883 cm^{-1}, that is, no evidence for metal–boron π back-donation in solution.[1, 7a,b] Monitoring the progress of this reaction by ^{11}B NMR spectroscopy revealed that already after one hour the boryloxycarbyne complexes **4a**, **b** had formed, as proven by the characteristic shielded resonance signals for the oxygen-bound boron atoms at $\delta = 31.1$ and 30.8 ppm, respectively.[13] The presence of an equimolar amount of unconverted $B_2(NMe)_2I_2$ was deduced from the second ^{11}B NMR signal at $\delta = 36.2$ ppm.[14] The characteristic ^{11}B NMR signals of the diborane(4)yl complexes **6a**,**b** could be detected after an additional hour in very low intensities, which however continually increased over a period of several days. This observation provides evidence that even in the presence of surplus $B_2(NMe)_2I_2$ the formation of the boryloxycarbyne complexes **4a**, **b** with nucleophilic attack of carbonyl oxgen atoms at both boron centres of the same diborane(4) molecule is favoured. Additionally, it must be concluded that the complexes **4a**, **b** are not stable in the presence of $B_2(NMe)_2I_2$, but transfer one $(\eta^5\text{-}C_5H_5)(OC)_3M$ moiety with formation of the diborane(4)yl complexes **6a**, **b**. This assumption was proven by treating the isolated and purified complexes **4a**,**b** with one equivalent of $B_2(NMe_2)_2I_2$. After stirring the two reactants in benzene at ambient temperatures for 5 d, the diborane(4)yl complexes **6a**, **b** were obtained according to Equation (5) and isolated in yields of about 30%.

Monitoring the progress of this reaction with ^1H and ^{11}B NMR spectroscopy showed **6a**, **b** to be the major products after five days. Besides, only traces of the unconverted boryloxycarbyne complexes **4a**,**b** together with some unidentified boron-containing products, presumably originating from the degradation of $B_2(NMe_2)_2I_2$, were detected. The absence of significant amounts of **5a**, **b** during the reaction, as proven by ^1H and ^{11}B NMR spectroscopy, implies that 1) $(\eta^5\text{-}C_5H_5)(OC)_3M$ transfer to $B_2(NMe_2)_2I_2$ proceeds faster than the rearrangement of **4a**, **b** and 2) **6a**, **b** are not formed via **5a**, **b** as intermediates.

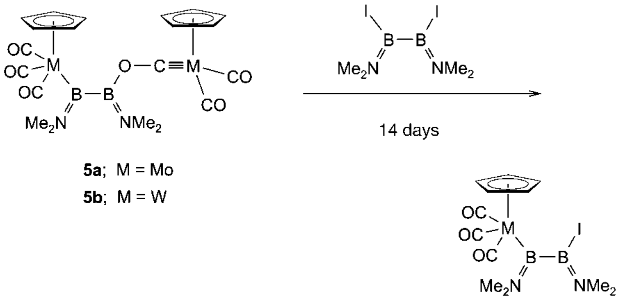


4a; M = Mo
4b; M = W

(5)

6a; M = Mo
6b; M = W

Further evidence for this was provided by an experiment in which the reactivity of the rearranged complexes **5a**,**b** towards an equimolar amount of $B_2(NMe)_2I_2$ was investigated. Monitoring corresponding solutions in benzene with ^1H and ^{11}B NMR spectroscopy showed that **5a**, **b** also transfer one $(\eta^5\text{-}C_5H_5)(OC)_3M$ moiety to $B_2(NMe_2)_2I_2$ with formation of the diborane(4)yl complexes **6a**,**b** according to Equation (6). This reaction, however, is complete only after 14 days at ambient temperature, and is thus significantly slower than the corresponding transfer from the boryloxycarbyne complexes **4a**, **b**.



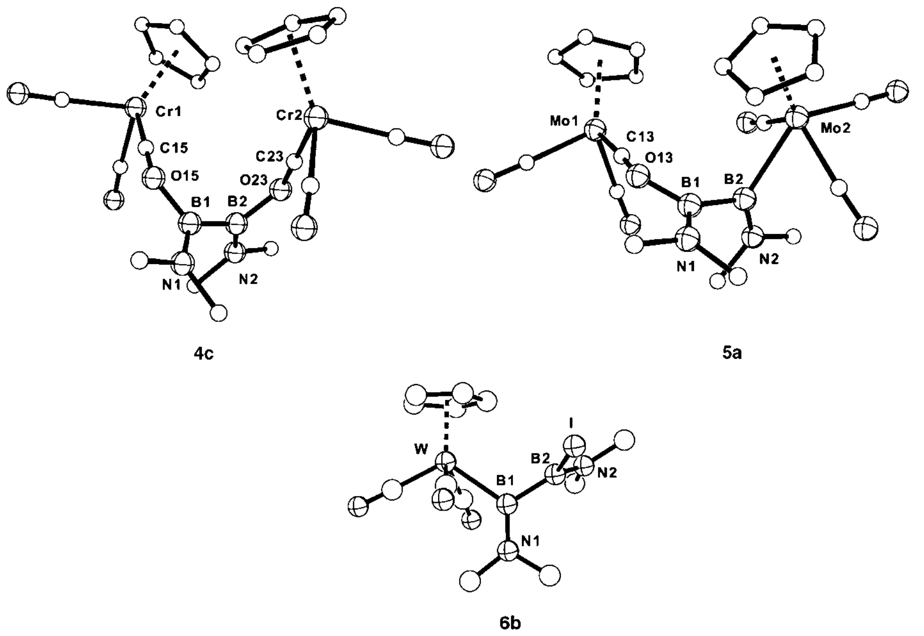
5a; M = Mo
5b; M = W

(6)

6a; M = Mo
6b; M = W

Density functional calculations were carried out on the chromium carbyne complex **4c**, the rearranged products **5a**, **b**, M = W) and the diborane(4)yl complexes **6a**, **b** with ECP basis sets for transition metals, 6-311G(d, p) basis sets for iodine and 6-31G(d, p) basis sets for all other nonmetal atoms. The structures shown in Figure 2 were calculated to be minima, as proven by vibrational analysis.

The chromium complex **4c** was optimised in C_2 symmetry and an unobtrusive geometry was found for the central diborane(4) moiety (Table 1). The boron–boron and boron–nitrogen distances are in the expected range for single and double bonds, respectively, and the two bonding planes around the boron centres enclose an angle of approximately



4c 5a 6b

Figure 2. Calculated structures of **4c**, **5a** and **6b**.

80°C, that is, somewhat distorted from an ideal orthogonal arrangement. The oxycarbyne ligand shows the expected linear geometry with a Cr-C-O angle of 178.5°.

The geometry calculated for **5a** is in very good agreement with the experimental data; as expected, the calculated interatomic distances are slightly longer. The related tungsten complex **5b** was optimised in C_1 symmetry, and the structural data match those of its molybdenum counterpart (Table 1).

The diborane(4)yl complexes **6a**, **b** were optimised in C_1 symmetry, and their overall geometry resembles that of the closely related tungsten complex $[(\eta^5\text{-}C_5H_5)(OC)_3W\{B(NMe_2)B(NMe_2)Cl\}]$ (**7**), the structure of which was derived from X-ray crystallography.[7a] In particular, the tungsten–boron, boron–boron and boron–nitrogen distances of **6b** and **7** differ by less than 3 pm.

The NMR shifts for all five compounds were calculated with the GIAO method (Table 1) and are generally in good agreement with the experimental data (Table 1). However, more pronounced deviations between calculated and experimental shifts are observed in the case of the tungsten-bound carbyne carbon and iodine-bound boron atoms.

Conclusion

The reactivity of the diiododiborane(4) $B_2(NMe_2)_2I_2$ towards $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Cr, Mo, W) proved to be rather complex and in sharp contrast to the common reactions of $B_2(NMe_2)_2Hal_2$ (Hal = Cl, Br) with transition metal carbonylates.

The various reactions and rearrangements observed and described here are summarized in Scheme 1.

The formation of the dinuclear boryloxycarbyne complexes $[\{(\eta^5\text{-}C_5H_5)(OC)_2M{\equiv}CO\}_2B_2(NMe_2)_2]$ (**4a**, M = Mo; **b**, M = W; **c**, M = Cr) with two boron–oxygen bonds clearly proves the intrinsic nucleophilic character of the carbonyl oxygen centre in the transition metal carbonylates. In the case of molybdenum and tungsten these complexes undergo an unprecedented rearrangement with formation of the thermodynamically favoured diborane(4)yl complexes **5a**,**b** with one boron–oxygen and one boron–metal linkage. The failure of the corresponding chromium complex **4c** to undergo the same rearrangement remains to be explained. However, this observation is well in line with the fact that chromium boryl complexes are unknown as yet and could not be obtained by salt elimination reactions or any other synthetic method.

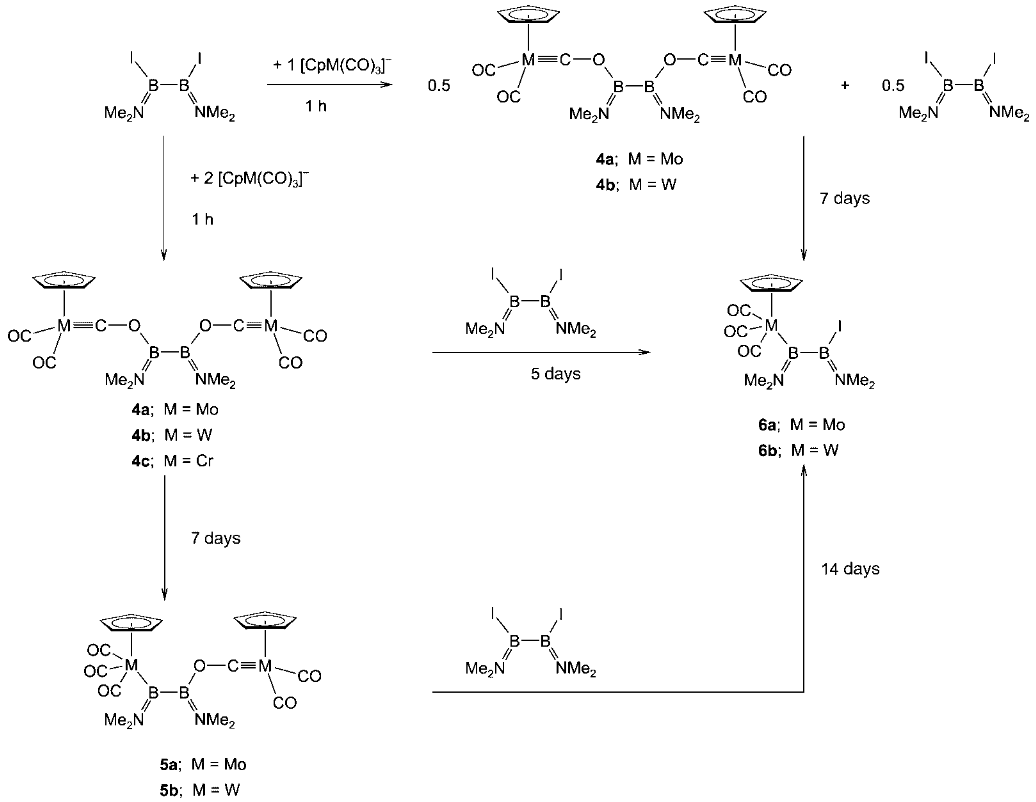
The reaction of **4a**,**b** and **5a**,**b** with $B_2(NMe_2)_2I_2$ to give the diborane(4)yl complexes **6a**, **b** is of some significance, as it represents a novel, albeit not very specific, method for the generation of classical metal–boron bonds. Future investigations will focus on the exploitation of this potentially useful method.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere with common Schlenk techniques. Solvents and reagents were dried by standard procedures, distilled and stored under nitrogen over molecular sieves. $B_2(NMe_2)_2I_2$,[14] $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$,[15] $K[(\eta^5\text{-}C_5H_5)W(CO)_3]$[15] and $K[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$[16] were obtained according to literature procedures. NMR: Varian Unity 500 at 499.843 (^1H, standard TMS, internal), 150.364 (^{11}B, standard $BF_3 \cdot OEt_2$ in C_6D_6, external), 125.639 MHz ($^{13}C\{^1H\}$, APT, standard TMS, internal). All NMR spectra were recorded at 25°C in C_6D_6 unless otherwise stated. Mass spectra were recorded on a Finnigan MAT 95 (70 eV), and elemental analyses (C, H, N) were obtained from a Carlo-Erba elemental analyzer, model 1106.

4a: A solution of $B_2(NMe_2)_2I_2$ (0.98 g, 2.70 mmol) in benzene (10 mL) was added dropwise to a suspension of $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ (1.53 g, 5.30 mmol) in benzene (10 mL). After the mixture had been stirred for 1 h at ambient temperature, all volatile materials were removed under high vacuum. The residue was suspended in hexane (30 mL), filtered and the remaining solid was rinsed with hexane (10 mL). The filtrate was concentrated in vacuo to 20 mL and stored at −30°C. After 48 h **4a** (0.53 g, 32.7 %) was obtained as a yellow, very air- and moisture-sensitive, crystalline material. ^1H NMR: $\delta = 2.31, 2.37$ (s, 6H; $N(CH_3)_2$), 5.22 ppm (s, 10H; C_5H_5); ^{11}B NMR: $\delta = 31.1$ ppm (BO); ^{13}C NMR: $\delta = 35.28, 39.33$ ($N(CH_3)_2$), 91.31 (C_5H_5), 229.49 (CO), 245.18 ppm (carbyne C); elemental analysis (%) calcd for $C_{20}H_{22}B_2Mo_2N_2O_6$ (599.90): C 40.04, H 3.70, N 4.67; found: C 39.52, H 3.83, N 4.66.

4b: As described for **4a**, a suspension of $K[(\eta^5\text{-}C_5H_5)W(CO)_3]$ (1.19 g, 3.20 mmol) in benzene was treated with a solution of $B_2(NMe_2)_2I_2$ (0.58 g, 1.60 mmol) in benzene. **4b** (0.40 g, 32.2 %) was obtained as yellow, very air- and moisture-sensitive crystals. ^1H NMR: $\delta = 2.39, 2.41$ (s, 6H; $N(CH_3)_2$), 5.15 ppm (s, 10H; C_5H_5); ^{11}B NMR: $\delta = 30.8$ ppm (BO); ^{13}C NMR: $\delta = 35.31, 39.44$ ($N(CH_3)_2$), 89.80 (C_5H_5), 220.11 (CO), 242.72 ppm (carbyne C);



Scheme 1. Summary of reactions and rearrangements described.

elemental analysis (%) calcd for $C_{20}H_{22}B_2N_2O_6W_2$ (775.72): C 30.97, H 2.86, N 3.61; found: C 30.17, H 2.84, N 3.37.

4c: As described for **4a**, a suspension of K[(η^5-C_5H_5)Cr(CO)$_3$] (1.39 g, 5.78 mmol) in benzene was treated with a solution of $B_2(NMe_2)_2I_2$ (1.05 g, 2.89 mmol) in benzene. **4c** (0.92 g, 62.3 %) was obtained as green, very air- and moisture-sensitive crystals. ^{1}H NMR: $\delta = 2.29$, 2.37 (s, 6H; N(CH$_3$)$_2$), 4.72 ppm (s, 10H; C_5H_5); ^{11}B NMR: $\delta = 31.3$ ppm (BO); ^{13}C NMR: $\delta =$ 35.21, 39.31 (N(CH$_3$)$_2$), 87.32 (C_5H_5), 238.90 (CO), 250.39 ppm (carbyne C); elemental analysis (%) calcd for $C_{20}H_{22}B_2Cr_2N_2O_6$ (512.02): C 46.92, H 4.33, N 5.47; found: C 46.20, H 4.48, N 5.35.

5a: A solution of **4a** (0.20 g, 0.33 mmol) in benzene (10 mL) was stirred for seven days at ambient temperature, after which all volatile materials were removed under high vacuum. The residue was dissolved in hexane (20 mL), and the resulting yellow solution was concentrated in vacuo to 10 mL and stored at −30 °C. After 48 h **5a** was obtained in quantitative yield as yellow crystals. ^{1}H NMR: $\delta = 2.16$, 2.24, 2.79, 2.84 (s, 3H; N(CH$_3$)), 5.03, 5.20 ppm (s, 5H; C_5H_5); ^{11}B NMR: $\delta = 31.5$ (BO), 65.2 ppm (BMo); ^{13}C NMR: $\delta =$ 34.78, 38.32, 42.84, 48.95 (N(CH$_3$)), 91.50, 93.68 (C_5H_5), 224.11, 226.58, 229.75, 229.97, 233.78, (CO), 241.20 ppm (carbyne C); elemental analysis (%) calcd for $C_{20}H_{22}B_2Mo_2N_2O_6$ (599.90): C 40.04, H 3.70, N 4.67; found: C 39.59, H 3.65, N 4.66.

5b: As described for **5a**, a solution of **4b** (0.20 g, 0.26 mmol) in benzene (10 mL) was stirred for seven days. Compound **5b** was obtained in quantitative yield as yellow crystals. ^{1}H NMR: $\delta = 2.21$, 2.26, 2.80, 2.87 (s, 3H; N(CH$_3$)), 5.04, 5.12 (s, 5H, C_5H_5); ^{11}B NMR: $\delta = 32.6$ (BO), 62.7 (BW); ^{13}C NMR: $\delta = 34.74$, 38.46, 43.46, 49.29 (N(CH$_3$)), 89.92, 92.51 (C_5H_5), 215.47, 218.04, 220.38, 220.68, 223.42 (CO), 239.02 ppm (carbyne C); elemental analysis (%) calcd for $C_{20}H_{22}B_2N_2O_6W_2$ (775.72): C 30.97, H 2.86, N 3.61; found: C 30.39, H 3.07, N 3.50.

6a: A solution of $B_2(NMe_2)_2I_2$ (1.03 g, 2.83 mmol) in benzene (10 mL) was added dropwise to a suspension of K[(η^5-C_5H_5)Mo(CO)$_3$] (0.81 g, 2.81 mmol) in benzene (10 mL). After the mixture had been stirred for seven days at ambient temperature, all volatile materials were removed under high vacuum. The remaining residue was suspended in hexane (40 mL), filtered and the remaining solid was rinsed with hexane (5 mL). The filtrate was concentrated in vacuum to 15 mL and stored at −30 °C. After several days **6a** (0.40 g, 29.3 %) was obtained as a red, very air- and moisture-sensitive, crystalline material.

Alternative 1: A solution of **4a** (0.86 g, 1.42 mmol) in benzene (10 mL) was treated with a solution of $B_2(NMe_2)_2I_2$ (0.52 g, 1.42 mmol) in benzene (10 mL) and stirred for five days at ambient temperature. All volatiles were removed in high vacuum, and the remaining solid repeatedly recrystallised from hexane at −30 °C to yield pure **6a** (0.40 g, 29.1 %).

Alternative 2: A solution of **5a** (0.59 g, 0.97 mmol) in benzene (10 mL) was treated with a solution of $B_2(NMe_2)_2I_2$ (0.36 g, 0.97 mmol) in benzene (10 mL) and stirred for 14 days at ambient temperature. All volatiles were removed in high vacuum, and the remaining solid repeatedly recrystallised from hexane at −30 °C to yield pure **6a** (0.26 g, 27.6 %).

^{1}H NMR: $\delta = 2.49$, 2.63, 2.70, 2.80 (s, 6H; N(CH$_3$)$_2$), 5.00 ppm (s, 5H; C_5H_5); ^{11}B NMR: $\delta = 35.5$ (BI), 66.0 ppm (BMo); ^{13}C NMR: $\delta = 42.45$, 42.58, 44.27, 47.58 (N(CH$_3$)$_2$), 93.65 (C_5H_5), 224.72, 227.96, 233.39 ppm (CO); IR (hexane): $\tilde{\nu} = 1992$ (m), 1916 (m), 1895 cm^{-1} (m) (C=O); elemental analysis (%) calcd for $C_{12}H_{17}B_2IMoN_2O_3$ (481.74): C 29.92, H 3.56, N 5.82; found: C 29.90, H 3.59, N 5.71.

6b: As described for **6a**, $B_2(NMe_2)_2I_2$ (1.00 g, 2.75 mmol) was treated with a suspension of K[(η^5-C_5H_5)W(CO)$_3$] (1.02 g, 2.75 mmol) in benzene for seven days at ambient temperature. Compound **6b** (0.43 g, 27.4 %) was obtained as a maroon, very air- and moisture-sensitive, crystalline material.

Alternative 1: As described for **6a**, **4b** (0.75 g, 0.98 mmol) was treated with $B_2(NMe_2)_2I_2$ (0.36 g, 0.98 mmol) to yield **6b** (0.34 g, 30.5 %).

Alternative 2: As described for **6a**, **5b** (0.68 g, 0.88 mmol) was treated with $B_2(NMe_2)_2I_2$ (0.33 g, 0.88 mmol) to yield **6b** (0.29 g, 28.5 %). ^{1}H NMR: $\delta =$ 2.47, 2.67, 2.72, 2.85 (s, 6H; N(CH$_3$)$_2$), 4.97 ppm (s, 5H; C_5H_5); ^{11}B NMR: $\delta = 37.4$ (BI), 63.3 ppm (BW); ^{13}C NMR: $\delta = 42.45$, 43.21, 44.20, 47.95 (N(CH$_3$)$_2$), 92.39 (C_5H_5), 216.31, 219.39, 222.58 ppm (CO); IR (toluene): $\tilde{\nu} = 1992$ (m), 1899 (m), 1883 cm^{-1} (m) (C=O); elemental analysis (%) calcd for $C_{12}H_{17}B_2IN_2O_3W$ (569.65): C 25.30, H 3.01, N 4.92; found: C 24.93, H 3.09, N 4.51.

X-ray structure determination of 5b: X-ray quality crystals were removed from a Schlenk tube and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber and instantly placed in the low-temperature N_2 stream of a P4 four-circle diffractometer (Siemens). $C_{20}H_{22}B_2Mo_2N_2O_6$; formula mass 599.90 $g\,mol^{-1}$, monoclinic space group $P2_1/c$ (no. 14); $a=17.607(4)$, $b=8.456(2)$, $c=18.242(4)$ pm, $\beta=117.55(3)^\circ$, $V=2.4080(9)$ mm^3, $Z=4$, $\rho_{calcd}=1.655$ $g\,cm^{-3}$; $Mo_{K\alpha}$ radiation ($\mu=1.078$ mm^{-1}). Data collection at 173 K on a yellow crystal of about $0.4\times0.5\times0.2$ mm by using ω scans in the diffraction range $4.48<2\theta<58^\circ$ yielded 7899 reflections. Empirical absorption correction by ψ scans; 6412 of 6415 unique reflections were used for refinement of 293 parameters; max./min. residual electron density: $-786/715$ $e\,nm^{-3}$. $R1=0.045$ ($F>4\sigma(F)$) and $wR2=0.101$ (all data) with $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR2=\{\Sigma_w(F_o^2F_c^2)^2/\Sigma_w(F_o^2)^2\}^{0.5}$. Calculations were carried out with the SHELXTL PC 5.03[17] and SHELXL-97[18] program suites. The phase problem was solved by direct methods, and the structures were refined on F_o^2 by full-matrix least-squares techniques. Anisotropic thermal parameters were included for all non-hydrogen atoms. H atoms were placed geometrically and refined using a riding model, including free rotation of methyl groups. Their isotropic thermal parameters were constrained to 1.2 (cyclopentadienyl H) or 1.5 (methyl groups) times U_{eq} of the bonded carbon atom. CCDC-116236 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

SCF calculations: all calculations were performed by using Gaussian98 package with the Becke three-parameter hybrid exchange functionals and Lee–Young–Parr correlation functionals (B3LYP) of DFT.[19] All the geometries have been fully optimised with CEP-31G basis set for chromium, molybdenum and tungsten, 6-311G(d,p) basis set for iodine, and 6-31G(d,p) basis set for other non-metal atoms. For the obtained stationary points, harmonic frequency analysis at the same level of theory were performed. Optimisation following the negative eigenvector was carried out for geometries with imaginary frequencies. The calculations utilized C_1 symmetry for all molecules except **4c**, which was calculated in C_2 symmetry. The total energies E_h and the ZPVE (in Hartrees, in parentheses) are as follows; **4c**: −1559.207902 (0.401361); **5a**: −1522.139270 (0.397303); **5b**: −1521.728002 (0.365861); **6a**: −7840.099668 (0.286767); **6b**: −7839.902147 (0.287680).

Acknowledgement

We thank DFG, Fonds der Chemischen Industrie, EPSRC and the RSoc for financial support. We are grateful to the Rechenzentrum of Aachen University of Technology (RWTH) for generously placing computational time at our disposal.

---

[1] For reviews on borane, boryl and borylene complexes, see: a) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882 – 1898, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1786 – 1801; b) G. I. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685 – 2722; c) H. Braunschweig, M. Colling, *J. Organomet. Chem.* **2000**, *614*, 18 – 26; d) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1 – 51; e) H. Braunschweig in *Inorganic Chemical Highlights* (Eds.: G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, New York, **2001**, pp. 213 – 218.

[2] For reviews on transition-metal-catalysed hydroboration, see :a) K. Burgess, M. J. Ohlmeyer, *Chem. Rev.* **1991**, *91*, 1179 – 1191; b) H. Wadepohl, *Angew. Chem.* **1997**, *109*, 2547 – 2550, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1787 – 1790; c) I. Beletskaya, A. Pelter, *Tetrahedron* **1997**, *97*, 4957 – 5026; d) T. B. Marder, N. C. Norman, *Top. Catal.* **1998**, *5*, 63 – 73.

[3] a) J. F. Hartwig, K. M. Waltz, *Science* **1997**, *277*, 211 – 213; b) K. M. Waltz, C. N. Muhoro, J. F. Hartwig, *Organometallics* **1999**, *18*, 3383 – 3393; c) H. Chen, J. F. Hartwig, *Angew. Chem.* **1999**, *111*, 3597 – 3599, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 3391 – 3393.

[4] a) D. A. Robertus, G. L. Geoffrey in *Comprehensive Organometallic Chemistry*, *Vol. 2* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**, pp. 763 – 879; b) R. B. King, *Acc. Chem. Research*, **1970**, *3*, 417 – 427.

[5] a) M. J. Bennet, W. A. G. Graham, R. A. Smith, R. P. Stewart, *J. Am. Chem. Soc.* **1973**, *95*, 1684 – 1686; b) D. F. Shriver, *J. Organomet. Chem.* **1975**, *94*, 259 – 271; c) A. A. Pasinskii, I. L. Eremenko, G. Z. Suleimanov, Y. A. Nuriev, I. P. Beletskaya, V. E. Shklover, Y. T. Struchkov, *J. Organomet. Chem.* **1984**, *266*, 45 – 52; d) U. Schubert, E. Kunz, M. Knorr, J. Müller, *Chem. Ber.* **1987**, *120*, 1079 – 1085.

[6] R. N. Vrtis, C. P. Rao, S. Warner, S. J. Lippard, *J. Am. Chem. Soc.* **1988**, *110*, 2669 – 2670.

[7] a) H. Braunschweig, B. Ganter, M. Koster, T. Wagner, *Chem. Ber.* **1996**, *129*, 1099 – 1101; b) H. Braunschweig, M. Koster, R. Wang, *Inorg. Chem.* **1999**, *38*, 415 – 416; c) H. Braunschweig, M. Koster, *J. Organomet. Chem.* **1999**, *588*, 213 – 234; d) H. Braunschweig, M. Koster, *Z. Naturforsch. B* **2002**, *57*, 483 – 487.

[8] H. Braunschweig, M. Koster, K. W. Klinkhammer, *Angew. Chem.* **1999**, *111*, 2368 – 2370, *Angew. Chem. Int. Ed.* **1999**, *38*, 2229 – 2231.

[9] K. C. Brinkman, A. J. Blakeny, W. Krone – Schmidt, J. A. Gladysz, *Organometallics* **1984**, *3*, 1325 – 1332.

[10] Y. Kawano, T. Yasue, M. Shimoi, *J. Am. Chem. Soc.* **1999**, *121*, 11744 – 11747.

[11] G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc. Dalton Trans.* **1989**, S1 – S83.

[12] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1989**, S1 – S19.

[13] After one hour, the boryloxycarbyne complexes **4a**,**b** could be isolated and fully characterised from reactions of $B_2(NMe_2)I_2$ with only one equivalent of $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W).

[14] H. Schick, Dissertation, Ludwig-Maximilians Universität, München, **1966**.

[15] E. O. Fischer, W. Hafner, *Z. Naturforsch. B* **1955**, *10*, 140 – 143.

[16] J. A. Gladysz, G. M. William, W. Tam, D. L. Johnson, D. W. Parker, J. C. Selover, *Inorg. Chem.* **1979**, *18*, 553 – 558.

[17] SHELXTL PC 5.03, Siemens Analytical X – Ray Instruments Inc., Madison, WI, **1994**.

[18] G. M. Sheldrick, SHELXL – 97, Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, **1997**.

[19] Gaussian98, Revision a11, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.

Received: September 11, 2002 [F4406]