DALTON
FULL PAPER

Hydroboration of metal–carbon triple bonds†

Hubert Wadepohl,* Ulrich Arnold, Ute Kohl, Hans Pritzkow and Andreas Wolf

*Anorganisch-Chemisches Institut der Ruprecht-Karls-Universität, Im Neuenheimer Feld 270,
D-69120 Heidelberg, Germany. E-mail: bu9@ix.urz.uni-heidelberg.de*

Received 30th May 2000, Accepted 21st August 2000
First published as an Advance Article on the web 2nd October 2000

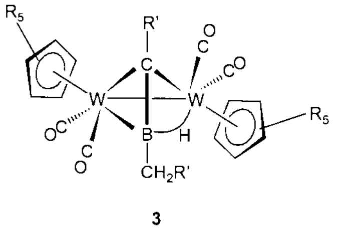
Hydroboration reactions of Fischer carbyne metal complexes [M(≡CR)X(CO)$_2$] (X = η-C$_5$R$_5$ or tpb′; tpb′ = tris(3,5-dimethylpyrazolyl)hydroborate) were studied. Depending on R and X two types of hydroboration products were formed, namely the α-boryl-η^3-benzyl metal complexes [M(C$_5$R$_5$)(CO)$_2${(BEt$_2$)C(H)(C$_6$H$_4$Me-4)}] (M = W, R$_5$ = Me$_4$Et; M = Mo, R = Me) and the novel borylmetal complexes [M(tpb′)(CO)$_2${η^2-B(R′)CH$_2$R}] (M = W, R′ = Et, R = C$_6$H$_4$Me-4 or Me; M = Mo, R′ = Et, R = C$_6$H$_4$Me-4; M = W, R′ = Ph, R = C$_6$H$_4$Me-4 or Me). β-Agostic CHM interactions are present between the metal and the boryl ligands. Labelling experiments involving "DBEt$_2$" showed selective transfer of deuterium to the former carbyne carbon, with only deuterium participating in the agostic interaction. From [W(≡CR)(C$_5$Me$_5$)(CO)$_2$] **2** (R = Me or SiPh$_3$) and "HBEt$_2$" the complex *trans*-[W(C$_5$Me$_5$)(CO)$_2$(H)(C$_2$H$_4$)] was obtained as the sole organometallic compound. Deuterium labelling experiments confirmed transfer of hydrogen from the borane to the carbyne complex. In polar solvents, [W(η-C$_5$Me$_5$)(CO)$_2${(BEt$_2$)C(H)C$_6$H$_4$Me-4}] and the η-C$_5$Me$_4$Et analogues were at least partially (30–100%) converted into [W(η-C$_5$R′$_5$)(CO)$_2$(H)(C$_2$H$_4$)] (R′ = Me, R′$_5$ = Me$_4$Et) and unknown boron containing products. From an acetone solution of the α-borylbenzyl η-C$_5$Me$_4$Et complex crystals of a new product were isolated. Its unusual structure results from disruption of the boryl group, incorporation of two molecules of acetone to give a 1,3-dioxa-2-boracyclohexane ring system, conversion of the benzyl ligand into an η^4-2-methyl-5-*exo*-methylenehexa-1,3-diene ligand and the formation of an acetyl group on the tungsten.

Introduction

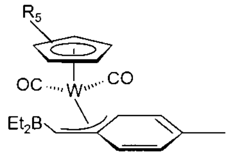
More than 25 years ago the synthesis of the first alkylidyne (carbyne) metal complexes by Fischer *et al.* was a true milestone of organometallic chemistry.[1] The chemistry of the transition metal–carbon triple bond, present in such complexes, has meanwhile developed into a major field of research.[2–11] Particularly helpful in understanding the diverse reactivity of the M≡C bond was Stone's recognition of the synthetic utility of the isolobal relationship[12] between alkynes and carbyne metal complexes, which quickly gave them a new role as versatile organometallic building blocks.[13] Isolobality often relates organometallic (*e.g.* the metal–carbon triple bond) to organic functionalities (*e.g.* the carbon–carbon triple bond). It does, however, not necessarily implicate identical reactivity.

Hydroboration is a very powerful tool for the functionalization of carbon–carbon multiple bonds. Much of the usefulness of this reaction stems from its predictability and wide applicability.[14] However, attempts to hydroborate metal–carbon triple bonds have shown a much higher complexity in these systems, as compared to the alkynes.[15]

When treated with BH$_3$·thf the carbynemetal complexes of the type [W(≡CR′)(η-C$_5$R$_5$)(CO)$_2$] (R′ = C$_6$H$_4$Me-4 **1** or Me **2**) gave the ditungsten compounds [{W(η-C$_5$R$_5$)(CO)$_2$}$_2$(μ-R′CB-(H)CH$_2$R′)] **3**, which are analogs of the well known μ-alkyne complexes (or dimetallatetrahedranes) [{W(η-C$_5$R$_5$)(CO)$_2$}$_2$-(μ-R′CCR′)].[16] Reaction of **1** with dialkylboranes [9-borabicyclo[3.3.1]nonane (9-BBN) or diethylborane ("HBEt$_2$")] gave the mononuclear complexes [W(η-C$_5$R$_5$)(CO)$_2${η^3-CH-(BR″$_2$)C$_6$H$_4$Me-4}], *e.g.* **4**.[16,17] Here, the gross reaction amounts to a 1,1 hydroboration of the metal–carbon triple bond at the carbyne carbon atom, generating an α-borylbenzyl ligand.



3



4a R = H
4b R = Me

More recently we communicated the hydroboration with "HBEt$_2$" of the tris(3,5-dimethylpyrazolyl)hydroborate (tbp′) substituted carbyne metal complexes [M(≡CR)(tpb′)(CO)$_2$] (M = W **5** or Mo **6**) to give the boryl metal complexes [M(tpb′)(CO)$_2${η^2-B(Et)CH$_2$R}] **7**, **8** (R = Me or C$_6$H$_4$Me-4).[18] In this reaction the former carbyne carbon is reduced to a methylene group and becomes separated from the metal by a borylene (BR) moiety. In the present paper we give a full account of this work, along with a report of further investigations of hydroboration reactions involving some of the classical Fischer-type carbyne metal complexes [M(≡CR′)-(η-C$_5$R$_5$)(CO)$_2$] (M = Mo or W).

Results

Hydroboration of the carbynemetal complexes [M(≡CC$_6$H$_4$Me-4)-(η-C$_5$R$_5$)(CO)$_2$] (M = Mo or W)

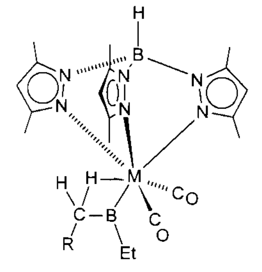
Reaction of the *p*-tolylcarbyne metal complexes [M(≡CC$_6$H$_4$-

---

† Dedicated to Professor Günter Helmchen on the occasion of his 60th birthday.

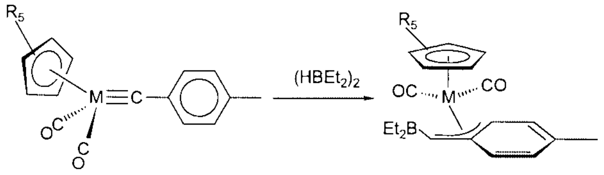
Electronic supplementary information (ESI) available: IR data and preparative details for some of the complexes. See http://www.rsc.org/suppdata/dt/b0/b004256k/

DOI: 10.1039/b004256k



7 M = W
8 M = Mo

Me-4)(η-C$_5$R$_5$)(CO)$_2$] **1c** (M = W, R$_5$ = Me$_4$Et) and **9** (M = Mo, R = Me) with a two- to four-fold excess of “HBEt$_2$” in thf at low temperature (−50 to −30 °C) gave the α-boryl-η^3-benzyl metal complexes [M(η-C$_5$R$_5$)(CO)$_2${(α-BEt$_2$)C(H)(C$_6$H$_4$-Me-4)}] **4c** (M = W, R$_5$ = Me$_4$Et) and **10** (M = Mo, R = Me), respectively (Scheme 1). The products were characterized by spectroscopic methods and, in the case of **10**, by a single crystal structure analysis. Unfortunately, due to the poor crystallinity of the material, the quality of the reflection data set was poor. The structure could be solved, and the connectivity of the non-hydrogen atoms established. However, refinement to an acceptable level was not possible.



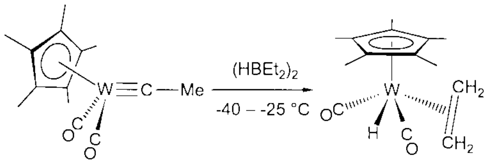
1c M = W, R$_5$ = Me$_4$Et
9 M = Mo, R = Me

4c M = W, R$_5$ = Me$_4$Et
10 M = Mo, R = Me

Scheme 1

Hydroboration of the carbynemetal complexes [W(≡CR)(η-C$_5$Me$_5$)(CO)$_2$] (R = Me 2 or SiPh$_3$ 13)

Reaction of the methylidynetungsten complex **2** with an excess of “HBEt$_2$” in thf solution took place above −40 °C, as indicated by a deepening of the yellow colour of the solution and the appearance of two new ν_{CO} absorptions at 1957 and 1876 cm^{-1} in the infrared spectrum. The only organometallic product of this reaction was the known[19] hydridoethylenetungsten complex *trans*-[W(η-C$_5$Me$_5$)(CO)$_2$(H)(C$_2$H$_4$)] **11b** (62% yield) (Scheme 2). When “HBEt$_2$” was added dropwise to a thf solution of **2** at −40 °C the only observable change in the IR (ν_{CO}) spectrum was a decrease in intensity of the bands due to **2** (at 1972 and 1893 cm^{-1}), accompanied by a proportional growth of those due to the product **11b**. Quantitative conversion of **2** into **11b** required approximately 2.2 molar BH equivalents. Reaction of **2** with “HB^{n}Pr$_2$” in thf both at −40 °C and ambient temperature took a very similar course. 1.7 molar BH equivalents were needed for the quantitative conversion of **2** into **11b**, which was identified by mass and ^{1}H NMR spectroscopy. Treatment of **2** with a large excess (5.7 BH equivalents) of “HB^{n}Pr$_2$” at −10 °C in thf gave a yellow crystalline product which was an approximately 7.5 : 1 mixture of the ethylene and propenehydrido complexes **11b** and **12**, respectively.



2

11b

Scheme 2

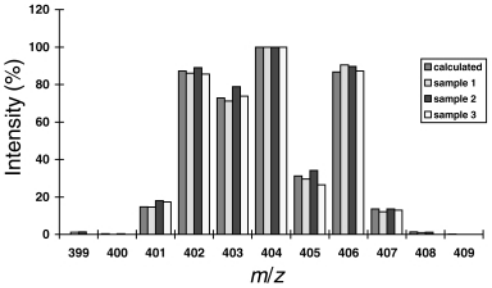


Fig. 1 Experimental and calculated (M^+ 84%, $[M - \mathrm{H}]^+$ 16%) mass distributions of the parent ion of [W(η-C$_5$Me$_5$)(CO)$_2$(H)(C$_2$H$_4$)] **11b**. Experimental data from three separate mass spectroscopic analyses are shown.

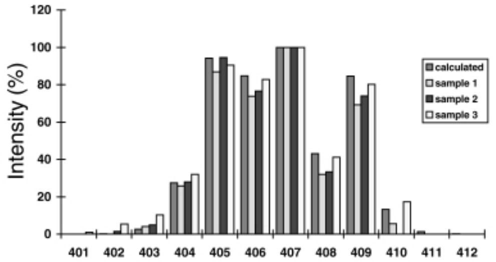
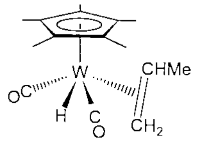


Fig. 2 Experimental and calculated (n = 0, 86%, n = 1, 14%; M^+ 84%, $[M - \mathrm{H}]^+$ 16%) mass distributions of the parent ion of [W(η-C$_5$Me$_5$)(CO)$_2$(C$_2$H$_{2+n}$D$_{3-n}$)] **11b-D**, generated from complex **2-D** with 1.7 equivalents of “HBEt$_2$”. Experimental data from three separate mass spectroscopic analyses are shown.



12

A sample of the deuterium labelled ethylidyne complex [W(≡CCD$_{3-n}$H$_n$)(η-C$_5$Me$_5$)(CO)$_2$] **2-D** was prepared from the labelled carbene complex [W{=C(OMe)CD$_{3-n}$H$_n$}(CO)$_5$][20] according to Fischer's method. Using mass spectroscopy, the isotopic composition of **2-D** was evaluated as 86% [W(≡CCD$_3$)(η-C$_5$Me$_5$)(CO)$_2$] and 14% [W(≡CCD$_2$H)(η-C$_5$Me$_5$)(CO)$_2$]. After reaction of this mixture of isotopomers with 1.2 equivalents of “HBEt$_2$” in thf at −25 °C the IR spectrum indicated complete conversion into the hydridoethylene complex [W(C$_2$H$_{2+n}$D$_{3-n}$)(η-C$_5$Me$_5$)(CO)$_2$] **11b-D**. The determination of the deuterium content of **11b-D** by electron impact mass spectroscopy was complicated by partial loss of hydrogen from the parent ion. In a number of experiments carried out under identical conditions with several samples of non-deuteriated **11b** this process was found reproducibly to give a 84 : 16 mixture of the M^+ and $[M - \mathrm{H}]^+$ ions (Fig. 1). Keeping the same ratio of M^+ and $[M - (\mathrm{H, D})]^+$, the parent peak envelope of a 86 : 14 mixture of [W(η-C$_5$Me$_5$)(CO)$_2$(C$_2$H$_2$D$_3$)] and [W(η-C$_5$Me$_5$)(CO)$_2$(C$_2$H$_3$D$_2$)] was calculated. The resulting pattern and the one actually observed from **11b-D** were in excellent agreement (Fig. 2), indicating that the deuterium labels in **2-D** were completely retained after reaction with “HBEt$_2$”.

When the reaction was carried out with an excess (3.4 equivalents) of “HBEt$_2$”, the isotope pattern of the parent ion(s) in

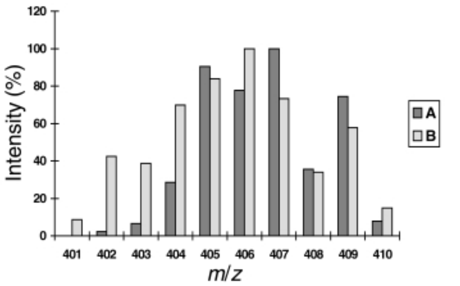
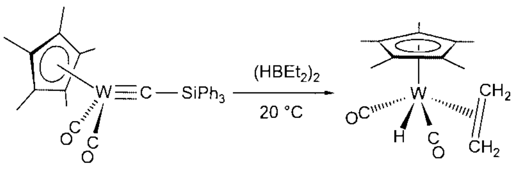


Fig. 3 Experimental mass distributions of the parent ions of [W(η-C_5Me_5)$(CO)_2$($C_2H_{2+n}D_{3-n}$)] **11b-D**, generated from complex **2-D** with 1.7 (A) and 3.4 equivalents of "$HBEt_2$" (B), respectively.

the mass spectrum of the product was different from that observed after the reaction with a 1 : 1.7 molar ratio of the carbyne complex and "$HBEt_2$" (Fig. 3). The presence of significant intensity at *m*/*z* = 402 and 401 is strongly indicative of the presence of the non-deuteriated complex **11b**, along with [W(η-C_5Me_5)$(CO)_2$($C_2H_{2+n}D_{3-n}$)] (n = 0 or 1), *i.e.* significant loss of deuterium. The product resulting from the reaction of **2-D** and "$HBEt_2$" in a 1 : 1.7 molar ratio (*i.e.* [W(η-C_5Me_5)-$(CO)_2$($C_2H_{2+n}D_{3-n}$)] (n = 0 or 1)) was stirred in the presence of an excess of "$HBEt_2$" (14.4 equivalents) in thf for two hours at ambient temperature. IR spectroscopy was employed to verify the stability of this complex under these conditions. After work-up, mass spectroscopic analysis again indicated partial loss of the deuterium labels.

The triphenylsilylcarbynetungsten complex [W(≡$CSiPh_3$)-(η-C_5Me_5)$(CO)_2$] **13** was markedly less reactive than the *p*-tolyl and methyl derivatives. No reaction with an excess of "$HBEt_2$" was observed in thf solution at −40 °C. Stirring of the mixture at ambient temperature caused a slow deepening of the yellow colour, accompanied by a decrease in intensity of the IR (ν_{CO}) bands of **13**, with a concurrent growth of two bands at 1957 and 1877 cm^{-1}, characteristic of the formation of **11b** (Scheme 3). After several hours conversion was quantitative, with only the absorptions of **11b** present in the carbonyl region of the infrared spectrum. After work-up, complex **11b** was isolated in 43% yield.

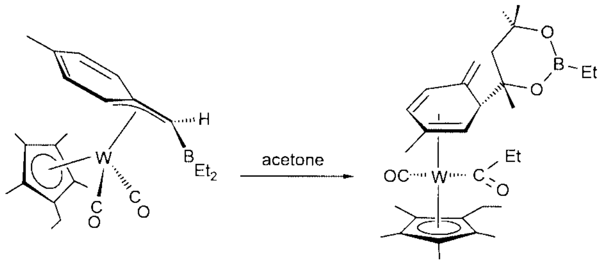


13 **11b**

Scheme 3

Decomposition of the α-boryl-η^3-benzyl metal complexes [W(η-C_5R_5)$(CO)_2${(α-BEt_2)C(H)(C_6H_4Me-4)}] 4b (R = Me) and 4c (R_5 = Me_4Et)

In certain solvents, solutions of the α-borylated η^3-benzyl complex **4b**[17] changed from orange to yellow on standing at ambient temperature. In the infrared (ν_{CO}) spectrum this was accompanied by a decrease in intensity of the two bands due to **4b** and by the appearance and subsequent growth of two new bands at lower frequency (1956 and 1875 cm^{-1} in thf). The rate and extent of this reaction markedly depended on the solvent. Whereas in benzene and diethyl ether an equilibrium with 30–40% conversion was reached after about ten hours at room temperature, the reaction went to completion in thf, methylene chloride and acetone after about 20 hours. Below 0 °C an equilibrium was reached even in the last mentioned solvents. Below −20 °C solutions of **4b** were stable over extended periods in all the solvents mentioned. In the NMR spectra the ^{1}H and ^{13}C resonances of **4b** decreased with time. A new set of resonances appeared and gained intensity. Most of the new signals could be attributed to the hydridoethylene complex **11b**, which appeared to be the sole organometallic product of the reaction. The infrared spectrum is also consistent with **11b** being the only carbonyl containing species formed. Other resonances in the proton and carbon spectra depended on the particular solvent and also on the initial concentration of **4b**. The ^{11}B NMR resonance of the product mixture was a broad feature centered at δ 54 and did not change when proton decoupled.



4c **14**

Scheme 4

In acetone solution [W(η-C_5Me_4Et)$(CO)_2${(α-BEt_2)C(H)-(C_6H_4Me-4)}] **4c** showed the same changes in the IR and NMR spectra as were observed for complex **4b**. However, during attempted work-up of the product by crystallization from acetone, a new product, **14**, was obtained in several batches with a total yield of 63% (Scheme 4). Other products, isolated in small yields, were [W(C_5Me_4Et)$(CO)_2$]$_2$ and [W$(CO)_6$]. The molecular structure of **14** was determined by a single crystal structure analysis. A view of the molecule is presented in Fig. 4, along with important bond lengths and angles. The structure shows little resemblance to the starting material **4c** and to its 'decomposition product' [W(η-C_5Me_4Et)$(CO)_2$(H)(C_2H_4)] **11c**. The original *p*-tolylcarbyne has been transformed into a

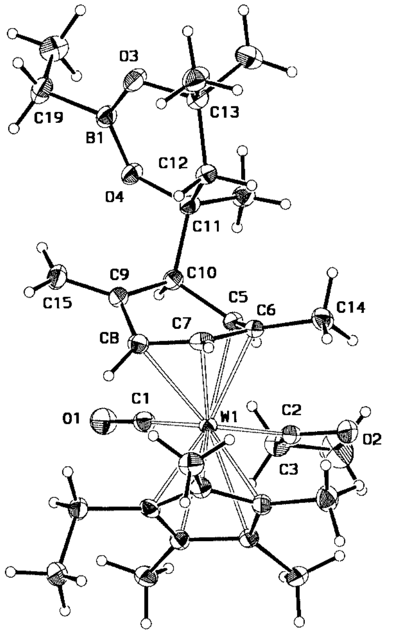


Fig. 4 Molecular structure of complex **14**. Selected bond lengths [Å] and angles [°]: W1–C1 1.959(5), W1–C2 2.222(5), W1–C5 2.330(6), W1–C6 2.260(6), W1–C7 2.244(5), W1–C8 2.365(5), C1–O1 1.160(5), C2–O2 1.218(5), C2–C3 1.543(6), C5–C6 1.436(6), C6–C7 1.417(6), C6–C14 1.509(6), C7–C8 1.424(6), C8–C9 1.479(6), C9–C10 1.525(6), C9–C15 1.337(6), C10–C11 1.560(6), C11–C12 1.525(6), C11–O4 1.457(5), C12–C13 1.531(6), C13–O3 1.458(6), B1–O3 1.359(6), B1–O4 1.363(6) and B1–C19 1.579(7); W1–C1–O1 174.9(4), W1–C2–O2 123.4(3), W1–C2–C3 119.6(3), O2–C2–C3 117.0(4), O3–B1–O4 123.7(4), O3–B1–C19 119.3(4) and O4–B1–C19 117.0(4).

2-methyl-5-*exo*-methylenehexa-1,3-diene ligand, which bonds to the tungsten atom in the η^4 fashion. A second six-membered substituted 1,3-dioxa-2-boracyclohexane ring system is attached to the cyclohexadiene ligand at the 6 position. Of the two ethyl groups formerly attached to boron one has been transferred to a carbonyl on tungsten, thus forming an η^1-acyl ligand.

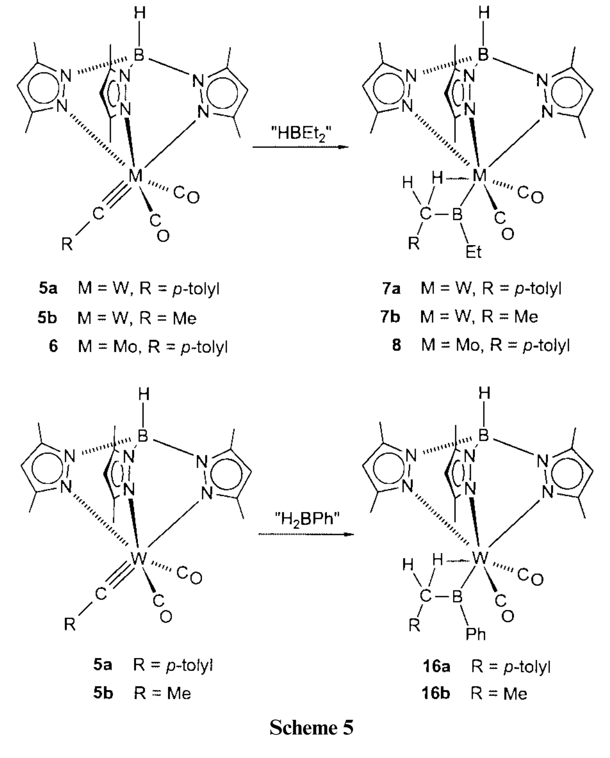
The spectra of complex **14** in solution are consistent with this structure, notably the presence of only one carbonyl stretch at 1910 cm^{-1} due to the carbonyl ligand, and a second band at 1611 cm^{-1} arising from the acyl ligand. The ^{11}B NMR spectrum shows a resonance at δ 30.2.

Surprisingly, the molybdenum complex $[Mo(\eta\text{-}C_5Me_5)(CO)_2\{(\alpha\text{-}BEt_2)C(H)(C_6H_4Me\text{-}4)\}]$ **10** and the cyclopentadienyltungsten derivative $[W(\eta\text{-}C_5H_5)(CO)_2\{(\alpha\text{-}BEt_2)C(H)(C_6H_4Me\text{-}4)\}]$ **4a**[17] were stable in solutions of common solvents at room temperature for long periods.

Hydroboration of the carbynemetal complexes $[W(\equiv CC_6H_4\text{-}Me\text{-}4)(tpb)(CO)_2]$ 15 and $[M(\equiv CR)(tpb')(CO)_2]$ (M = W, R = C_6H_4Me-4 5a, Me 5b or Ph 5c); (M = Mo, R = C_6H_4Me-4 6; tpb = hydrotris(pyrazol-1-yl)borate)

The complex $[W(\equiv CC_6H_4Me\text{-}4)(tpb)(CO)_2]$ **15** slowly reacted in thf solution with "$HBEt_2$" between −30 °C and room temperature. However, about 20 equivalents of the hydroborane were necessary until no residual carbyne could be detected by infrared spectroscopy. In toluene, reaction of **15** with "$HBEt_2$" took place between −10 and +5 °C; the starting material **15** was consumed after addition of about 6 equivalents of "$HBEt_2$". According to the IR and NMR spectra, further reaction occurred in this mixture when heated above 25 °C. In any case, no characterizable product could be isolated. Three equivalents of BH_3·thf were required for the total consumption of **15** in thf solution at ambient temperature. The primary product showed IR (ν_{CO}) absorptions at 2004, 1964, 1930 and 1850 cm^{-1}. After chromatography on deactivated alumina a 9% yield of the complex $[\{W(tpb)(CO)_2\}_2]$ was isolated.

No reaction took place between the carbyne metal complex **5a** and diethylborane in thf solution up to 65 °C. In toluene solution, reaction between **5a** or its molybdenum analog **6** and an excess of "$HBEt_2$" occurred at 60 °C, to give the yellow boryl metal complexes **7a** and **8**, respectively in about 70% yield (Scheme 5). The considerably more reactive ethylidyne tungsten complex **5b** gave product **7b** at room temperature. In all cases, triethylborane was detected by NMR spectroscopy in the reaction mixtures as a second product. Reaction of **5a** and **5b** in toluene solution with phenylborane "H_2BPh" at ambient temperature gave the products **16a**, **16b** in high yields. These reactions were notably faster than those with diethylborane. With **5a** and "H_2BPh" the reaction proceeded smoothly at ambient temperature and was complete within about one hour. Reaction between **5b** and "H_2BPh" was instantaneous. The products **7**, **8** and **16** are air and moisture sensitive yellow crystalline solids, soluble in polar organic solvents. Single crystal structure determinations were carried out for **7a**, **7b** and **16a**, **16b**.



Scheme 5

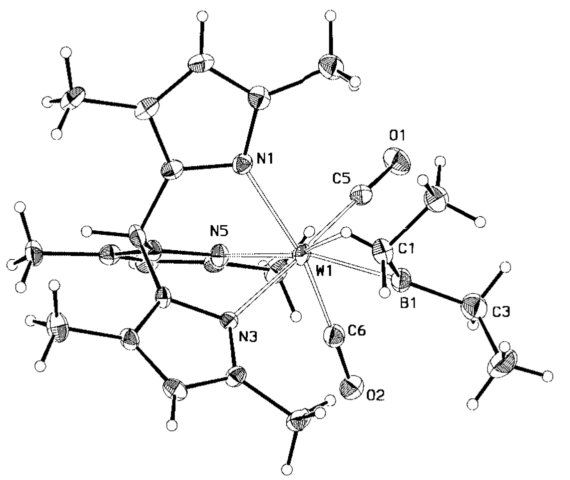


Fig. 5 Molecular structure of complex **7b**. Selected bond lengths [Å] and angles [°]: W1–B1 2.064(9), W1 ··· C1 2.475(8), W1–C5 1.959(8), W1–C6 1.928(9), W1–N1 2.250(6), W1–N3 2.251(6), W1–N5 2.188(6), B1–C1 1.613(14), B1–C3 1.561(13), C5–O1 1.158(9) and C6–O2 1.191(10); W1–B1–C1 83.6(5), W1–B1–C3 154.2(7), C1–B1–C3 122.1(8), W1–C5–O1 179.4(7) and W1–C6–O2 177.4(7).

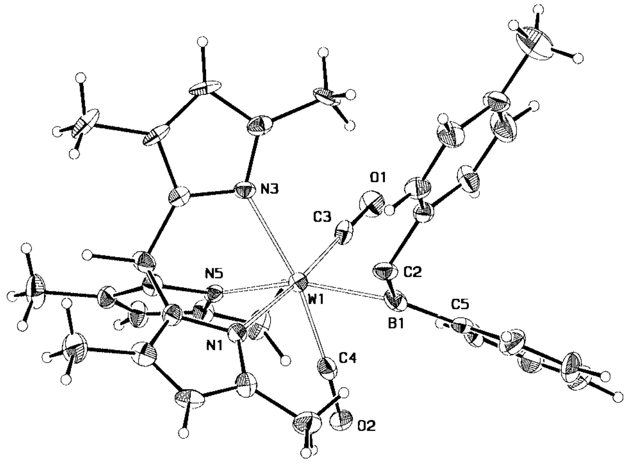


Fig. 6 Molecular structure of complex **16a**. Selected bond lengths [Å] and angles [°]: W1–B1 2.058(13), W1 ··· C2 2.511(13), W1–C3 1.961(11), W1–C4 1.958(11), W1–N1 2.209(8), W1–N3 2.250(8), W1–N5 2.174(9), B1–C2 1.648(17), B1–C5 1.567(16), C3–O1 1.170(12) and C4–O2 1.161(12), W1–B1–C2 84.5(7), W1–B1–C5 150.8(9), C2–B1–C5 124.7(10), W1–C3–O1 178.6(9) and W1–C4–O2 176.4(9).

The crystal structure of complex **7a** has been communicated.[18] The molecular structures of **7b** and **16a**, **16b** are depicted in Figs. 5–7.

The molecules consist of $(tpb')(OC)_2W$ complex fragments which are ligated by a diorganyl boryl ligand $BR'(CH_2R)$ (R′ = Et or Ph; R = *p*-tolyl or Me). β-Agostic interactions are present between the metal and a CH bond of the methylene group of the boryl ligands, as evident by the acute angle W–B–C(H_2) (82–85°), the relatively short distance W ··· C(H_2) (2.45–2.51 Å) and, in the case of **7a, 7b** and **16b**, by the direct location and refinement of the agostic hydrogen atoms ($d_{W\text{-}H}$ = 2.17(8) (**7a**),

Table 1 ^{1}H NMR spectroscopic data (δ) for the complexes [M(tpb′)(CO)$_2${B(R′)CH$_2$R}] **7**, **8** and **16** (in C$_6$D$_6$, ambient temperature)

		tpb′			
Complex	M, R, R′	CH	CH$_3$	R′	CH$_2$R
8	Mo, *p*-tolyl, Et	5.41(s, 1), 5.48(s, 2)	1.99(s, 6), 2.05(s, 3); 2.07(s, 6), 2.11(s, 3)	2.33(q, 2), 1.54(t, 3)	2.41(s, 2), 6.87(m,^{a} 2), 7.11(m,^{a} 2), 2.71(s, 3)
7a	W, *p*-tolyl, Et	5.38(s, 1), 5.45(s, 2)	2.00(s, 3), 2.01(s, 6), 2.06(s, 6), 2.07(s, 3)	2.44(q, 2), 1.57(t, 3)	2.75(s, 2), 6.88(m,^{a} 2), 7.14(m,^{a} 2), 2.79(s, 3)
7b	W, Me, Et^{b}	5.87(s, 1), 5.93(s, 2)	2.27(s, 6), 2.34(s, 3), 2.40(s, 6), 2.50(s, 3)	1.92(q, 2), 1.28(t, 3)	1.03(q, 2), 1.44(t, 3)
7b-D	W, Me, Et^{b}	5.80(s, 1), 5.86(s, 2)	2.20(s, 6), 2.28(s, 3), 2.33(s, 6), 2.43(s, 3)	1.85(q, 2), 1.22(t, 3)	1.36(br s, 3)
7c-D	W, Ph, Et	5.87(s, 1), 5.88(s, 2)	1.95(s, 6), 2.34(s, 3), 2.40(s, 6), 2.54(s, 3)	2.03(q, 2), 1.26(t, 3)	7.18(m, 5)
16a	W, *p*-tolyl, Ph^{b}	5.88(s, 2), 5.94(s, 1)	1.91(s, 6), 2.37(s, 3), 2.42(s, 6), 2.69(s, 3)	7.43(m, 3), 7.89(m, 2)	3.02(s, 2), 6.95(m,^{a} 2), 7.09(m,^{a} 2), 2.25(s, 3)
16b	W, Me, Ph^{b}	5.94(s, 1), 5.99(s, 2)	2.34(s, 6), 2.40(s, 3), 2.46(s, 6), 2.65(s, 3)	7.53(m, 3), 7.99 M, 2)	1.35(q, 2), 1.55(t, 3)

^{a} (AB)$_2$ pattern. ^{b} In CD$_2$Cl$_2$.

Table 2 ^{13}C NMR spectroscopic data for the complexes [M(tpb′)(CO)$_2${B(R′)CH$_2$R}] **7**, **8** and **16** (in CD$_2$Cl$_2$ ambient temperature)

			tpb′				
Complex	M, R, R′	CO	CH	CH$_3$	C^{a}	R′	CH$_2$R
8	Mo, *p*-tolyl, Et	221.8	106.8, 107.2	12.6, 13.1, 14.4, 14.9	135.5, 136.3, 145.4, 145.5, 152.0, 153.6	20.1,^{b} 9.2^{c}	−11.0,^{b} 128.9,^{d} 130.6,^{d} 20.7^{c}
7a	W, *p*-tolyl, Et	216.4	106.7, 106.9	12.5, 13.0, 14.5, 152.	135.2, 136.3, 145.0, 145.3, 152.0, 153.5	19.3,^{b} 9.4^{c}	−14.8,^{b} 128.5,^{d} 130.2,^{d} 20.6^{c}
7b	W, Me, Et	216.7	107.39, 107.42	12.7, 13.2, 15.2, 15.7	145.2, 145.7, 152.6, 154.3	18.8,^{b} 9.4^{c}	−30.2,^{b} 15.9^{c}
7b-D	W, Me, Et	216.5	107.21, 107.24	12.4, 12.9, 15.0,^{e} 15.43^{e}	145.0, 145.5, 152.5, 154.3	18.9,^{b,e,f} 9.9^{c,f}	15.45^{c}
16a	W, *p*-tolyl, Ph^{b}	219.0	107.5, 107.7	12.8, 13.3, 14.6, 16.0			−16.6^{b}
16b	W, Me, Ph	219.1	107.58, 107.64	12.8, 13.3, 15.3, 15.9			−30.0,^{b} 17.5^{c}

^{a} Quaternary carbons of the pyrazolyl and phenyl rings. ^{b} CH$_2$. ^{c} CH$_3$. ^{d} CH. ^{e} Broad resonance. ^{f} Assigned by ^{13}C/^{1}H, ^{11}B triple resonance (see text).

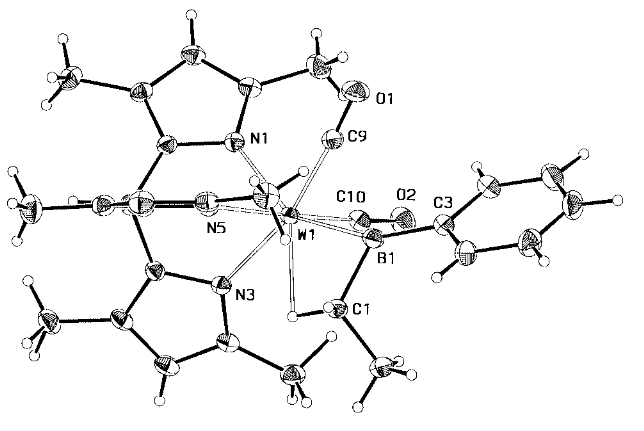


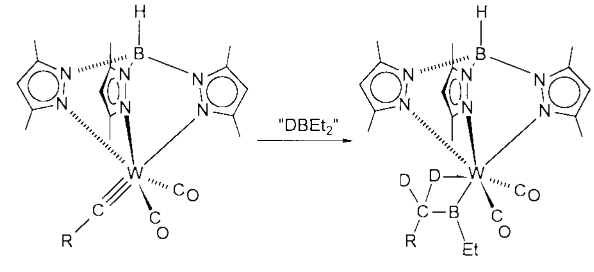
Fig. 7 Molecular structure of complex **16b**. Selected bond lengths [Å] and angles [°]: W1–B1 2.070(4), W1 · · · C1 2.476(4), W1–C9 1.941, W1–C10 1.951(4), W1–N1 2.183(3), W1–N3 2.255(3), W1–N5 2.257, B1–C1 1.619(5), B1–C3 1.557(5), C9–O1 1.168(4) and C10–O2 1.174(4); W1–B1–C1 83.4(2), W1–B1–C3 154.7(3), W1–C9–O1 176.3(3), W1–C10–O2 177.2(3) and C1–B1–C3 121.7(3).

2.22(4) (**7b**), 2.22 (8) Å (**16b**)). In all the structures the boron atom of the boryl group is planar configurated (root mean square deviations from the best planes through boron, tungsten and the two carbon atoms bonded to B: 0.0002–0.018 Å).

Broad ^{11}B resonances are detected for the agostic boryl ligands at δ 76–77, along with the sharper resonance at $\delta \approx -9$ due to the quaternary boron of the tpb′ ligand. A 2 : 1 pattern is displayed by the resonances of the dimethylpyrazolyl groups (*i.e.* two sets of resonances each for the ring hydrogens and the two inequivalent methyl groups). When measured in a magnetic field of 4.7 T the proton and carbon spectra are not notably dependent on temperature between 350 and 210 K (Tables 1, 2). In the proton coupled 125.8 MHz carbon spectrum at 190 K the resonance at δ −18.8 due to the agostic methylene group of **16a** could be resolved into a doublet of doublets with the corresponding coupling constants J_{CH} = 97 and 129 Hz.

Reaction of [W(≡CR)(tpb′)(CO)$_2$] (R = Me 5b or Ph 5c) with "DBEt$_2$"

Reaction of the carbyne metal complexes [W(≡CR)(tpb′)(CO)$_2$] (R = Me **5b** or Ph **5c**) with "DBEt$_2$" gave a single product in each case (Scheme 6). The proton spectrum of the product **7b-D** was very similar to that of **7b**, except for the region $1.0 \leqslant \delta \leqslant 1.5$, where the quartet/triplet pattern at δ 1.03 (intensity 2 H)/1.44 (intensity 3 H) due to the agostic ethyl group of **7b** had been replaced by a slightly broadened singlet at δ 1.36 (intensity 3H). The assignment of the methylene proton resonance at δ 1.85 to the non-agostic ethyl group was confirmed by a series of selectively ^{1}H and ^{11}B decoupled ^{13}C triple resonance experiments, which correlated the proton resonances at δ 1.85(a quartet) and 1.22(a triplet) with the carbon signals at δ 18.9 and 9.9, respectively. The proton spectrum of **7c-D** resembled that of the related *p*-tolyl complex **7a** (disregarding the differences caused by the replacement of the *p*-tolyl by a phenyl group), except that the singlet at δ 2.75 due to the methylene group of



5b R = Me
5c R = Ph

7b-D R = Me
7c-D R = Ph

Scheme 6

7a was missing. Only broad features with no resolvable ^{1}H or ^{2}D coupling could be detected for the agostic methylene groups in the 125.8 MHz carbon spectra of **7b-D** and **7c-D**, even at low temperature (220 K).

Discussion

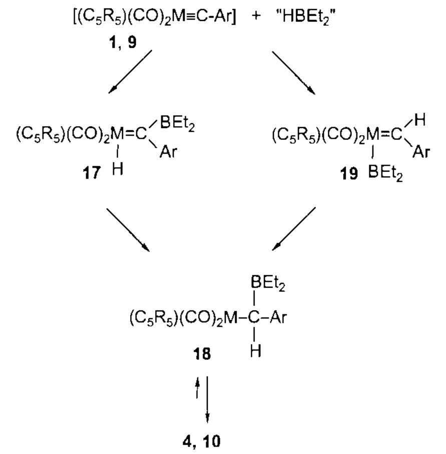
Formation of the boron-containing products

The reactivity of low-valent (*i.e.* Fischer-type) carbyne metal complexes towards electrophiles and nucleophiles has been subject to much discussion.[2,7,8,11,21] Atomic charges on the carbyne carbons are calculated to be negative by both semi-empirical and *ab initio* molecular orbital methods.[7,22] From the numerous theoretical studies some important generalizations can be made.[2,8] The highest occupied molecular orbital (HOMO) is largely metal centered (mainly metal d), whereas the lowest unoccupied molecular orbital (LUMO) is an anti-bonding π^* orbital of the metal–carbon multiple bond. The MC π orbitals are lower in energy than the metal d orbital, but chemically active. Hence, under frontier orbital control, electrophilic attack is expected to take place at the metal, nucleophilic attack is expected at the carbyne carbon (the LUMO has a larger coefficient there), or 'across' the metal carbyne bond, *i.e.* more or less simultaneously on M and C. In charge controlled reactions, however, electrophiles will become attached to the carbyne carbon.

Based on its reactivity in a variety of coupling reactions, the carbyne carbon in the complexes $[\text{d}^6\text{-M}(\equiv\text{CR})(\eta\text{-C}_5\text{R}_5)(\text{CO})_2]$ is considered to be 'nucleophilic', *i.e.* susceptible to electrophilic attack.[11] Correspondingly, protonation of $[(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}\equiv\text{C(aryl)}]$ (*e.g.* **1a**) gives products derived from protonation at C.[23] However, reaction of $[\text{Mo}(\equiv\text{CCH}_2\text{CMe}_3)(\eta\text{-C}_5\text{H}_5)\{\text{P(OMe)}_3\}_2]$ with HBF$_4$ led to the alkylidyne hydrido complex $[\text{Mo}(\equiv\text{CCH}_2\text{CMe}_3)(\eta\text{-C}_5\text{H}_5)\{\text{P(OMe)}_3\}_2(\text{H})]^+$, with only indirect evidence for the site of kinetic attack by protons being the alkylidyne carbon or the "π electrons of the metal–carbon triple bond".[8,24] This was rationalized in terms of the donor/acceptor properties of the other ligands, P(OMe)$_3$ being much worse a π acceptor than CO.[8]

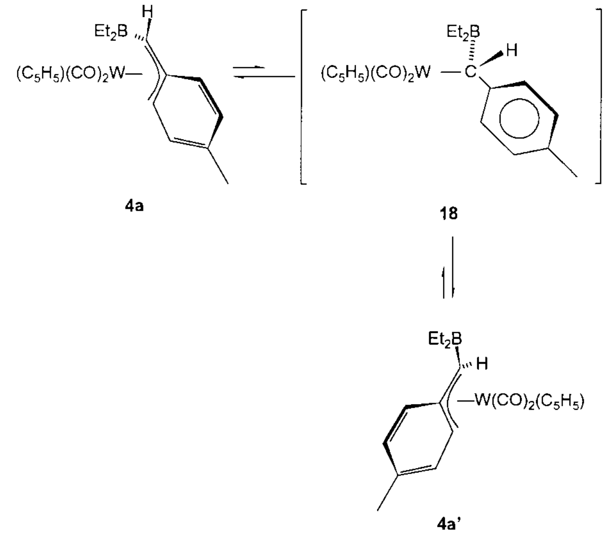
Organic hydroboration is generally assumed to be initiated by an attack of the organic substrate by the electrophilic boron atom of the borane.[25] In our reactions it is however very difficult if not impossible to decide on the initial site of attack of the borane. Furthermore, in solution the organohydroboranes "$\text{H}_n\text{BR}_{3-n}$" ($n = 1$ or 2) are normally equilibrium mixtures of organyldiborane-6 derivatives $\text{H}_m\text{B}_2\text{R}_{6-m}$ ($m = 1$–6), due to the exchange of organic groups being catalysed by the BH functions.[26] Phenylborane "H$_2$BPh" was reported forty years ago, but only poorly characterized.[27] For the solid state, the originally postulated[27a] composition HPhB(μ-H)$_2$BPhH has recently been confirmed by a crystal structure analysis.[28] As shown by the ^{11}B NMR spectra, several species exist in solutions in non-donor solvents. Additional complications may arise due to the equilibrium between all diborane-6 derivatives and their corresponding monoborane solvent adducts in donor solvents.

For the cyclopentadienyl substituted carbyne complexes mechanistic speculations have been made[16b] involving a hydrido-carbene[29] intermediate **17**, which would undergo hydride migration to give an η^1-benzyl species **18**. The latter could however form equally well from a borylcarbene primary product **19** (Scheme 7). The co-ordinatively unsaturated 16 valence electron (VE) α-boryl-η^1-benzyl complex **18** very likely is in equilibrium with the final products **4** and **10**, respectively.



Scheme 7

The equilibrium between the η^3- and η^1-benzyl structures also satisfactorily accounts for the observed formation of a second isomer **4a′** when solid **4a** is dissolved at −80 °C and then allowed to warm (Scheme 8).[17]

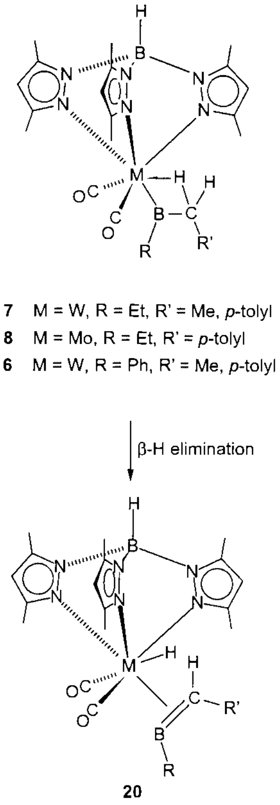


Scheme 8

The formation of agostic boryl complexes from tris(pyrazolyl)borate substituted carbyne complexes is more difficult to explain. The composition of the products **7**, **8** and **16** formally requires addition of a dihydromonoorganoborane H$_2$BR to the carbyne complex, even in the reactions with the monohydrodiorganoborane HBEt$_2$. In our preliminary communication this was tentatively accounted for by the well known dismutation of (HBEt$_2$)$_2$, to give H$_2$BEt and BEt$_3$, the latter of which was indeed detected in the reaction mixtures.[18] However, ethylborane is considered less reactive than diethylborane, and its equilibrium concentration in the "HBEt$_2$" reagent is quite low.[30] On the one hand this may favour attack of the carbyne by HBEt$_2$ or its dimer, exchange of ethyl groups with an excess of unchanged borane still being possible elsewhere along the reaction path. On the other hand, the observed much faster reaction at lower temperatures with phenylborane

"H_2BPh" appears to support our initial view of attack of the carbyne by an H_2BR (or $[H_2BR]_2$) moiety.

Apart from the question of the reactive species, the primary site of attack is equally difficult to elucidate. Two possibilities (electrophilic attack of boron at the metal or at the carbyne carbon atom) have speculatively been discussed in a recent review.[31] Following the latter pathway, which was believed to be more firmly grounded in literature precedent,[31] intermediate **20** with an η^2-co-ordinated boraalkene was proposed (Scheme 9).



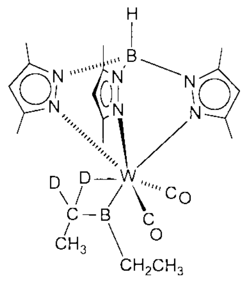
7 M = W, R = Et, R' = Me, *p*-tolyl
8 M = Mo, R = Et, R' = *p*-tolyl
16 M = W, R = Ph, R' = Me, *p*-tolyl

20

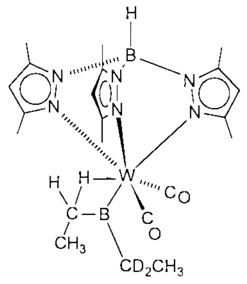
Scheme 9

This formal β-hydrogen elimination product of the agostic boryl complexes **7**, **8** and **16** strongly resembles the intermediates proposed below for some of the reactions leading to the boron free hydridoethylene complexes **11**.

Our deuterium labelling studies essentially rule out an intermediate with a conventional (*i.e.* non-agostic) boryl ligand. From such a species the formation of two isomers of **7b-D** and **7b-D′** would be expected, with deuterium in the agostic and non-agostic methylene group, respectively. Owing to the thermodynamic preference of deuterium for the stronger bond the latter isomer should even prevail, in marked contrast to the experimental observation.

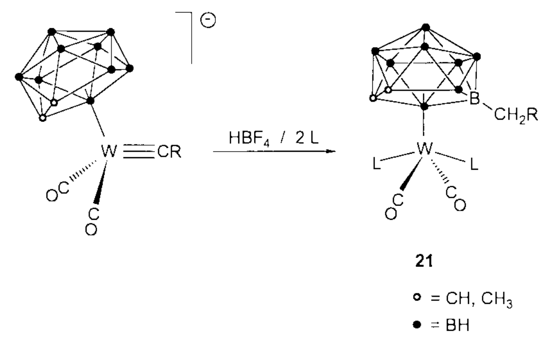


7b-D



7b-D′

Intramolecular hydroborations of carbaboranyl-substituted carbyne metal complexes (*e.g.* $[(C_2B_9H_{11})(OC)_2(d^6\text{-}M){\equiv}CR]^-$) have been reported by Stone.[13b,c] In these proton induced reactions the carbyne moiety CR is assumed to be protonated first, whereupon the resulting carbene species C(H)R inserts into a B–H bond of the carbaboranyl cage, adjacent to the metal. The products, *e.g.* **21** (Scheme 10), are related to **7**, **8** and **16** inasmuch as the carbyne ligand is converted into a CH_2R group and separated from the metal by a boron atom.



21

○ = CH, CH_3
● = BH

Scheme 10

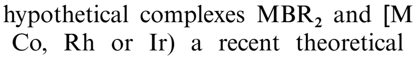
Structure and spectra of $[Mo(\eta\text{-}C_5Me_5)(CO)_2\{(\alpha\text{-}BEt_2)C(H)(C_6H_4Me\text{-}4)\}]$ 10

The IR and NMR spectroscopic data of complex **10** closely resemble those of its tungsten analog **4b**.[17] In particular, only one species is detected in solutions of both **4b** and **10**, whereas two isomers were observed for the sterically less hindered cyclopentadienyl complex **4a**. The molecular structure of **10** in the solid state is also quite similar to that of **4b**. An *exo*-like orientation (with respect to the carbonyl ligands)[32] of the η^3-*p*-methylbenzyl ligand is adopted in the crystal. The diethylboryl group is attached to the terminal carbon of the η^3-benzyl moiety in the *anti* position.

Structure and spectra of the agostic boryl complexes $[M(tpb')(CO)_2\{B(R')(CH_2R)\}]$ 7, 8 and 16

NMR spectroscopic and X-ray crystallographic evidence strongly supports the presence of a β-agostic interaction[33] between the metal atom and a methylene group of the diorganyl boryl ligand $B(R')(CH_2R)$. In the crystal structures of complexes **7a**, **7b** and **16b** the agostic hydrogen atoms could be located and refined successfully. However, due to their vicinity to the heavy tungsten atom, their positions (and correspondingly also distances and angles to other atoms) are not very accurate. More reliably, the angle $WBC(H_2$, agostic) is quite acute (82–85°), and results in a short distance between the carbon atom of this methylene group and the metal (2.45–2.51 Å). Both features are characteristic of β-agostic systems.[33] Of the two methylene groups of the ethyl substituents in **7b** the one involved in the interaction with the metal has a somewhat larger distance to boron (1.61(1) *vs.* 1.56(1) Å). The tungsten–boron bond in **7a**, **7b** and **16a**, **16b** (2.06–2.07 Å) is quite short. Linkages between tungsten and heterosubstituted boryl ligands in comparable complexes are considerably longer, *e.g.* 2.190(7) Å in $[W(\eta\text{-}C_5H_5)_2(H)\{B(cat)\}]$,[34] 2.19(1), 2.23(1) Å in $[W(\eta\text{-}C_5H_5)_2\{B(cat)\}_2]$,[35] and 2.370(8) Å in $[W(\eta\text{-}C_5H_5)(CO)_3\{B(NMe_2)B(NMe_2)Cl\}]$[36] (cat = catecholate).

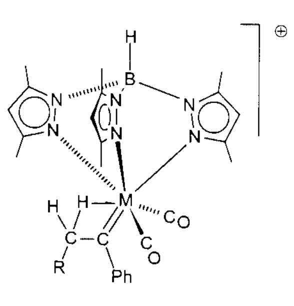
A lot of thought has been given to the possible presence of significant metal-to-boron back bonding in boryl metal complexes.[37–40] This has been the subject of much speculation



$$L_nM{-}B\langle \longleftrightarrow L_nM{=}\overset{\oplus\ \ominus}{B}\langle$$

ever since the first reports of transition metal–boron linkages. For a series of hypothetical complexes MBR_2 and $[MBR_2]^+$ (where M = Sc, Co, Rh or Ir) a recent theoretical study emphasized the importance of π-back donation in the M–boryl bonds.[41] In another theoretical study of the more realistic complexes *cis*-[Pt(PH$_3$)$_2$(BR$_2$)$_2$] the calculated surprisingly small difference between Pt–BH$_2$ and Pt-B(OH)$_2$ bond energies was attributed to the effect of delocalization of the d$_\pi$ electrons of Pt to the p$_\pi$ orbital of BR$_2$.[42] Experimental evidence for such π interactions is however very scarce. In fact, most observations which could be interpreted as due to the presence or absence of this effect can also be explained by other reasons. The short W–B distance in **7** and **16** (about 5% less than the sum of the covalent radii) despite the steric crowding implies a strong bond. Moreover, the ^{11}B NMR resonances of the complexes **7**, **8** and **16** are shifted to high field ($\Delta\delta \approx 10$) with respect to those of the triorganoboranes (alkyl)BRR′, whereas a low field shift is generally observed with most other borylmetal complexes.[39] Although due to the paramagnetic shielding effect of the metal the boron chemical shifts must be approached with caution, both observations appear to be consistent with a significant contribution of the dipolar resonance structure.

The structures of complexes **7** and **16** are quite similar to that of the cationic carbene complex [W{=C(Ph)(CH$_3$)}(tpb′)(CO)$_2$]$^+$ **22a**.[43] Formally, **22** may be derived from **7** or **16** by the isolobal and isoelectronic substitution of the boryl BR$_2$ by the cationic carbene ligand CR$_2$$^+$. The short W–C distance in **22a** (1.94(2) Å, 94% of the sum of the covalent radii) is consistent with a strong metal-to-carbon π interaction. As expected, CR$_2$$^+$ is a much stronger acceptor than BR$_2$, as can be seen from the carbonyl stretching frequencies, which are at considerably higher wavenumbers for the cationic carbene complexes.

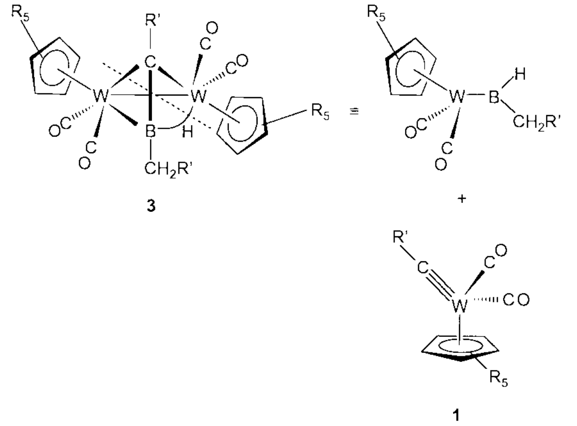


22a R = H
22b R = Me

The agostic interaction of the methylene group with the metal centre in complexes **7**, **8** and **16** is highly fluxional, involving in turn either of its two CH bonds. Only one NMR resonance is normally observed for these protons even at low temperature. Its position in the spectrum ($1.4 \leqslant \delta \leqslant 2.8$) is not indicative of an unusual bonding scheme. The corresponding carbon resonance however is at rather high field ($-30 \leqslant \delta \leqslant -11$). This signal is broad at ambient temperature, due to coupling with the quickly relaxing boron nuclei.

For complex **16a** the dynamic switch of the methylene hydrogens could be frozen out on the high field (500 MHz) NMR timescale at −90 °C. The observed multiplet structure and C–H coupling constants (97 and 129 Hz) for the methylene carbon atom are consistent with slowly (on the NMR timescale) interconverting terminal and agostic CH bonds. In any case, no sign of exchange of the two organic substituents on boron between the agostic and normal positions was observed in the NMR spectra up to 60 °C. Furthermore, no site exchange took place between the CD$_2$CH$_3$ and CH$_2$CH$_3$ groups in complex **7b-D**, even after prolonged heating in solution at 60 °C. Clearly, the barrier for exchange of the two ethyl groups must be of a considerable height.

At first sight, the μ-‘boraalkyne’ ditungsten complexes [{W(η-C$_5$R$_5$)(CO)$_2$}$_2$(μ-R′CB(H)CH$_2$R′)] **3**, obtained from the carbyne metal complexes **1** or **2** and BH$_3$·thf, and the boryl metal complexes **7**, **8** and **16** seem unrelated. However, the dinuclear products **3** may formally be considered addition products of the starting metal carbyne and a boryl metal complex [W(η-C$_5$R$_5$)(CO)$_2${B(H)(CH$_2$R′)}], which is essentially equal to **7**, **8** and **16**.



3

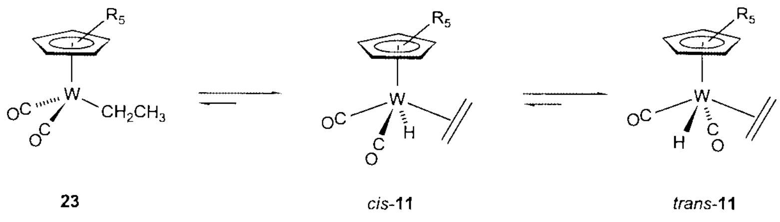
1

Decomposition of the α-boryl-η^3-benzyl metal complexes 4b and 4c

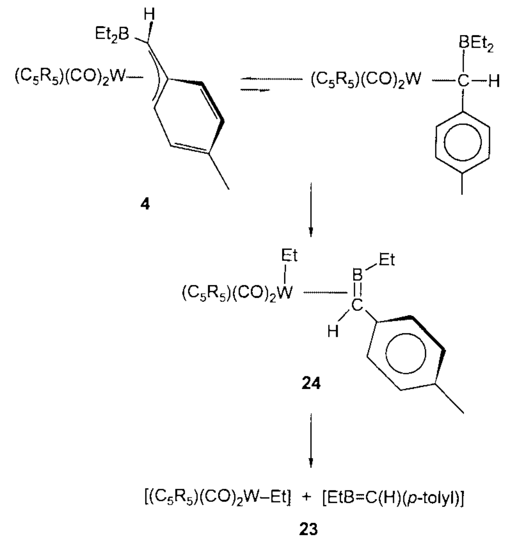
The formation of the ethylenehydridotungsten complexes **11b**, **11c** from **4b** and **4c**, respectively, in polar solvents is a clean process, according to our IR and NMR spectroscopic evidence. The only possible source of the ethylene ligand in the product **11** is an ethyl group from the boryl substituent in **4**. The unsaturated complexes [W(η-C$_5$R$_5$)(CO)$_2$(C$_2$H$_5$)] **23** are known very rapidly to β-eliminate and form *cis*-[W(η-C$_5$R$_5$)(CO)$_2$(C$_2$H$_4$)(H)], which then rearranges to give the final product **11** with a *trans* configuration of the ethylene and hydride ligands (Scheme 11).[19,44] Magnetization transfer experiments carried out with complex **11b** showed slow exchange between the hydridic and all of the olefinic proton sites.[45] This observation is consistent with an equilibrium between the ethylene hydride **11** and the unsaturated ethyl complex **23**, which may be stabilized by an additional agostic interaction.

Hence, formation of complex **23** from **4** appears to be the pathway leading to the product **11**. This could take place *via* migration of an ethyl group from boron to tungsten (β-ethyl elimination), resulting in the formation of a boraalkene in the co-ordination sphere of the metal (complex **24**, Scheme 12). Boraalkenes are very reactive and can only be isolated when stabilized by large groups or non-classical interactions.[46] Some metal π complexes of boraalkenes are known.[47] In the present case, **24** can only be a short-lived intermediate, or else it would be observable in the IR and NMR spectra. Loss of boraalkene from **24** leads to the ethyl complex **23**, which β-hydrogen eliminates to give the final product **11**. We are uncertain about the fate of the boron containing product. The postulated boraalkene EtB=CHR is expected to be highly unstable and is very unlikely to survive in solution. The dependence of the NMR spectra on the respective solvent indeed indicates further reactions.

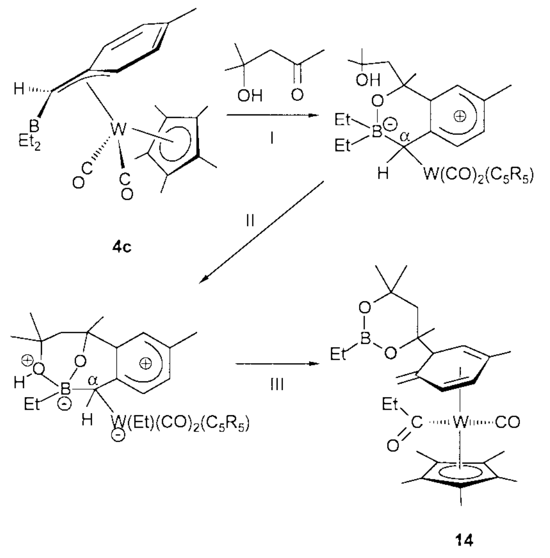
During the formation of complex **14** transfer of an ethyl group from boron to the tungsten centre must also be involved somewhere along the reaction coordinate. Formally, **14** can be derived from **4c** and two molecules of acetone. A speculative mechanism is proposed in Scheme 13. Diacetone alcohol Me$_2$C(OH)CH$_2$C(O)Me can be generated by a Lewis acid catalysed aldol condensation from acetone.[48] The reaction with **4c** could be initiated by an attack of the oxygen of the keto group at boron, followed by electrophilic addition of the carbon to the arene (I, Scheme 13). Transfer of an ethyl group from boron to the metal and subsequent addition of the hydroxyl group to the then three-co-ordinate boron (II, Scheme 13) leads to another intermediate. From there, after a proton shift from OH to C$_\alpha$, cleavage of the B–C$_\alpha$ bond, migration of the ethyl group from the metal to a carbonyl ligand and even-



Scheme 11



Scheme 12



Scheme 13

tual co-ordination of the cyclohexadiene system by the metal the final product **14** could be formed (III, Scheme 13). Alternatively, the second intermediate could be arrived at with an analogous sequence of reactions starting from **24** and diacetone alcohol.

Reaction of [W(≡CR)(η-C_5Me_5)$(CO)_2$] (R = Me 2 or $SiPh_3$ 13) with "$HBEt_2$"

Attempted hydroboration of [W(≡CMe)(η-C_5Me_5)$(CO)_2$] **2** clearly leads to hydrogenation (*i.e.* reduction) of the ethylidyne ligand by the hydroborane, most likely involving [W(η-C_5Me_5)$(CO)_2$(C_2H_5)] **23** as an intermediate, which then rapidly β-eliminates to give the final product **11b**. The partial loss of the deuterium label in the reactions with an excess of the borane, and the formation of the propene complex [W(η-C_5Me_5)$(CO)_2$(H)(C_3H_6)] **12**, can be explained by **11b** undergoing exchange of alkyl groups with the hydroborane, again probably *via* the unsaturated intermediate **23**.

Reports on reductions of carbyne metal complexes to give carbene and alkyl species are quite rare. The cationic complex $[Re(\equiv CPh)(\eta\text{-}C_5H_5)(CO)_2]^+$ can be reduced in a stepwise fashion by $HAlEt_2$ (formation of [Re(=CHPh)(η-C_5H_5)$(CO)_2$] and [Re(η-C_5H_5)$(CO)_2$(H)(CH_2Ph)]).[49] The above mentioned intramolecular hydroboration reactions of certain anionic carbaboranyl-substituted carbyne metal complexes involving a proton and a BH function of the carbaboranyl cage also lead to reduction of the carbyne moiety. However, in these products (*e.g.* complex **21**) the CH_2R group resulting from the carbyne ligand is now attached to a boron atom and separated from the metal. Hence, there are similarities to the reactions of "$HBEt_2$" with both **2** (formation of an alkylmetal complex) and **5**, **6** (formation of a CH_2R substituted borylmetal complex).

Hydrogenation of the carbyne ligand does not explain the formation of complex **11b** from [W(≡$CSiPh_3$)(η-C_5Me_5)$(CO)_2$] **13** and "$HBEt_2$". Although the isolated yield of **11b** was only slightly more than 40%, the infrared spectrum of the reaction mixture leaves little doubt about the complete conversion of **13** into **11b**. Compared to **2**, a different mechanism must be operational in this case. This is also indicated by the observation that there is no reaction below room temperature, in contrast to **2**, where smooth reaction occurs even at −40 °C. A possible explanation of the experimental facts is transfer of an ethyl group from the hydroborane to the metal, accompanied by loss of the carbyne ligand. In view of the decomposition pathway of the α-boryl-η^3-benzyl complexes **4b**, **4c**, 1,1 hydroboration of the carbyne ligand in **13** might be involved as one of the first steps (*cf.* Scheme 12).

Conclusion

We have demonstrated that hydroboration of metal-to-carbon triple bonds may follow any of several reaction channels, each leading to a different type of product. Even in the series of Fischer-type carbynemetal complexes studied in the present investigation large qualitative and quantitative differences in reactivity are apparent. It appears likely that most of the reactions are initiated by electrophilic attack of the borane at the carbyne carbon, but complex rearrangements occur, both involving the metal containing species and sometimes also the borane. In addition, hydrogenation activity of the boranes also seems to play a role. Despite their being involved in catalytic hydro- and di-boration reactions of olefins,[38] and in the stoichiometric and catalytic functionalization of alkanes,[50] relatively little is known about the reactivity of borylmetal complexes, and most of the available data stems from complexes with heteroatom substituents (O, N) on boron.[37–40] To date, the agostic boryl metal complexes **7**, **8** and **16** are the only dialkylboryl metal species known. Their stoichiometric and catalytic chemistry is presently being explored.

Experimental

General procedures

All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Alumina used as a stationary phase for column chromatography was heated to 180–200 °C under vacuum for several days, deactivated with 5% of water and then stored under nitrogen. The carbyne metal complexes [W(CMe)(η-C_5Me_5)$(CO)_2$] **2**,[51] [W($CSiPh_3$)(η-C_5Me_5)$(CO)_2$] **13**,[52] [W(CC_6H_4Me-4)(tpb′)$(CO)_2$] **5a**,[53] and [W(CPh)(tpb′)$(CO)_2$] **5c**[54] were prepared according to published procedures as were the organohydroboranes "$HBEt_2$",[55] "HB^nPr_2"[55] and "H_2BPh".[27]

NMR spectra were obtained on Bruker AC 200 and AVANCE DRX200 instruments (200.1 MHz for ^1H, 64.2 MHz for ^{11}B, 50.3 MHz for ^{13}C) and on a AVANCE DRX500 spectrometer (125.8 MHz for ^{13}C). ^1H and ^{13}C chemical shifts are reported *vs.* $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. The multiplicities of the ^{13}C resonances were routinely determined using the DEPT technique and are indicated as even (*e*) or odd (*o*). External BF_3·OEt_2 was used to reference ^{11}B chemical shifts. Mass spectra were recorded in the electron impact ionization (EI) mode at 70 eV using Finnigan MAT 8400 and JEOL JMS-700 instruments. If not stated otherwise, *m*/*z* values for the ions with the most abundant molybdenum (^{98}Mo, 24.1%) and tungsten (^{184}W, 30.7%) isotopes are given. Elemental analyses were performed locally by the microanalytical laboratory of the organisch-chemisches Institut der Universität Heidelberg and by Mikroanalytisches Labor Beller, Göttingen.

Preparations

[W(η-C_5Me_4Et)$(CO)_2${$η^3$-C(H)(BEt_2)C_6H_4Me-4}] 4c. A 1.4 ml sample (9.8 mmol) of $(HBEt_2)_2$ was slowly added to a thf (250 ml) solution of 5.0 g (10.1 mmol) of [W(CC_6H_4Me-4)(η-C_5Me_4Et)$(CO)_2$] **1c** at −50 °C. The solution was kept at −50 °C for another hour and then slowly warmed to room temperature (changing from orange to deep red). After stirring overnight all volatiles were removed under vacuum. The dark orange residue was treated with 350 ml of hexane and separated from a small amount of yellow insoluble material by filtration. Cooling of the solution to −20 °C gave 3.1 g (55%) of [W(η-C_5Me_4Et)$(CO)_2${C(H)(BEt_2)C_6H_4Me-4}] **4c** as dark orange microcrystals. ^1H NMR (C_6D_6): δ 0.79 (t, 3 H, CH_2CH_3), 1.30 (br m, 10 H, BEt_2), 1.43 (s, 6 H, CH_3), 1.47 (s, 6 H, CH_3), 1.98 (s, 3 H, CH_3-4), 2.15 (q, 2 H, CH_2CH_3), 2.75 (s, 1 H, benzyl CH), 5.48 (d, 1 H, CH), 6.26 (d, 1 H, CH), 6.63 (d, 1 H, CH) and 6.77 (d, 1 H, CH). ^{11}B-{^1H} NMR (C_6D_6): δ 51.0. Calc. for $C_{25}H_{35}BO_2W$: C, 53.41; H, 6.28. Found: C, 52.95; H, 6.00%.

[Mo(η-C_5Me_5)$(CO)_2${$η^3$-C(H)(BEt_2)C_6H_4Me-4}] 10. A 280 mg sample (2.00 mmol) of $(HBEt_2)_2$ was slowly added to a thf solution (40 ml) of 570 mg (1.46 mmol) of [Mo(CC_6H_4-Me-4)(η-C_5Me_5)$(CO)_2$] **9** at −50 °C. The mixture was slowly warmed to room temperature. It deepened in colour gradually, accompanied by a change in the IR (ν_{CO}) spectrum, which was complete at −40 °C (bands at 1982 and 1906 cm^{-1} are replaced by new bands at 1979 ([$Mo(CO)_6$]), 1931 and 1841 cm^{-1}). After warming to room temperature solvent was removed under reduced pressure. The residue was redissolved in *n*-hexane and filtered. Cooling of the filtrate to −20 °C gave a 390 mg (58%) yield of red crystalline [Mo(η-C_5Me_5)$(CO)_2${C(H)(BEt_2)-C_6H_4Me-4}] **10**. ^1H NMR (C_6D_6): δ 1.26 (br m, 10 H, BEt_2), 1.34 (s, 15 H, C_5Me_5), 1.95 (s, 3 H, Me-4), 2.89 (s, 1 H, C*H*BEt_2), 5.10 (d, 1 H, CH), 6.41 (d, 1 H, CH), 6.78 (d, 1 H, CH) and 6.82 (d, 1 H, CH). ^{13}C-{^1H} NMR (C_6D_6): δ 10.1 (C_5*Me*$_5$), 11.9 (BCH_2*C*H_3), 15.3 (br, B*C*H_2CH_3), 21.3 (Me-4), 91.6 (CH), 102.9 (*C*$_5Me_5$), 109.2 (C), 128.8 (CH), 129.7 (CH), 130.3 (CH), 136.3 (CH), 243.8 (CO) and 250.8 (CO). ^{11}B-{^1H} NMR (C_6D_6): δ 45.7. MS (EI, 70 eV): *m*/*z* (rel. intensity %) 462 (M^+), 434 ($[M - CO]^+$), 406 (100, $[M - 2CO]^+$) and 91 ($[C_7H_7]^+$). Calc. for $C_{24}H_{33}BMoO_2$: C, 62.63; H, 7.23. Found: C, 62.21; H, 5.95%.

Complex 14. A solution of 3.0 g (5.3 mmol) of [W(η-C_5Me_4Et)$(CO)_2${C(H)(BEt_2)C_6H_4Me-4}] **4c** in 50 ml of acetone was allowed to stand at room temperature for 24 h. Cooling to −20 °C afforded a small amount of yellow crystals, which were separated from the mother liquor by filtration. Reduction of the volume of the mother liquor under vacuum, followed by cooling to −20 °C, gave another crop of yellow crystalline material. This procedure was repeated four times to give a total yield of 2.3g (63%) of yellow complex **14**. ^1H NMR (thf-d_8): δ 0.52 (q, 2 H, CH_2), 0.79 (t, 3 H, CH_3), 0.80 (q, 2 H, CH_2), 0.99 (t, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.65 (br s, 2 H, CH_2), 1.78 (s, 3 H, CH_3), 1.79 (s, 3 H, CH_3), 1.84 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3), 2.15 (m, 2 H, CH_2), 2.17 (s, 3 H, CH_3), 2.74 (m, 5 H, BEt), 2.80 (d, 1 H, CH), 2.89 (d, 1 H, CH), 3.66 (dd, 1 H, CH) and 4.44 (dd, 1 H, CH). ^{13}C-{^1H} NMR (thf-d_8): δ 8.10 (*e*, CH_3), 10.38 (*e*, CH_3), 10.42 (*e*, CH_3), 10.53 (*e*, CH_3), 10.73 (*e*, CH_3), 14.12 (*e*, CH_3), 14.83 (*e*, CH_3), 15.01 (*o*, C), 18.14 (*e*, CH_3), 19.56 (*o*, CH_2), 25.32 (*o*, C), 25.71 (*o*, C), 27.84 (*e*, CH_3), 30.58 (*e*, CH_3), 33.83 (*e*, CH_3), 43.97 (*o*, CH_2), 57.46 (*e*, CH), 61.16 (*o*, CH_2), 65.88 (*e*, CH), 68.84 (*e*, CH), 80.02 (*e*, CH), 99.98 (*o*, C), 100.05 (*o*, C), 102.82 (*o*, CH_2), 129.13 (*o*, C), 130.08 (*o*, C), 150.83 (*o*, C_{acyl}) and 259.54 (*o*, CO). ^{11}B-{^1H} NMR (thf-d_8): δ 30.2. Calc. for $C_{31}H_{47}BO_4W$: C, 54.89; H, 6.98. Found: C, 55.21; H, 7.20%.

Reaction of [W(CMe)(η-C_5Me_5)$(CO)_2$] 2 with $(HBEt_2)_2$. A thf solution (40 ml) of 260 mg (0.65 mmol) of [W(CMe)(C_5Me_5)$(CO)_2$] **2** was treated with 210 mg (1.5 mmol) of $(HBEt_2)_2$ at −60 °C and slowly warmed to room temperature. A change from yellow to golden-yellow took place around −40 °C, accompanied by a change in the IR (ν_{CO}) spectrum (bands at 1972 and 1893 cm^{-1} are replaced by two new bands at 1957 and 1876 cm^{-1}). After warming to room temperature all volatiles were removed under reduced pressure. The remaining dark yellow oil was redissolved in *n*-hexane, filtered and cooled to −20 °C. The product [W(η-C_5Me_5)$(CO)_2$(H)(C_2H_4)] **11b** (160 mg, 62%) precipitated as yellow microcrystals.

Reaction of [W($CCD_{3-n}H_n$)(η-C_5Me_5)$(CO)_2$] 2-D (*n* = 0 or 1) with $(HBEt_2)_2$. *(a) Stoichiometric ratio metal carbyne: hydride ≈ 1 : 1.* A thf solution (30 ml) of 287 mg (0.71 mmol) of [W($CCD_{3-n}H_n$)(η-C_5Me_5)$(CO)_2$] **2-D** (*n* = 0, 86%; *n* = 1, 14%) was cooled to −25 °C and treated with 46 mg (0.66 mmol hydride) of $(HBEt_2)_2$. The course of the reaction was monitored by IR spectroscopy. After addition of 37 mg (0.53 mmol hydride) of $(HBEt_2)_2$ the reaction was complete, and the solution changed from yellow to brownish yellow. After warming to room temperature all volatiles were removed under reduced pressure and collected in a low temperature trap. The brown residue was dried in a stream of argon to give 290 mg (100%) of [W($C_2H_{2+n}D_{3-n}$)(η-C_5Me_5)$(CO)_2$] **11b-D**. ^1H NMR (thf-d_8): δ 1.99 (s, 15 H, C_5Me_5), 1.46 (br s, 1.2 H, $C_2H_{2+n}D_{3-n}$) and −4.98 (m, 0.6 H, $J(^{183}WH)$ = 30 Hz, WH). ^{13}C NMR (thf-d_8): δ 10.8 (q, C_5*Me*$_5$), 27.7 (br m, $C_2H_{2+n}D_{3-n}$), 102.3 (s, *C*$_5Me_5$) and 219.3 (CO). The contents of the cooling trap gave an ^{11}B-{^1H} NMR resonance at δ 54.

(b) With excess of $(HBEt_2)_2$. A thf solution (20 ml) of 155 mg (0.38 mmol) of [W(CCH_nD_{3-n}(η-C_5Me_5)$(CO)_2$] **2-D** (*n* = 0, 86%; *n* = 1, 14%) was cooled to −50 °C and treated with 90 mg (1.29 mmol hydride) of $(HBEt_2)_2$. After slow warming to room temperature most of the solvent was removed under reduced pressure to give a red-brown oil. Hexane (1 ml) was added and the mixture cooled to −20 °C. The brownish yellow precipitate was separated by filtration and dried in a stream of argon to give 80 mg (53%) of microcrystalline complex **11b-D**. ^1H NMR (CD_2Cl_2): δ 1.99 (s, 15 H, C_5Me_5), 1.50 (s, br, 2.4 H, $C_2H_{2+n}D_{3-n}$) and −4.99 (br s, 0.75 H, W–H).

Table 3 Details of the crystal structure determinations of complexes **14**, [W(CO)$_2$(tpb′)(BEt$_2$)] **7b**, [W(tpb′)(CO)$_2${B(Ph)R}] (R = C$_6$H$_5$Me-4 **16a** or Me **16b**)

	14	**7b**	**16a**	**16b**
Formula	$C_{31}H_{47}BO_4W$	$C_{21}H_{32}B_2N_6O_2W$	$C_{41}H_{46}B_2N_6O_2W$	$C_{34}H_{41}B_2N_6O_2W$
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/a$	$P\bar{1}$
a/Å	8.829(14)	14.425(7)	19.664(11)	10.308(8)
b/Å	12.33(2)	10.168(6)	8.005(5)	12.342(8)
c/Å	14.24(2)	16.623(8)	26.158(16)	13.508(10)
α/°	103.00(13)			84.29(6)
β/°	97.29(13)	92.35(4)	95.63(5)	81.00(6)
γ/°	97.15(13)			81.62(6)
V/Å^3	1480(4)	2436(2)	4098(4)	1674(2)
Z	2	4	4	2
M_r	678.35	606.00	860.31	771.20
μ(Mo-Kα)/mm^{-1}	3.94	4.77	2.86	3.49
Data collection temperature/°C	−55	−70	−70	−70
Reflections measured unique	6129	6418	7224	9760
observed [$I \geqslant 2\sigma(I)$]	5762	4136	4645	8813
R (obs. reflections only)	0.026	0.049	0.058	0.031
$wR2$ (all reflections)	0.075	0.112	0.141	0.077

Reaction of [W(CMe)(η-C$_5$Me$_5$)(CO)$_2$] 2 with (HB″Pr$_2$)$_2$. *(a) Stoichiometric ratio metal carbyne : hydride ≈ 1 : 1.* (HB″Pr$_2$)$_2$ was added dropwise to a thf solution (20 ml) of 175 mg (0.43 mmol) of [W(CMe)(η-C$_5$Me$_5$)(CO)$_2$] **2** at room temperature. The course of the reaction was monitored by IR spectroscopy. After addition of 71 mg (0.72 mmol hydride) of (HB″Pr$_2$)$_2$ the reaction was complete. ^{11}B NMR analysis of the mixture gave a resonance at δ 54. All volatiles were removed under reduced pressure. The brown residue was dried in a stream of argon to give 170 mg (100%) of [W(η-C$_5$Me$_5$)(CO)$_2$(H)(C$_2$H$_4$)] **11b** (characterization by ^{1}H NMR and IR spectroscopy).

(b) With an excess of (HB″Pr$_2$)$_2$. A hexane solution (20 ml) of 110 mg (0.27 mmol) of [W(CMe)(η-C$_5$Me$_5$)(CO)$_2$] **2** was treated with 150 mg (1.53 mmol) of (HB″Pr$_2$)$_2$ at −10 °C. The solution changed from yellow to yellow-brown. After slow warming to room temperature the volume was reduced under vacuum to 5 ml. Cooling to −20 °C resulted in the precipitation of a yellow crystalline solid, which was collected, washed with cold (−50 °C) hexane and dried under vacuum to give 40 mg of a 7.5 : 1 mixture of **11b** and [W(η-C$_5$Me$_5$)(CO)$_2$(H)(C$_2$H$_3$CH$_3$)] **12**. IR (hexane): ν_{CO} 1967 (s + sh) and 1891 (s + sh) cm^{-1}. **11b**: ^{1}H NMR (C$_6$D$_6$) δ 1.58 (s, C$_5$Me$_5$), 1.48 (br s, C$_2$H$_4$) and −4.59 (m, W–H); ^{13}C-{^{1}H} NMR (C$_6$D$_6$) δ 10.7 (C$_5$*Me*$_5$), 27.5 (C$_2$H$_4$), 101.5 (*C*$_5$Me$_5$) and 219.3 (CO). **12**: ^{1}H NMR (C$_6$D$_6$) δ 1.83 (m, C$_2$H$_3$CH$_3$), 1.59 (s, C$_5$Me$_5$) and −4.93 (m, W–H); ^{13}C-{^{1}H} NMR (C$_6$D$_6$) δ 10.7 (C$_5$*Me*$_5$), 22.4 (C$_2$H$_3$*C*H$_3$), 32.0 (*C*$_2$H$_3$CH$_3$), 40.2 (*C*$_2$H$_3$CH$_3$), 102.5 (*C*$_5$Me$_5$), carbonyl C not observed. MS (EI, 70 eV): *m*/*z* (relative intensity, %) 404 (18, **11b**, *M*$^+$) and 418 (5, **12**, *M*$^+$).

Reaction of [W(CSiPh$_3$)(η-C$_5$Me$_5$)(CO)$_2$] 13 with (HBEt$_2$)$_2$. A 85 mg sample (1.21 mmol of hydride) of (HBEt$_2$)$_2$ was added to a thf solution (40 ml) of 180 mg (0.28 mmol) of [W(CSiPh$_3$)(η-C$_5$Me$_5$)(CO)$_2$] **13** at −50 °C. The reaction was monitored by IR spectroscopy. It started around 15 °C and the solution changed from yellow to yellow-brown. All volatiles were removed under reduced pressure, the residue was washed with a little cold (−20 °C) hexane and dried under vacuum to give 49 mg (43%) of complex **11b** (characterization by ^{1}H NMR and IR spectroscopy).

Reaction of [W(η-C$_5$Me$_5$)(CO)$_2$(C$_2$H$_{2+n}$D$_{3-n}$)] 11b-D with (HBEt$_2$)$_2$. A thf solution (20 ml) of [W(η-C$_5$Me$_5$)(CO)$_2$(C$_2$H$_{2+n}$D$_{3-n}$)] **11b-D** ($n = 0$, 86%; $n = 1$, 14%) was treated with 91 mg (1.30 mmol) of (HBEt$_2$)$_2$ at ambient temperature. The IR (ν_{CO}) spectrum of this mixture did not change over 2 h. Removal of all volatiles under vacuum gaves 40 mg (100%) of a yellow-brown solid which was analysed by mass spectroscopy.

Preparation of [Mo(tpb′)(CO)$_2${η^2-B(Et)CH$_2$C$_6$H$_4$Me-4}] 8. A 770 mg (5.5 mmol) sample of (HBEt$_2$)$_2$ was added dropwise to a solution of 770 mg (1.4 mmol) of [Mo(CC$_6$H$_4$-Me-4)(tpb′)(CO)$_2$] **6** at ambient temperature. Heating the solution to 60 °C for 15 min resulted in a change from orange to yellow. After cooling solvent was removed under vacuum. The pale yellow residue was washed several times with hexane–toluene (10 : 1) and dried under vacuum to give 590 mg (71%) of [Mo(tpb′)(CO)$_2${B(Et)CH$_2$C$_6$H$_4$Me-4}] **8**. MS (EI, 70 eV): *m*/*z* (relative intensity, %) 594 (7, *M*$^+$), 566 (12, [*M* − CO]$^+$) and 538 (20, [*M* − 2CO]$^+$). Calc. for C$_{27}$H$_{36}$B$_2$-MoN$_6$O$_2$: C, 54.58; H, 6.11; N, 14.4. Found: C, 54.00; H, 6.08; N, 13.70%.

Preparation of [W(tpb′)(CO)$_2${η^2-B(Et)CH$_2$Me}] 7b. A 230 mg (1.64 mmol) sample of (HBEt$_2$)$_2$ was added dropwise to a toluene solution (10 ml) of 385 mg (0.68 mmol) [W(CMe)-(tpb′)(CO)$_2$] **5b**. The mixture was stirred for 3 hours at ambient temperature. The precipitated product was collected, washed with a little pentane and dried under vacuum. A second product fraction can be obtained from the mother liquor after cooling to −20 °C. Combined yield 345 mg (84%) of pale yellow [W(tpb′)(CO)$_2${B(Et)CH$_2$Me}] **7b**. MS (EI, 70 eV): *m*/*z* (relative intensity, %) 606 (100, *M*$^+$), 578 (9, [*M* − CO]$^+$) and 550 (51, [*M* − 2CO]$^+$). Calc. for C$_{21}$H$_{32}$B$_2$N$_6$O$_2$W: C, 41.62; H, 5.32; N, 13.87. Found: C, 41.49; H, 5.39; N, 13.87%.

[W(tpb′)(CO)$_2${η^2-B(Ph)CH$_2$Me}] 16b. A 370 mg (2.06 mmol) sample of (H$_2$BPh)$_2$ was added to a toluene solution (40 ml) of 2.0 g (3.54 mmol) of [W(CMe)(tpb′)(CO)$_2$] **2** at ambient temperature. The colour of the solution deepened within a few seconds. Solvent was removed under reduced pressure, the residue washed with five 20 ml portions of pentane and dried under vacuum to give 2.03 g (88%) of yellow [W(tpb′)(CO)$_2$-{B(Ph)CH$_2$Me}] **16b**. MS (EI, 70 eV): *m*/*z* (relative intensity, %) 654 (5, *M*$^+$) and 598 (3, [*M* − 3CO]$^+$). Calc. for C$_{25}$H$_{32}$B$_2$-N$_6$O$_2$W: C, 45.91; H, 4.93; N, 12.84. Found: C, 44.03; H, 5.05; N, 12.22%.

Crystal structure determinations

Single crystals of the agostic boryl metal complexes were obtained from solutions in benzene (**7b**; a solution saturated at 50 °C was slowly cooled to 10 °C) or mixtures of toluene, benzene and methylene chloride (**16a**·toluene·0.5 benzene, at −20 °C; **16b**·1.5 C$_6$H$_6$, solvent was slowly evaporated at ambient temperature). Complex **14** crystallized from an acetone solution of **4c** after several days at −20 °C. Crystal data are compiled in Table 3. Intensity data were collected on a Siemens-

Stoe AED2 four circle diffractometer at low temperature. The structures were solved by direct methods, and refined by full matrix least squares based on F^2 using all measured unique reflections. Most non-hydrogen atoms were given anisotropic displacement parameters. Some of the hydrogen atoms were localized in Fourier difference syntheses and refined isotropically. The remainder were input in calculated positions. One of the solvent molecules in the structure of **16a** was strongly disordered and could not be identified with certainty (toluene or benzene). It was refined as half a benzene with isotropic displacement parameters and all carbon–carbon bond lengths restrained to be equal. The calculations were performed using the programs SHELXS 86 and SHELXL 97.[56] Graphical representations were drawn with ORTEP II (anisotropic displacement ellipsoids scaled to 30% probability).[57]

CCDC reference number 186/2150.

See http://www.rsc.org/suppdata/dt/b0/b004256k/ for crystallographic files in .cif format.

Acknowledgements

This work was supported by the Sonderforschungsbereich 247 der Universität Heidelberg and the Fonds der Chemischen Industrie. The award of a Heisenberg Fellowship to H. W. is gratefully acknowledged.

References and notes

1 E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem.*, 1973, **85**, 618; E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem.*, 1974, **86**, 651; E. O. Fischer, *Adv. Organomet. Chem.*, 1976, **14**, 1.

2 M. A. Gallop and W. R. Roper, *Adv. Organomet. Chem.*, 1986, **25**, 121.

3 R. R. Schrock, *Acc. Chem. Res.*, 1986, **19**, 342.

4 W. E. Buhro and M. H. Chisholm, *Adv. Organomet. Chem.*, 1987, **27**, 311.

5 H. P. Kim and R. Angelici, *Adv. Organomet. Chem.*, 1987, **27**, 51.

6 H. Fischer, P. Hofmann, F. R. Kreissl, R. R. Schrock, U. Schubert and K. Weiss, *Carbyne Complexes*, VCH, Weinheim, 1988.

7 W. A. Nugent and J. A. Mayer, *Metal–Ligand Multiple Bonds*, Wiley & Sons, New York, 1988.

8 A. Mayr, *Comments Inorg. Chem.*, 1990, **10**, 227.

9 A. Mayr and H. Hoffmeister, *Adv. Organomet. Chem.*, 1991, **32**, 227.

10 A. Mayr and C. M. Bastos, *Prog. Inorg. Chem.*, 1992, **40**, 1.

11 P. F. Engel and M. Pfeffer, *Chem. Rev.*, 1995, **95**, 2281.

12 M. Elian, M. M. L. Chen, D. M. P. Mingos and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148; R. Hoffman, *Angew. Chem.*, 1982, **94**, 725; T. A. Albright, *Tetrahedron*, 1982, **38**, 1339.

13 (*a*) F. G. A. Stone, *Angew. Chem.*, 1984, **96**, 85; (*b*) F. G. A. Stone, *Adv. Organomet. Chem.*, 1990, **31**, 53; (*c*) S. A. Brew and F. G. A. Stone, *Adv. Organomet. Chem.*, 1993, **35**, 135.

14 H. C. Brown, *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, 1972.

15 H. Wadepohl, U. Arnold, H. Pritzkow and A. Wolf, in *Advances in Boron Chemistry*, ed. W. Siebert, Special Publication No. 201, The Royal Society of Chemistry, Cambridge, 1997, p. 385.

16 (*a*) G. A. Carriedo, G. P. Elliot, J. A. K. Howard, D. D. Lewis and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1984, 1585; (*b*) D. Barratt, S. J. Davies, G. P. Elliot, J. A. K. Howard, D. B. Lewis and F. G. A. Stone, *J. Organomet. Chem.*, 1987, **325**, 185.

17 H. Wadepohl, G. P. Elliott, H. Pritzkow, F. G. A. Stone and A. Wolf, *J. Organomet. Chem.*, 1994, **482**, 243.

18 H. Wadepohl, U. Arnold and H. Pritzkow, *Angew. Chem.*, 1997, **109**, 1009.

19 R. J. Kazlauskas and M. S. Wrighton, *J. Am. Chem. Soc.*, 1982, **104**, 6005.

20 C. G. Kreiter, *Angew. Chem.*, 1968, **80**, 402.

21 P. Hofmann, in ref. 6, p. 59.

22 G. Frenking, S. Dapprich, A. W. Ehlers, W. Otto and S. F. Vyboishchikov, in *Metal–Ligand Interactions*, eds. N. Russo and D. R. Salahub, Kluwer, Dordrecht, 1996, p. 185.

23 J. C. Jeffery, J. C. V. Laurie, I. Moore and F. G. A. Stone, *J. Organomet. Chem.*, 1983, **258**, C37; J. A. K. Howard, J. C. Jeffery, J. C. V. Laurie, I. Moore, F. G. A. Stone and A. Stringer, *Inorg. Chim. Acta*, 1985, **100**, 23; J. A. K. Howard, J. C. Jeffery, S. Li and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1992, 627; J. C. Jeffery, S. Li and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1992, 635.

24 M. Bottrill, M. Green, A. G. Orpen, D. R. Saunders and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1989, 511.

25 N. J. van Eikema Hommes and P. von R. Schleyer, *J. Org. Chem.*, 1991, **56**, 4074.

26 R. Köster, G. Bruno and P. Binger, *Liebigs Ann. Chem.*, 1961, **644**, 1.

27 (*a*) E. Wiberg, J. E. F. Evans and H. Nöth, *Z. Naturforsch., Teil B*, 1958, **13**, 263; (*b*) B. M. Mikhailov and V. A. Dorokov, *Dokl. Akad. Nauk SSSR*, 1961, **136**, 356; (*c*) F. G. Thorpe, G. M. Pickles and J. C. Podesta, *J. Organomet. Chem.*, 1977, **128**, 305; (*d*) T. E. Cole, R. K. Bakshi, M. Srebnik, B. Singaram and H. C. Brown, *Organometallics*, 1986, **5**, 2303.

28 U. Arnold, H. Pritzkow and H. Wadepohl, unpublished work.

29 M. J. Winter, *Polyhedron*, 1989, **8**, 1583; H. Adams, N. A. Bailey, M. J. Winter and S. Woodward, *J. Organomet. Chem.*, 1991, **418**, C39.

30 B. Wrackmeyer, *J. Organomet. Chem.*, 1976, **117**, 313; R. Contreras and B. Wrackmeyer, *Spectrochim. Acta, Part A*, 1982, **38**, 941.

31 M. R. Smith III, *Prog. Inorg. Chem.*, 1999, **48**, 505.

32 A. Davison and W. C. Rode, *Inorg. Chem.*, 1967, **6**, 2124; J. W. Faller and M. Incorvia, *Inorg. Chem.*, 1968, **7**, 840.

33 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395; M. Brookhart, M. L. H. Green and L. L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.

34 J. F. Hartwig and S. R. De Gala, *J. Am. Chem. Soc.*, 1994, **116**, 3661.

35 P. R. Rablen, J. F. Hartwig and S. P. Nolan, *J. Am. Chem. Soc.*, 1994, **116**, 4121.

36 H. Braunschweig, B. Ganter, M. Koster and T. Wagner, *Chem. Ber.*, 1996, **129**, 1099.

37 G. Schmid, *Angew. Chem.*, 1970, **82**, 920.

38 H. Wadepohl, *Angew. Chem.*, 1997, **109**, 2547.

39 G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685.

40 H. Braunschweig, *Angew. Chem.*, 1998, **110**, 1882.

41 D. G. Musaev and K. Morokuma, *J. Phys. Chem.*, 1996, **100**, 6509; Q. Cui, D. G. Musaev and K. Morokuma, *Organometallics*, 1998, **17**, 742.

42 S. Sakaki and T. Kikuno, *Inorg. Chem.*, 1997, **36**, 226.

43 S. G. Feng, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1990, **112**, 8192; S. G. Feng, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1992, *114*, 2951.

44 H. G. Alt and M. E. Eichner, *Angew. Chem.*, 1982, **94**, 77; K. A. Mahmoud, A. J. Rest, H. G. Alt, M. E. Eichner and B. M. Jansen, *J. Chem. Soc., Dalton Trans.*, 1984, 175; K. A. Mahmoud, A. J. Rest and H. G. Alt, *J. Chem. Soc., Dalton Trans.*, 1984, 187; G. K. Yang, K. S. Peters and V. Vaida, *J. Am. Chem. Soc.*, 1986, **108**, 2511; F. P. A. Johnson, C. M. Gordon, P. M. Hodges, M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1991, 833.

45 U. Arnold and H. Wadepohl, unpublished work.

46 P. Jutzi, *Angew. Chem.*, 1975, **87**, 269; A. Berndt, *Angew. Chem.*, 1993, **105**, 1034; J. J. Eisch, *Adv. Organomet. Chem.*, 1996, 355.

47 D.-Y. Jan and S. G. Shore, *Organometallics*, 1987, **6**, 428; S. Helm and H. Nöth, *Angew. Chem.*, 1988, **100**, 1378; S. Channareddy, G. Linti and H. Nöth, *Angew. Chem.*, 1990, **102**, 222; D. P. Workman, H.-B. Deng and S. G. Shore, *Angew. Chem.*, 1990, **102**, 328.

48 H. H. Emons and K. Pollmer, *Z. Anorg. Allg. Chem.*, 1981, 473, 208.

49 E. O. Fischer and A. Frank, *Chem. Ber.*, 1978, **111**, 3740.

50 K. M. Waltz and J. F. Hartwig, *Science*, 1997, **277**, 211; H. Chen and J. F. Hartwig, *Angew. Chem.*, 1999, **111**, 3597; K. M. Waltz, C. N. Muhoro and J. F. Hartwig, *Organometallics*, 1999, **18**, 3383.

51 E. O. Fischer, F. J. Gammel, J. O. Besenhard, A. Frank and D. Neugebauer, *J. Organomet. Chem.*, 1980, **191**, 261.

52 H. Wadepohl, U. Arnold, H. Pritzkow, M. J. Calhorda and L. F. Veiros, *J. Organomet. Chem.*, 1999, **587**, 233.

53 J. C. Jeffery, F. G. A. Stone and G. K. Williams, *Polyhedron*, 1991, **10**, 215.

54 J. H. Davis, Jr., C. M. Lukehart and L. Sacksteder, *Organometallics*, 1987, **6**, 50.

55 H. I. Schlesinger, L. Horvitz and A. B. Burg, *J. Am. Chem. Soc.*, 1936, **58**, 407.

56 SHELXS 86, G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; SHELXL 97, G. M. Sheldrick, Universität Göttingen, 1997.

57 ORTEP II, C. K. Johnson, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.