The *cis*-Insertion of Diphenylacetylene into an *exo*-Polyhedral Boron–Hydrogen Bond of a Molybdenacarbaborane Cage

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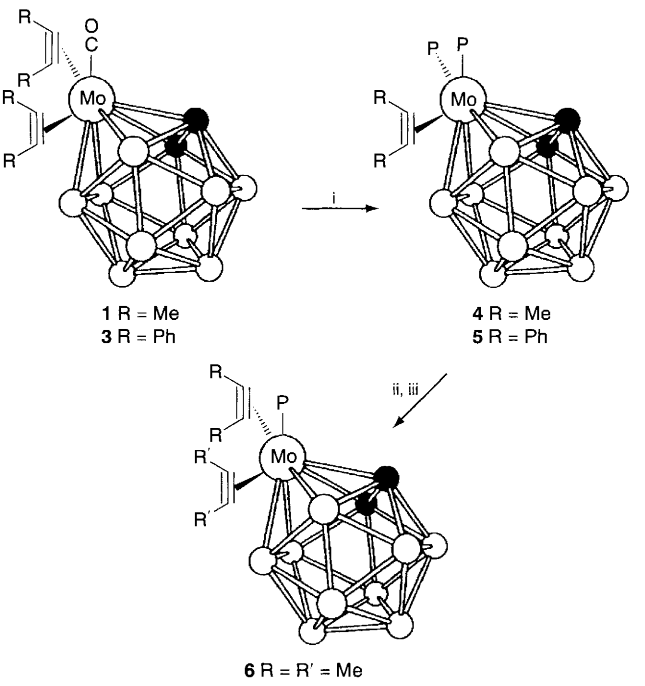
The η^2(4e)-alkyne bis(trimethylphosphite) substituted complexes [*closo*-3-(η^2-alkyne)-3,3-{P(OMe)$_3$}$_2$ 31,2-$MoC_2B_9H_{11}$] react with alkynes to form either monophosphite bis(alkyne) or mixed alkyne complexes [*closo*-3,3-(η^2-alkyne)(η^2-alkyne)-3-{P(OMe)$_3$}-3,1,2-$MoC_2B_9H_{11}$]; however, an attempt to extend the reaction to the bis(diphenylacetylene) system resulted in a novel *cis*-insertion of the alkyne into an *exo*-polyhedral B–H bond, which is explained by a bimetallic reaction pathway.

Recently,[1–3] *closo*-molybdenacarbaborane complexes have been characterised which incorporate η^2(4e)- and η^2(3e)-bonded alkyne ligands. Because of the isolobal relationship[3,4] between *nido*-$C_2B_9H_{11}{}^{2-}$ and $C_5H_5{}^-$ it might, therefore, be expected that the chemistry of bis(alkyne) complexes such as [*closo*-3,3-(η^2-MeC_2Me)-3-(CO)-3,1,2-$MoC_2B_9H_{11}$] **1** would parallel that of the cationic cyclopentadienyl analogue [Mo(η^2-MeC_2Me)$_2$(CO)(η-C_5H_5)][BF_4] **2**; a type of compound which has played a pivotal role in our studies[6,7] of the chemistry of η^2(4e)-bonded alkyne ligands. We have found, however, in exploring the chemistry of **1** and its diphenylacetylene analogue **3**, that there are significant differences in reaction chemistry; moreover, X-ray crystallographic studies show that *cis*-insertion of diphenylacetylene into an *exo*-polyhedral B–H bond can intervene.

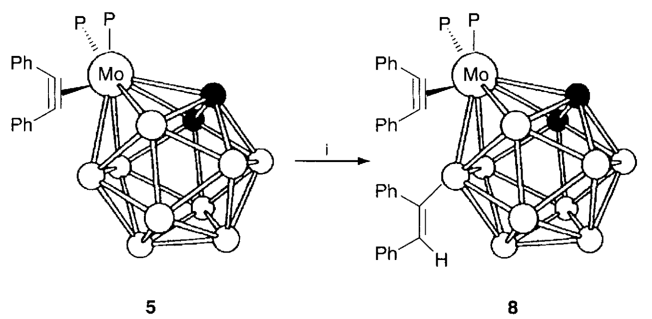
When a solution of **1** and 2 mol equiv. of P(OMe)$_3$ in dichloromethane is heated under reflux for 12 h the colour changes from yellow to blue, and on column chromatography (alumina) the η^2(4e)-but-2-yne bis(trimethylphosphite) complex **4**† (Scheme 1) is isolated as a relatively air-stable blue crystalline compound in 83% yield. A similar reaction between trimethylphosphite and **3** affords green crystals of **5** (55% yield). Thus, in these reactions there is a parallel with cationic cyclopentadienyl chemistry.[7,8] However, there is no parallel to the reaction which occurs when a mixture of **4** and an excess of but-2-yne in toluene contained in a sealed tube is heated to 90 °C. There is an immediate change in colour from blue to yellow, and on cooling bright yellow crystals of the mono-trimethylphosphite bis(but-2-yne) complex **6** are obtained. This reaction can also be extended to the synthesis of complexes with two different alkynes. For example, **4** reacts with diphenylacetylene, or **5** reacts with but-2-yne to give in excellent yield (73 and 90% respectively) bright yellow crystals of the mixed bis(alkyne)complex **7**.



Scheme 1 P = P(OMe)$_3$, ○ = BH, ● = CH. *Reagents and conditions*: i, + P(OMe)$_3$; ii, + R′C_2R′, toluene, 90 °C, iii, –P(OMe)$_3$.

An even more unusual reaction occurred when an attempt was made to make the analogous mono-phosphite bis(diphenylacetylene)complex [*closo*-3,3-(η^2-PhC_2Ph)$_2$-3-{P(OMe)$_3$}-3,1,2-$MoC_2B_9H_{11}$] by treating **5** with PhC_2Ph. On heating the reactants (12 h, 90 °C, toluene) the expected change in colour did not occur, but on chromatographic workup (alumina) a new green crystalline complex **8** (Scheme 2) was isolated (76% yield). Elemental analysis and NMR spectroscopy† showed that **8** carried two P(OMe)$_3$ ligands, and that two diphenylacetylene molecules had been incorporated into the product. The structural identity of **8** was revealed by a single-crystal X-ray diffraction study.‡ As is shown in Fig. 1 complex **8** contains a 3,1,2-$MoC_2B_9H_{11}$ cage, in which there are two trimethylphosphite ligands and one diphenylacetylene coordinated onto the molybdenum centre. The alkyne, which is η^2(4e)-bonded, is orientated in the solid state such that the C–C bond lies parallel to one of the Mo–P vertices. Importantly, the second diphenylacetylene has undergone a formal *cis*-insertion into an *exo*-polyhedral B–H bond thus forming an 8-substituted *cis*-BC(Ph)=C(Ph)H group.

Although there are a number of reported examples[9,10] of alkylidene and alkylidyne ligands formally 'inserting' into an *exo*-polyhedral B–H bond of a metallacarbaborane there is only one example[3] of the 'insertion' of an alkyne,§ and this involves the rearrangement of [*closo*-1,2-Me_2-3,3-(η^2-Me_3SiC_2H)$_2$-3-(CO)-3,1,2-$MoC_2B_9H_9$] into the *trans*-vinyl substituted cage [*closo*-1,2-Me_2-3,3-(η^2-Me_3SiC_2H)-3-(CO)-8,3-{σ: η^2-*trans*-CH=C(SiMe$_3$)H}-3,1,2-$MoC_2B_9H_9$]. However, this reaction has been shown[3] to involve the initial rearrangement of η^2-bonded Me_3SiC_2H into the vinylidene Mo=C=C(SiMe$_3$)H, and can therefore be viewed as a further example of the insertion of an alkylidene into a B–H bond. Clearly, the formation of the complex **8** is unlikely to involve an analogous phenyl migration to give Mo=C=CPh$_2$, and even if this was the case it would then



Scheme 2 P = P(OMe)$_3$, ○ = BH, ● = CH. *Reagents and conditions*: i, + PhC_2Ph, toluene, 90 °C.

be difficult to explain the regioselective formation of a *cis*-BC(Ph)=C(Ph)H group.

The earlier work of Stone and coworkers[9,10] together with the observations reported here lead us to suggest that the formation of **8** requires the involvement of two metal centres. Thus, it is proposed that in solution at 90 °C the complex **5** is in equilibrium with free $P(OMe)_3$ and the 16e species [*closo*-3-(η^2-PhC_2Ph)-3-{$P(OMe)_3$}-3,1,2-$MoC_2B_9H_{11}$], which is stabilised by dimerisation assisted by the establishment of an agostic B(μ-H)Mo interaction.[11,12]¶ As is shown in Scheme 3 the resulting dimer **A** contains two diphenylacetylene ligands, η^2(4e)- and η^2(2e)-bonded to adjacent molybdenum centres. Complete transfer of the hydrogen, which is involved in the original agostic interaction to the second metal centre, then affords intermediate **B**, in which there is an η^2(2e)-bonded alkyne adjacent to a Mo–H bond. Coordination of trimethylphosphite to this metal centre would then be expected to promote migration (**B**→**C**) of the hydrogen from the metal to the coordinated alkyne thus generating **C**, in which there are now boron–molybdenum and *cis*-MoC(Ph)=C(Ph)H fragments in a relative *cis*-configuration to each other. The boron–vinyl moiety present in the final product **8** can then be generated by a reductive elimination step (**C**→**D**), which is followed by disproportionation of **D** in the presense of diphenylacetylene to give **5** and **8**. In this way all of complex **5** is converted into **8** *via* a reaction sequence which involves the interplay of two metal centres, and where the *cis*-vinyl group is created at one centre before transfer to a cage boron. Thus, the overall effect is to achieve a formal hydroboration of an alkyne.

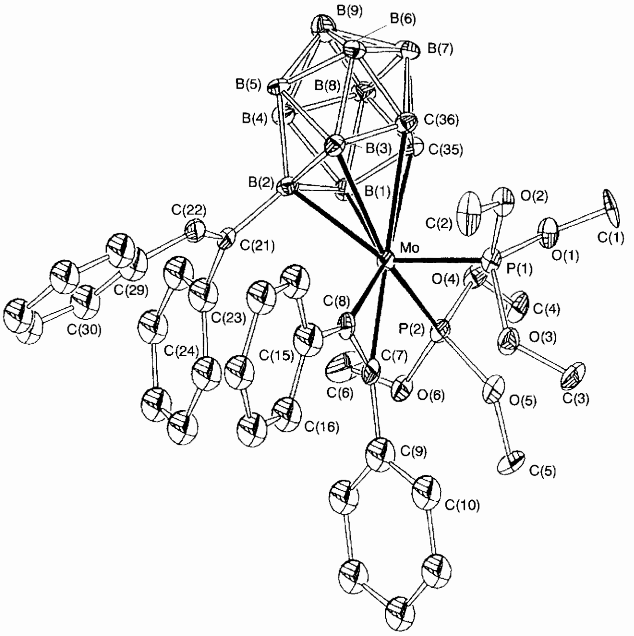
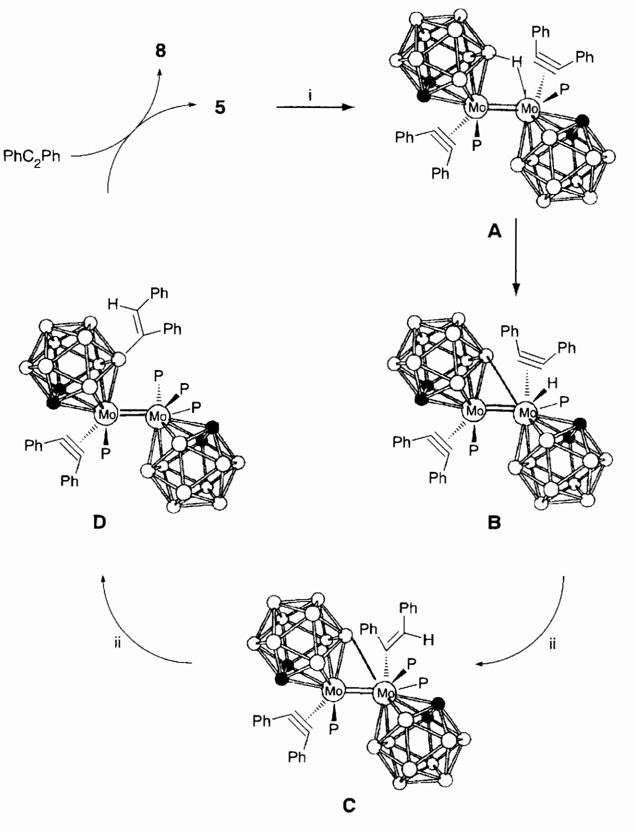


Fig. 1 Molecular structure of **8**. Pertinent bond lengths (Å) and angles (°) are as follows: Mo–C(35) 2.407(8), Mo–C(36) 2.466(8), Mo–B(1) 2.380(8), Mo–B(2) 2.441(8), Mo–B(3) 2.464(9), Mo–P(1) 2.427(4), Mo–P(2) 2.398(4), Mo–C(7) 2.046(8), Mo–C(8) 2.026(8), C(7)–C(8) 1.333(9), B(2)–C(21) 1.582(10), C(21)–C(22) 1.362(9), P(1)–Mo–P(2)84.3(2), C(7)–C(8)–C(15) 132.9(5), C(8)–C(7)–C(9) 136.4(5).



Scheme 3 P = $P(OMe)_3$, ○ = BH, ● = CH. *Reagents and conditions*: i, −$P(OMe)_3$, dimerisation; ii, +$P(OMe)_3$.

With this new insight it is suggested that related dinuclear pathways are also involved in the reactions observed by Stone and coworkers where there is an apparent 'insertion' of alkylidene, alkylidyne[9,10] and also norbornadiene[13] into a *exo*-BH bond of a variety of metallacarbaboranes.

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Footnotes

† *Selected NMR spectroscopic data* for compound **4**: ^1H (CD_2Cl_2), δ 3.52 [vt, 18 H, *N*(PH) 10.6 Hz, $POCH_3$], 3.05 [t, 6 H, *J*(PH) 1.3 Hz, $\equiv CCH_3$], 2.79 (br s, 2 H, cage-CH); $^{11}B\{^1H\}(CD_2Cl_2)$, −0.7 (s, 1 B), −7.6 (s, 2 B), −9.8 (s, 3 B), −17.1 (s, 2 B), −20.1 (s, 1 B); $^{13}C\{^1H\}(CD_2Cl_2)$, δ 222.0 (br s, $\equiv CCH_3$), 53.2 (s, OCH_3), 46.8 (br s, cage-C), 21.3 (s, CCH_3); $^{31}P\{^1H\}(CD_2Cl_2)$, δ 180.6 (s). Compound **5**: $^1H(CD_2Cl_2)$, δ 7.45–7.29 (m, 10 H, Ph), 3.54 [vt, 18 H, *N*(PH) 10.6 Hz, $POCH_3$], 3.13 (br s, 2 H, cage-CH); $^{11}B\{^1H\}(CD_2Cl_2)$, δ −1.2 (s, 1 B), −8.7 (s, 3 B), −11.3 (s, 2 B), −18.1 (s, 2 B), −22.5 (s, 1 B); $^{13}C\{^1H\}$ (CD_2Cl_2), δ 220.7 [t, *J*(PC) 16.3 Hz, C≡C], 142.0–124.6 (Ph), 53.7 (s, OCH_3), 47.9 (br s, cage-C); $^{31}P\{^1H\}(CD_2Cl_2)$, δ 174.7 (s). Compound **6**: $^1H(CD_2Cl_2)$, δ 4.36 [d, 9 H, *J*(PH) 10.4 Hz, $POCH_3$], 3.30 (s, 6 H, $\equiv CH_3$), 2.86 (s, 6 H, $\equiv CH_3$), 2.40 (br s, 2 H, cage-CH); $^{11}B\{^1H\}(CD_2Cl_2)$, δ −2.2 (s, 1 B), −5.3 (s, 1B), −9.4 (s, 2 B), −11.8 (s, 1 B), −12.4 (s, 1 B), −16.8 (s, 2 B), −21.4 (s, 1 B); $^{13}C\{^1H\}(CD_2Cl_2)$, δ 180.7 [d, *J*(PC) 8.1 H_2, C≡C], 154.1 [d, *J*(PC) 29.8 Hz, C≡C], 53.8 (s, OCH_3), 51.3 (br s, cage-C), 17.1 (s, CH_3), 16.6 [d, *J*(PC) 6.1 Hz, CH_3]; $^{31}P\{^1H\}(CD_2Cl_2)$, δ 167.6 (s). Compound **7**: $^1H(CD_2Cl_2)$, δ 7.47–6.89 (m, 10 H, Ph) 3.64 [d, 9 H, *J*(PH) 10.4 Hz, $POCH_3$], 3.10 (br s, 1 H, cage-CH), 2.85 (br s, 6 H, CH_3), 2.17 (br s, 1 H, cage-CH), $^{11}B\{^1H\}(CD_2Cl_2)$, δ −2.0 (s, 1 B), −6.1 (s, 1 B), −8.3 (s, 1 B), −10.9 (s, 1 B), −12.6 (s, 1 B), −15.8 (s, 2 B), −16.9 (s, 2 B), −20.6 (s, 1 B); $^{13}C\{^1H\}(CD_2Cl_2)$, δ 166.7 [d, *J*(PC) 8.1 Hz, $\equiv CPh$], 146.7 [d, *J*(PC) 27.1 H_2, $\equiv CPh$], 141.0 [d, *J*(PC) 10.8, $\equiv CMe$], 133.7–126.6 (Ph), 55.6 (br s, OCH_3), 52.1 (br s, cage-C), 49.6 (br s, cage-C), 19.1 (s, $\equiv C$–CH_3), $^{31}P\{^1H\}(CD_2Cl_2)$, δ 160.6 (s). Compound **8**: $^1H(CD_2Cl_2)$, δ 7.50–6.06 (m, 20 H, Ph), 5.88 (s, 1 H, =CH), 3.43 [vt, 18 H, *N*(PH) 10.6 Hz, $POCH_3$], 2.73 (br s, 2 H, cage-CH); $^{11}B\{^1H\}(CD_2Cl_2)$, δ 14.9 (s, 1 B), −4.6 (s, 1 B), −5.2 (s, 1 B), −9.5 (s, 2 B), −12.9 (s, 2 B), −17.8 (s, 2 B), $^{13}C\{^1H\}(CD_2Cl_2)$, δ 227.2 [t, *J*(PC) 16.3 Hz, C≡C], 145.8–124.6 (Ph), 54.2 (s, OCH_3), 46.8 (br s, cage-C), vinyl signals are obscured; $^{31}P\{^1H\}(CD_2Cl_2)$, δ 169.6 (s).

‡ *Crystal data*: $C_{36}H_{49}B_9MoO_6P_2$, M = 833.0, monoclinic, a = 11.736(2), b = 19.367(3), c = 17.781(3) Å, β = 100.67(2)°, U = 3971.6 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.39 g cm^{-3}, μ(Mo-Kα) = 4.2 cm^{-1}, $F(000)$ = 1720. Data were measured at 170 K on a CAD4 automatic four-circle diffractometer in the range $2 \leqslant \theta \leqslant 24°$. 6764 reflections were collected of which 4083 were unique with $I \geqslant 2\sigma(I)$. Data were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by

Patterson methods and refined using the SHELX suite of programs, to yield final $R = 0.0491$, $R_w = 0.0458$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ It is interesting to also note that it has been reported[3] that the complex [*closo*-1,2-Me_2-3-(η^2-PhC_2Ph)-3-(CO)-3-(PPh_3)-3-1-2-$MoC_2B_9H_9$] decomposes in solution to give an inseparable mixture (IR, NMR) of [*closo*-1,2-Me_2-3,3,3-$(CO)_3$-3-(PPh_3)-3,1,2-$MoC_2B_9H_9$] and [*closo*-1,2-Me_2-3,3-$(CO)_2$-3-(PPh_3)-8,3-{σ:η^2-C(Ph)= CHPh}-3,1,2-$MoC_2B_9H_9$], where the stereochemistry of the B–vinyl group was not defined.

¶ An alternative way in which a coordinatively unsaturated metal species can be stabilised has been demonstrated[14] by Hawthorne and coworkers for rhodium carbaborane species. This involves a *closo* $\rightleftharpoons$ *exo-nido* equilibrium process.

References

1 S. J. Dossett, S. Li and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1993, 1585.

2 S. Li and F. G. A. Stone, *Polyhedron*, 1993, **12**, 1689.

3 S. J. Dossett, S. Li, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1993, 3551.

4 K. P. Callahan and M. F. Hawthorne, *Adv. Organomet. Chem.*, 1976, **14**, 145.

5 T. A. Albright, J. K. Burdett and M. H. Whangbo, in *Orbital Interactions in Chemistry*, Wiley, 1985, p. 418.

6 C. Carfagna, M. Green, K. R. Nagele, D. J. Williams and C. M. Woolhouse, *J. Chem. Soc., Dalton Trans.*, 1993, 1761, and references therein.

7 M. Green, *J. Organomet. Chem.*, 1986, **300**, 93.

8 M. Bottrill and M. Green, *J. Chem. Soc., Dalton Trans.*, 1977, 2365.

9 F. G. A. Stone, *Adv. Organomet. Chem*, 1990, **31**, 53.

10 S. A. Brew and F. G. A. Stone, *Adv. Organomet. Chem.*, 1994, **35**, 135.

11 M. Green, J. A. K. Howard, A. N. de M. Jelfs, O. Johnson and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 73.

12 M. Green, J. A. K. Howard, A. P. James, A. N. de M. Jelfs, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 81.

13 M. Green, J. A. K. Howard, A. P. James, C. M. Nunn and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 61.

14 P. E. Behnken, J. A. Belmont, D. C. Busby, M. S. Delaney, R. E. King III, C. W. Kreimendahl, T. B. Marder, J. J. Wilczynski and M. F. Hawthorne, *J. Am. Chem. Soc.*, 106, **1984**, 3011, and references therein.