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Alkyne coupling in rhenacarbaborane chemistry. Structure of [1,2-μ-NHBu^t-2,2-(CO)$_2$-3,2-σ:η^2-{C(=CHBu^t)–CH=CHBu^t}-*closo*-2,1-ReCB$_{10}$H$_9$]

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The butadienyl moiety in the title compound is bound to both cage-boron and rhenium vertices, and arises from coupling of two alkyne molecules at the rhenium centre, unprecedented in metallacarbaborane chemistry.

Transition-element complexes in which the cyclopentadienide ligand $[C_5H_5]^-$ functions as a 6π-electron donor have played a pivotal role in the development of modern organometallic chemistry.[1] Formally isolobal with $[C_5H_5]^-$ are the carbaborane ligands [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ and [*nido*-7-$CB_{10}H_{11}]^{3-}$, and their derivatives, which for over 30 years have been known similarly to form metal complexes.[2,3] These metallacarbaboranes, however, are far fewer in number, and this is particularly so in the case of the latter, monocarbon carbaboranes.[4] We now report several new rhenium complexes of an amino-substituted *nido*-monocarbaborane ligand which functions as an 8-electron donor (6π electrons from the cluster open face plus 2σ electrons from the amino substituent). A facile two-alkyne coupling at the rhenium centre is demonstrated.

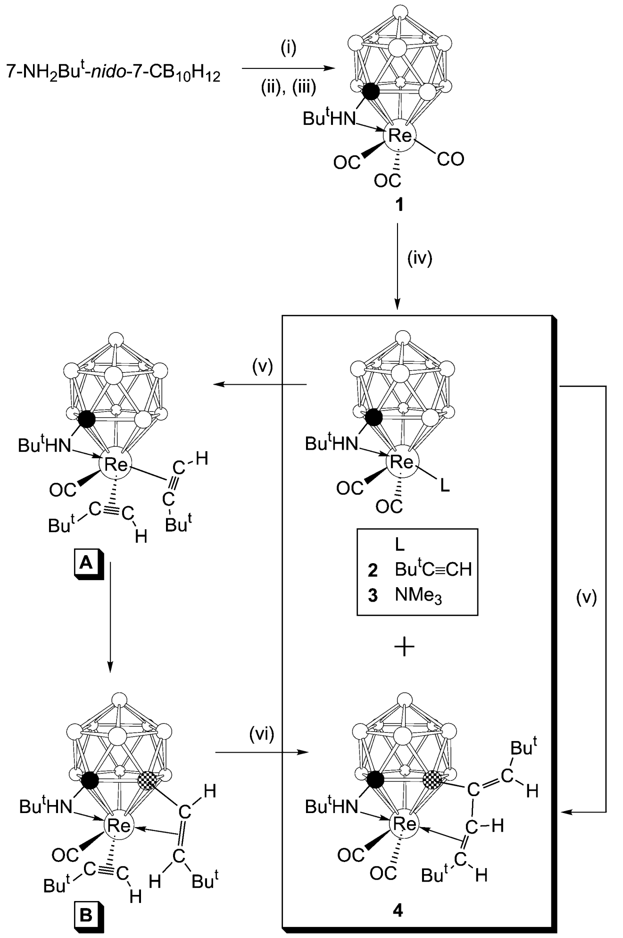
Treatment of 7-NH$_2$Bu^t-*nido*-7-CB$_{10}$H$_{12}$[5] in tetrahydrofuran (THF) with LiBu^n (3 equiv.) followed by [ReBr(THF)$_2$(CO)$_3$][6] ostensibly gives the dilithium salt of the dianionic rhenacarbaborane [1-NHBu^t-2,2,2-(CO)$_3$-*closo*-2,1-ReCB$_{10}$H$_{10}$]$^{2-}$, analogous to [2,2,2-(CO)$_3$-*closo*-2,1-ReCB$_{10}$H$_{11}$]$^{2-}$.[7] These two rhenacarbaboranes are oxidized by I$_2$ to Re^{III} species: the latter forms a monoanionic tricarbonyl-iodo complex,[7] whereas the former gives neutral [1,2-μ-NHBu^t-2,2,2-(CO)$_3$-*closo*-2,1-ReCB$_{10}$H$_{10}$] **1** (Scheme 1).† In **1** the NHBu^t group completes the metal coordination sphere by bridging between the cage-carbon atom and the rhenium vertex, as seen in the previously reported—and formally isoelectronic—anionic molybdenum and tungsten complexes.[8]

When compound **1** in CH$_2$Cl$_2$ is treated at room temperature for 12 h with one equiv. each of Bu^{t}C≡CH and Me$_3$NO, one CO is replaced by the alkyne affording [1,2-μ-NHBu^t-2-Bu^{t}C≡CH-2,2-(CO)$_2$-*closo*-2,1-ReCB$_{10}$H$_{10}$] **2**.† However, this is not the only product. Column chromatography on silica gel of the product mixture gave, in addition, small amounts of a trimethylamine complex [1,2-μ-NHBu^t-2,2-(CO)$_2$-2-NMe$_3$-*closo*-2,1-ReCB$_{10}$H$_{10}$] **3**† plus a third species which is formed in greatest proportion and is of most interest. This complex, [1,2-μ-NHBu^t-2,2-(CO)$_2$-3,2-σ:η^2-{C(=CHBu^t)–CH=CHBu^t}-*closo*-2,1-ReCB$_{10}$H$_9$] **4**,† contains a dienyl moiety that is bound to both the rhenium centre and to a boron vertex ligating the metal.

Under conditions similar to those by which it is formed, compound **2** does not by itself react with donors such as NEt$_3$ or PPh$_3$, and **3** is likewise unreactive towards Bu^{t}C≡CH. It may therefore be concluded that **2** and **3** are formed competitively from **1** following initial CO removal by Me$_3$NO. However, treatment of compound **2** with Me$_3$NO and one further equivalent of the alkyne affords **4** as the only observed product. All the compounds **1**–**4** show a broad ^{13}C{^{1}H} NMR resonance at *δ ca.* 103, diagnostic[8] of the cage-carbon atom involved in a C$_{cage}$–{μ-NHBu^t}–Re linkage. The asymmetry implied by their ^{11}B{^{1}H} NMR spectra is further consistent with this. In the NMR spectra of **4** the appearance of signals attributable to three Bu^t groups, allied with observation of multiple ^{1}H–^{1}H couplings, was suggestive of incorporation and linking of two alkynes. However, the additional attachment of the organic function to a cluster boron atom and the exact nature of this function were only confirmed by X-ray diffraction analysis.‡

The structure determined is shown in Fig. 1. A substituted 1,3-dien-2-yl moiety is coordinated to the rhenium vertex [Re–C(8) 2.316(7), Re–C(9) 2.445(7) Å] and is also bonded to an α boron atom in the $\overline{CBBBB}$ belt that η^5-ligates the rhenium [B(2)–C(14) 1.587(10) Å]. The bond lengths within the diene suggest little conjugation, consistent with the two double bonds being almost orthogonal [*ϕ*(C(9)C(8)C(14)C(15)) 70.9(10)°], although—as noted above—in solution NMR spectra some such communication is evidenced by the observed long range ^{1}H–^{1}H coupling.

Mechanistically, it is reasonably assumed that formation of **4** in the principal reaction proceeds by first conversion of **2** to a *bis*(alkyne) species (Scheme 1, **A**) from which—either subse-



Scheme 1 *Reagents and conditions*: i, Bu^{n}Li (3 equiv.), THF; ii, [ReBr(THF)$_2$(CO)$_3$], THF; iii, I$_2$, THF; iv, Me$_3$NO, Bu^{t}C≡CH, CH$_2$Cl$_2$; v, **2** with Me$_3$NO, Bu^{t}C≡CH, CH$_2$Cl$_2$; vi, CO scavenging. Key: (○ = BH, ▩ = B, ● = C.

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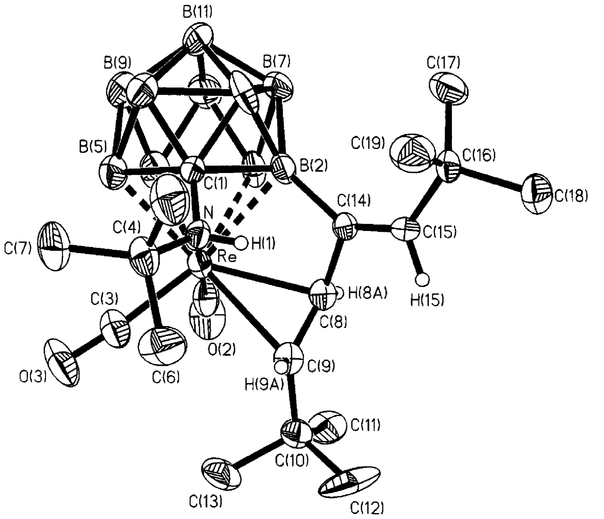

Fig. 1 Molecular structure of **4** with crystallographic labeling scheme (thermal ellipsoids with 40% probability). Selected distances (Å) and angles (°): Re–C(1) 2.145(7), Re–N 2.244(6), Re–C(8) 2.316(7), Re–B(2) 2.352(8), Re–C(9) 2.445(7), C(1)–N 1.422(8), B(2)–C(14) 1.587(10), C(8)–C(9) 1.383(9), C(8)–C(14) 1.508(9), C(14)–C(15) 1.331(9); C(1)–Re–C(8) 99.7(2), N–Re–C(8) 87.4(2), C(1)–Re–C(9) 113.2(2), N–Re–C(9) 83.3(2), C(8)–Re–C(9) 33.6(2), N–C(1)–B(2) 103.6(5), C(1)–N–Re 67.4(4), C(9)–C(8)–C(14) 128.0(6), C(9)–C(8)–Re 78.3(4), C(14)–C(8)–Re 94.6(4), C(8)–C(9)–Re 68.1(4), C(15)–C(14)–C(8) 119.6(6), C(15)–C(14)–B(2) 137.6(6), C(8)–C(14)–B(2) 102.7(6).

quently or concomitantly—one of the alkynes rearranges to a vinylidene[9] intermediate. The latter, in turn, inserts into an adjacent B–H bond, resulting in the *Re*-alkyne/*Re*,*B*-vinyl species **B**. Rearrangement of the remaining alkyne in **B** then affords a vinylidene which inserts into the nearby C–H bond at the boron-bound terminus of the B–C(H)=C(H)Bu^t group, giving **4**. This is consistent with the observed regio- and geometric specificity of the 'tail-to-tail' alkyne coupling. The present results contrast with previous observations in the related metalladicarbaborane systems based on $\{MoC_2B_9\}$[10] and $\{RuC_2B_9\}$[11] clusters, where multiple alkyne substitution results in mixed *Mo*-alkyne/*Mo*,*B*-vinyl or multiple *cage-B*-vinyl-substituted products, respectively, without diene formation. Moreover, in an allied iron–monocarbaborane complex only a single alkyne molecule is incorporated and converted to a σ:η^2-vinyl species, even with excess of this reagent.[12] Further investigations of the mechanism of formation of **4** and of its reactivity are at present under way.

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Notes and references

† **1**: Orange microcrystals; yield 46%. Anal. Calc. for $C_8H_{20}B_{10}NO_3Re$: C, 20.3; H, 4.3; N, 3.0. Found: C, 20.5; H, 4.3; N, 3.0%; IR (CH_2Cl_2): ν_{max}(CO) 2088s, 2040m, 2001s cm^{-1}; ^{1}H NMR (360.13 MHz, CD_2Cl_2), δ 3.87 (br s, 1H, NH), 1.26 (s, 9H, Bu^t); ^{13}C{^{1}H} NMR (90.56 MHz, CD_2Cl_2), δ 191.5, 190.8, 189.1 (CO × 3), 103.5 (br, cage C), 65.0 (*C*Me$_3$), 29.1 (C*Me*$_3$); ^{11}B{^{1}H} NMR (115.55 MHz, CD_2Cl_2, unit integral except where indicated), δ 18.9, 3.2, 0.8, −3.4, −6.6 (3B), −7.6, −15.3, −19.3.

2: Yellow microcrystals; yield 13%. Anal. Calc. for $C_{13}H_{30}B_{10}NO_2Re$: C, 29.6; H, 5.7; N, 2.7. Found: C, 29.8; H, 5.8; N, 2.6%; IR: ν_{max}(CO) 2077s, 2020s cm^{-1}; ^{1}H NMR, δ 7.42 (s, 1H, ≡CH), 1.69 (s, 9H, Bu^t), 1.00 (s, 9H, Bu^t), NH too broad to be observed; ^{13}C{^{1}H} NMR, δ 195.5 (CO), 182.2 (≡CH), 117.0 (≡*C*Bu^t), 104.2 (br, cage C), 61.4 (N*C*Me$_3$), 36.5 (C*C*Me$_3$), 32.0 (C*Me*$_3$), 28.9 (C*Me*$_3$); ^{11}B{^{1}H} NMR, δ 14.7, 2.0, −3.4, −5.1, −5.9, −8.3, −9.6, −10.1, −13.8, −19.9.

3: Brown microcrystals; yield 9%. Anal. Calc. for $C_{10}H_{29}B_{10}N_2O_2Re$: C, 23.8; H, 5.8; N, 5.6. Found: C, 23.8; H, 5.8; N, 5.3%; IR: ν_{max}(CO) 2028s, 1939s cm^{-1}; ^{1}H NMR, δ 3.24 (s, 9H, NMe$_3$), 3.12 (br s, 1H, NH), 1.25 (s, 9H, Bu^t); ^{13}C{^{1}H} NMR, δ 206.7, 204.7 (CO × 2), 102.8 (br, cage C), 63.5 (*C*Me$_3$), 61.1 (NMe$_3$), 29.5 (C*Me*$_3$); ^{11}B{^{1}H} NMR, δ 12.4, 3.7, −0.3, −1.9, −3.7, −9.0, −10.6, −12.1, −14.1, −19.1.

4: Orange microcrystals; yield 23% (unoptimised). Anal. Calc. for $C_{19}H_{40}B_{10}NO_2Re$: C, 37.5; H, 6.6; N, 2.3. Found: C, 37.5; H, 6.7; N, 2.3%; IR: ν_{max}(CO) 2045s, 1978s cm^{-1}; ^{1}H NMR, δ 5.77 (br, 1H, B–C=CH), 4.71 [dd, ^3J(HH) = 15, ^4J(HH) = 2, 1H, Re–(C*H*=CHBu^t)], 4.53 [d, ^3J(HH) = 15, 1H, Re–C*H*Bu^t], 2.79 (br s, 1H, NH), 1.42 (s, 9H, Re–CH*Bu^t*), 1.22 (s, 9H, NBu^t), 1.14 (s, 9H, B–C=CBu^t); ^{13}C{^{1}H} NMR, δ 200.2, 194.8 (CO × 2), 163.5 (B–C=*C*), 127.8 (v br, B–C), 104.3 (Re–*C*Bu^t), 103.6 (br, cage C), 64.8 (N*C*Me$_3$), 56.2 [Re–(*C*H=CHBu^t)], 36.1, 34.3 (C*C*Me$_3$ × 2), 32.6 (Re–CC*Me*$_3$), 31.1 (B–C=CC*Me*$_3$), 29.3 (NC*Me*$_3$); ^{11}B{^{1}H} NMR, δ 14.3, 3.8, −1.8, −2.8, −6.4, −7.3, *ca.* −9.2 [sh, B(3)] −9.7, −18.6, −19.1.

‡ *Crystal data* for **4**: Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo-Kα X-radiation (λ = 0.71073 Å); Lorentz, polarization and empirical absorption corrections; solution by direct methods and full-matrix least-squares refinement on F^2 (SHELXL97); crystals from CH_2Cl_2–light petroleum (bp 40–60 °C) (−30 °C); $C_{19}H_{40}B_{10}NO_2Re$, M = 608.82, monoclinic, space group $P2_1/n$, a = 11.440(2), b = 15.369(2), c = 15.377(2) Å, β = 92.828(12)°, U = 2700.2(7) Å^3, T = 293 K, Z = 4, μ(MoKα) = 4.517 mm^{-1}, 5032 reflections measured, 4777 unique (R_{int} = 0.0256) were used in all calculations. Final wR_2 (F^2) = 0.0808 (all data), R_1 [$F > 4\sigma(F)$] = 0.0393. CCDC reference number 181735. See http://www.rsc.org/suppdata/cc/b2/b201772p/ crystallographic data in CIF or other electronic format.

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