Further studies of the Enhanced Structural Carborane Effect: tricarbonylruthenium and related derivatives of benzocarborane, dihydrobenzocarborane and biphenylcarborane†

Samuel L. Powley, Georgina M. Rosair and Alan J. Welch*

Detailed comparison of the molecular structures of \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3,3,3-(CO)}\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_{11}]\) (1) and \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3,3,3-(CO)}\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_3]\) (2) reveals evidence for an Enhanced Structural Carborane Effect in 1 arising from the involvement of the cage \(p_z\) orbitals in the exopolyhedral ring to some degree. A minor co-product in the synthesis of 2 is \([\eta-(\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3,3,3-(CO)}\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_3]\) (3). Compounds 2 and 3 are readily interconverted, since heating 2 to reflux in THF or reaction with MesNO affords 3 which readily reacts with CO to regenerate 2. The \(\eta\)-ene bonding in 3 is also displaced by PMEs, P(OMe)\(_3\) and t-BuNC to yield \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3,3,3-(CO)}\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_3]\) (4), \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3,3,3-(CO)}\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_3]\) (5) and \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3,3,3-(CO)}\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_3]\) (6), respectively. Structural studies of 4–6, focussing on the Exopolyhedral Ligand Orientation of the \((\text{Ru(CO)}_3)\text{L}\) fragment relative to the \(\text{C}_2\text{B}_3\) carborane face, are discussed in terms of the structural trans effects of PMEs, P(OMe)\(_3\) and t-BuNC relative to that of CO. An improved synthesis of \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-1,2-closo-C}_2\text{B}_9\text{H}_3]\) , “biphenylcarborane”, is reported following which the first transition-metal derivatives of this species, \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3-Cp-3,1,2-closo-CoC}_2\text{B}_9\text{H}_3]\) (7) and \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3,3,3-(CO)}\text{-3,1,2-closo-RuC}_2\text{B}_9\text{H}_3]\) (8), are prepared. Comparisons of the structures of 7 and 8 with the corresponding benzocarborane derivatives \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3-Cp-3,1,2-closo-CoC}_2\text{B}_9\text{H}_3]\) and 1, respectively, suggest that Clar’s rule for aromaticity can be applied to polycyclic aromatic hydrocarbons fused onto carborane cages.

Introduction

We recently named the phenomenon whereby cage C atoms in metallacarboranes of the type \(3,1,2\text{-closo-MC}_2\text{B}_9\text{H}_{11}\) are less strongly bound to the metal atom than cage B atoms as the Structural Carborane Effect (SCE).\(^1\) The origin of the SCE is that in a carborane ligand the C atoms contribute relatively little to the cage frontier molecular orbitals.\(^2\) Although this effect was already very well-known, giving it this name allowed us subsequently to describe the Enhanced Structural Carborane Effect (ESCE).\(^2\) This arises when an exopolyhedral \(\{\text{C}_4\text{H}_4\}\) diene tethers the two carborane C atoms allowing the \(p_z\) orbitals of the cage C atoms to participate in a pseudoaromatic C ring at the expense of bonding to the metal atom. The effect is similar to the difference in metal-bonding of a Cp ligand and an indenyl ligand – in the former the M–C interactions are equivalent but in the latter the ring junction C atoms are weaker bound to the metal atom since their \(p_z\) orbitals are simultaneously part of two aromatic systems. In an attempt to observe an ESCE we compared molecular parameters in two pairs of related compounds, \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-1,2-closo-C}_2\text{B}_9\text{H}_{10}]\) (“benzocarborane”, I, Fig. 1) and \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-1,2-closo-C}_2\text{B}_9\text{H}_{10}]\) (“dihydrobenzocarborane”, II, Fig. 1) as one pair,\(^3,4\) and their \(\{\text{CoCp}\}\) derivatives \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3-Cp-3,1,2-closo-CoC}_2\text{B}_9\text{H}_3]\) (I-Co) and \([\text{1,2-} \mu-(\text{C}_4\text{H}_4)\text{-3-Cp-3,1,2-closo-CoC}_2\text{B}_9\text{H}_3]\) (II-Co) as the other.\(^5\) Although the differences were small they were significant – in the compounds with the \(\{\text{C}_4\text{H}_4\}\) tether the \(\text{C}_{\text{cage}}\)–B/M3 and \(\text{C}_{\text{cage}}\)–B6 distances were longer, and the \(\text{C}_{\text{cage}}\)–\(\text{C}_{\text{cage}}\) distances shorter, than those in the compounds with the \(\{\text{C}_4\text{H}_4\}\) tether, providing firm evidence for an ESCE.

Seeking to extend this work we herein describe the synthesis and complete characterisation, including structural studies, of \(\{\text{Ru(CO)}_3\}\) derivatives of benzocarborane and dihydrobenzocarborane, providing further evidence for an ESCE. During the course of these studies we unexpectedly discovered that the \(\{\text{C}_4\text{H}_4\}\) tricarbonyl compound can be interconverted...
with an \(\eta^1\text{-}(C_2H_6)\text{(CO)}_3\text{Cl}_2\) species and we have explored substitution of the ene of the latter compound with various 2\(e\) donor ligands. Finally we have prepared and characterised the first examples of metal derivatives of [1,2-\(\mu\text{-}(C_2H_4)\text{-}3,3,3\text{-}(\text{CO})_3\text{-}3,1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10}\)], “biphenylcarborane”. Analysis of their structures in comparison with those of analogous metal complexes of benzo-carborane provides evidence that the three fused \(C_6\) rings in biphenylcarborane can be discussed in terms of the Clar structure of phenanthrene.

### Results and discussion

The [\(\text{HNMe}_3\)]\(^+\) salt of [7,8-\(\mu\text{-}(C_4H_4)\text{-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}\)]
\([\text{deboronated I}]\) was synthesised analogously to the [\(\text{HNMe}_3\)]\(^+\) salt of [7,8-\(\mu\text{-}(C_4H_4)\text{-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10}\)]
\([\text{deboronated II}]\).\(^5\) Deprotonation of the former followed by reaction with [\(\text{Ru(CO)}_3\text{Cl}_2\)]\(_2\) in THF and work-up involving thin-layer chromatography (TLC) afforded, in low yield, the yellow compound [1,2-\(\mu\text{-}(C_4H_4)\text{-}3,3,3\text{-}(\text{CO})_3\text{-}3,1,2\text{-closo-Ru-C}_2\text{B}_9\text{H}_{10}\)] (1), according to Scheme 1. Compound 1 was characterised by microanalysis, IR spectroscopy, mass spectrometry and both \(^1\)H and \(^{11}\)B NMR spectroscopies, the analyses of all of which were fully consistent with the anticipated structure. However, since we targeted 1 to investigate the ESCE involving detailed structural comparison it was also necessary to characterise the compound crystallographically. Note that [\(\text{NMe}_4\)]\([1,2\text{-}\mu\text{-}(C_4H_4)\text{-}3,3,3\text{-}(\text{CO})_3\text{-}3,1,2\text{-closo-}\text{C}_2\text{B}_9\text{H}_{10}\)]\(^5\) was deprotonated and treated with [\(\text{Ru(CO)}_3\text{Cl}_2\)]\(_2\) in an analogous manner to that described above for 1, affording [1,2-\(\mu\text{-}(C_4H_4)\text{-}3,3,3\text{-}(\text{CO})_3\text{-}3,1,2\text{-closo-Ru-C}_2\text{B}_9\text{H}_{10}\)] (2), in somewhat better yield, Scheme 2. Following analytical and spectroscopic characterisation, compound 2 was also subjected to crystallographic analysis, the results of which are shown in Fig. 3. Note that in 2 the \(C_s\) symmetry (in the same sense as in 1) is crystallographically-imposed.

Key molecular parameters in compounds 1 and 2 are compared in Table 1. Both the \(\langle C_{\text{cage}}\text{-Ru}\rangle\) and \(\langle C_{\text{cage}}\text{-B6}\rangle\) distances are significantly shorter \([\text{differences }0.042(3)\text{ and }0.015(4)\text{ Å, respectively}]\) and the C1–C2 distance significantly longer \([\text{difference }0.036(4)\text{ Å}]\) in compound 2 compared to compound 1 providing clear evidence for an Enhanced Structural Carborane Effect and implying some degree of aromaticity in the \(C_6\) ring of 1; if the cage \(C_p\) orbitals in 1 are involved in an aromatic exopolyhedral ring they will be less involved in bonding to the Ru3 and B6 atoms. The same conclusion was reached when we compared molecular structures of I-Co and II-Co.\(^1\)

A colourless minor co-product, compound 3, was produced along with 2. Elemental analysis and mass spectrometry were consistent with only a dicarbonyl species. Both the \(^{11}\)B and
1H NMR spectra implied retention of $C_s$ symmetry, but in the 1H spectrum the resonance for the C$_H$ atoms had moved upfield, from $\delta$ 5.83 ppm in 2 to $\delta$ 4.09 ppm in 3. Collectively, these data were consistent with displacement of one CO ligand by an $\eta$-co-ordinated {HC$_v$CH} unit, and this was confirmed by a crystallographic study (Fig. 4).

Thus compound 3 is $[\eta_1(1,2-\mu-(C_4H_6))-3,3-(CO)_{2}3,1,2\text{-closo-RuC}_2B_9H_9]^- \text{ in which, formally, the C4=C5 ene unit in the tether has displaced the C31O31 ligand of 2, and the ability of the exopolyhedral C$_4$H$_6$ unit to do this adds an interesting dimension to the chemistry of transition-metal derivatives of dihydrobenzocarborane. In 3 the Ru–C4 and Ru–C5 bond lengths are 2.3005(11) and 2.3052(11) Å, respectively, and the C4–C5 distance is 1.4029(16) Å. The Ru–C1/C2 connectivities in 3 are significantly shorter than those in 2, 2.2086(10) and 2.1996(9) Å cf. 2.2783(16) Å, and the C1–C2 connectivity is significantly longer, 1.7011(13) Å cf. 1.6627(19) Å; these changes are presumably the consequences of these connectivities being constrained within new or modified cyclic systems in 3. The substitution of a CO ligand in 2 by an $\eta$-ene ligand in 3 might have been expected to result in stronger bonding of the two remaining CO ligands, but the evidence for this is somewhat contradictory; whilst the average C–O distance in 3, 1.1436(17) Å, is somewhat longer than the C32–O32 distance in 2, 1.1368(12) Å (consistent with stronger Ru–CO bonding in 3), the average Ru–CO distance in 3, 1.9274(14) Å is marginally longer than the Ru–C32 distance in 2, 1.9192(12) Å (leading to the opposite conclusion).

In forming compounds 2 and 3 the anion $[7,8\text{-}\mu-(C_4H_6)-7,8\text{-nido-C}_2B_9H_9]^- \text{ is treated with a source of } \{Ru(CO)_3\}^{2+} \text{ so presumably the first species formed is 2 which then loses CO to afford 3 as a minor co-product. Accordingly we have explored the interconversion of compounds 2 and 3, Scheme 3. The tri-}

\text{carbonyl 2 is readily converted into the dicarbonyl/ene 3 by reaction with Me}_3\text{NO in CH}_2\text{Cl}_2 \text{ or simply by heating to reflux in THF. In reverse, compound 3 is quantitatively converted into 2 by reaction with CO.}
The η-ene function in 3 is not displaced by THF or MeCN (even when heating to reflux in these solvents for 16 h) but is readily substituted by PMe3, P(OMe)3 and t-BuNC to afford the colourless products [1,2-μ-(C6H4)-3,3-(CO)2-3-PMe3-3,1,2-closo-RuC2B9H9](4), [1,2-μ-(C6H4)-3,3-(CO)2-3-P(OMe)3-3,1,2-closo-RuC2B9H9](5) and [1,2-μ-(C6H4)-3,3-(CO)2-3-t-BuNC-3,1,2-closo-RuC2B9H9](6), respectively. Compounds 4–6 were fully characterised by elemental analysis, mass spectrometry, and IR and 1H, 11B and (for 4 and 5) 31P NMR spectroscopies. Although, in all cases, these techniques fully confirmed the identity of the compounds they did not establish the orientation of the [Ru(CO)2L] fragment with respect to the carborane cage so finally all three compounds were subjected to X-ray diffraction studies. Fig. 5–7 show perspective views of single molecules of 4–6, respectively. These structures will be fully discussed in the following section but, briefly, in 4 and 5 one CO ligand lies effectively over the connectivity between the two cage C atoms whilst in 6 the isocyanide ligand occupies this position. In the structure of 5 there is an H-bond between H6B (part of one of the CH2 groups in the tether) and O10, H6B⋯O10 2.510(3) Å, C6–H6B⋯O10 151.0(3)°, H6B⋯O10–P1 106.21(18)°, H6B⋯O10–C10 125.6(3)° (note that these e.s.d.s are artificially small since H6B was not freely refined).

Fig. 5 Perspective view of compound 4 with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.

Fig. 6 Perspective view of compound 5 with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.

An obvious extension of the chemistry of benzocarborane I would be to consider analogues in which the C6 tether (which, as noted above, has a small degree of aromatic character) was extended to a polycyclic aromatic hydrocarbon (PAC). Recently Morisaki, Chujo and co-workers coupled the α-C atoms of the substituents of 1,2-(2′-BrC6H4)2-1,2-closo-C2B10H10 to afford the compound [1,2-μ-(C6H4)2-1,2-closo-C2B10H10] (“biphenylcarborane”, III), Fig. 8. The structure of III in relation to the structure of I is interesting in the context of Clar’s rule for the aromaticity in PACs. Briefly, considering phenanthrene (Fig. 9), Clar’s rule states that structure B with two disjoint aromatic π-sexets is a better description of the molecule than structure A with only one central π-sexet. The peripheral rings have more aromatic character, and the central ring less aromatic character, in B relative to A, and the C1C2 bond is more of a formal double bond in B than it is in A.

To a degree this is borne out when the structures of I and III are compared. Although the differences are small and not statistically significant, the average Ccage–B and Ccage–Ccage
distances in III, 1.739(7) and 1.643(3) Å respectively, are both shorter than those in I, 1.746(4) and 1.651(6) Å respectively. This is consistent with somewhat less aromatic character in the central C₆ ring of III and consequently less of a ESCE (hence shorter Ccage–B) but more localised double-bond character in the Ccage–Ccage link (hence shorter Ccage–Ccage).

We were interested if these minor differences in the structures of I and III would be replicated, or perhaps enhanced, in their metal derivatives. Although the debronation of III with wet fluoride has been reported and the nido product isolated as the [NMe₄]⁺ salt⁸ no metal derivatives are currently known. However, because the original synthesis of III is poor-yielding (ca. 7% based on B₁₀H₁₄)⁶ we have first developed an improved synthesis. Double deprotonation of 1,2-closo-C₂B₁₀H₁₂ followed by addition of CuCl/pyridine and then 2,2'-diiodobiphenyl, following the general procedure developed by Fox et al.,⁹ afforded III in 56% yield after work-up.

Subsequently we have deboronated III using EtOH/KOH and isolated the product as [HNMe₃][7,8-μ-(C₆H₄)₂-7,8-nido-C₂B₉H₁₀] (IV). From this we have subsequently prepared the {CoCp} species [1,2-μ-(C₆H₄)₂-3-Cp-3,1,2-closo-CoC₂B₉H₁₀] (7) and the {Ru(CO)₃} species [1,2-μ-(C₆H₄)₂-3,3,3-(CO)₃-3,1,2-closo-RuC₂B₉H₁₀] (8) in reasonable and trace yields, respectively (Scheme 4). Compounds 7 and 8, the first examples of metal derivatives of biphenylcarborane III, have been characterised by mass spectrometry and ¹H and ¹¹B NMR spectroscopies plus (for 7) microanalysis and (for 8) IR spectroscopy. Both 7 and 8 have also been studied crystallographically, and perspective views of single molecules are shown in Fig. 10 and 11, respectively.

Fig. 7 Perspective view of compound 6 with atomic numbering scheme. Only the major component of the partial disorder in the t-BuNC ligand is shown. Displacement ellipsoids as in Fig. 2.

Fig. 8 Biphenylcarborane (III).

Fig. 9 Alternative representations of phenanthrene. Representation B is favoured by Clar’s rule.

Fig. 10 Perspective view of compound 7 with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.

Scheme 4 Synthesis of compounds 7 ([M] = CoCp) and 8 ([M] = Ru(CO)₃).
Key average molecular dimensions for 7 and 8 are given in Table 1. In comparison with 1-Co compound 7 shows evidence of a reduced ESCE (shorter C\textsubscript{age-CO} and C\textsubscript{age-B6} distances) consistent with less aromaticity in the central C\textsubscript{6} ring. Moreover, the C1–C2 distance is significantly shorter in 7 in accord with Clar’s rule. Comparing the data for compound 8 with those of compound 1 we also note shorter C1–C2 and C\textsubscript{age-B6} distances in the former, but this time the C\textsubscript{age-Ru} distance is longer. A possible reason for this is suggested in the following section. Our overall conclusion, therefore, is that comparisons of III with 1, 7 with 1-Co and 8 with 1 indicate reasonable agreement with expectations based on the assumption that Clar’s rule can be applied to PACs fused onto carborane cages.

Exopolyhedral ligand orientations

Compounds 1–6 and 8 all contain a \{RuL\textsubscript{3}\} fragment attached to a carbons-adjacent C\textsubscript{2}B\textsubscript{4} carborane ligand. In 1, 2 and 8 the metal fragment is \{Ru(CO)\textsubscript{3}\} whilst in 3–6 the metal fragment is \{Ru(CO)\textsubscript{2}L\}. Since, as already noted, the carbon atoms in a carborane ligand contribute less to the cage frontier orbitals than do the facial boron atoms (the origin of the Structural Carborane Effect, SCE), the cage B atoms will exert a greater structural trans effect (trans influence) than the cage C atoms, and this should be evident in both the orientation and molecular dimensions of the exopolyhedral ligands.\textsuperscript{10}

There are five examples of \[3,3,3-(CO)\textsubscript{3}-3,1,2-closo-MC\textsubscript{2}B\textsubscript{6}H\textsubscript{11}\] species in the Cambridge Structural Database (CSD),\textsuperscript{11} summarised together with key structural information in Table 2. For each carbonyl ligand are given the M–CO distance and \(\theta\), the modulus of the torsion angle C–M–A–B where A is the centroid of the C1C2B7B8B4 face and B is the centroid of the C1–C2 connectivity (Fig. 12). A CO ligand with \(\theta = 0^\circ\) sits above the centre of the C–C connectivity whilst one with \(\theta = 180^\circ\) sits opposite that connectivity. Given that the cage C atoms exert a smaller structural trans effect than the B atoms one would expect to see this reflected in the M–CO distances, with stronger and shorter M–CO bonds opposite cage C atoms and weaker and longer M–CO bonds adjacent to cage C atoms. Table 2 also contains the \(\theta\) and M–CO distances for the tricarbonyl compounds 1, 2 and 8.

The literature data in Table 2 generally support the expectation of an inverse relationship between \(\theta\) and the M–CO bond length. Initially the data for HOSGIF and KOBLOC appear to contradict this pattern to some extent but, whilst

![Fig. 11](https://example.com/fig11.png)

**Fig. 11** Left, perspective view of compound 8 with atomic numbering scheme and displacement ellipsoids as in Fig. 2. Right, space-filling view of compound 8.
none of the literature structures analysed in Table 2 are particularly precise, both HOSGIF and KOBLOC are relatively imprecise, with high e.s.d.s on bond distances, so their value in this exercise is somewhat limited. Moreover, on checking the assignment of the cage C atoms in HOSGIF by the VCD method \(^{10}\) we believe that the published locations of the carbon atoms are suspect. With regard to the structures \(1A, 2\) and \(8\) there is again the clear pattern of reducing M–CO distance with increasing \(\theta\) angle; the more the CO ligand is trans to the cage C atoms the stronger it is bound to the metal. Unfortunately the same pattern is not evident for \(1B\), and we have no explanation for this. Fig. 13 shows the orientations of the \{Ru(CO)\}_3 fragments in \(1A, 1B, 2\) and \(8\) projected onto the C\(_2\)B\(_3\) carborane face.

The orientation of the \{Ru(CO)\}_3 fragment in \(8\) is unusual, having one CO lying opposite the C\(_{cage}\)-C\(_{cage}\) connectivity; a possible reason for this is that it minimises intramolecular crowding between the biphenyl substituent and the metal fragment (a space-filling representation of \(8\) is provided as part of Fig. 11). We tentatively suggest that this orientation, with a strong CO ligand directly trans to the cage C atoms, may be the reason why the C\(_{cage}\)-Ru distances in \(8\) are anomalously long as noted in the previous section.

The CSD contains seven compounds in which an \{M(CO)\}_2L\] fragment is bonded to a \((C\_2\_B\_9\_H\_11)\) carborane ligand as the 3,1,2-MC\(_2\)B\(_9\) isomer, and selected data on these are collected in Table 3. Also included are relevant data from compounds 3–6. In this tabulation there are two \(\theta_{CO}\) values and one \(\theta_L\) value, which together describe the orientation of the \{M(CO)\}_2L\] fragment \((\theta\) is calculated as above). Also listed are the corresponding M–CO distances. Fig. 14 shows the orientations of the \{Ru(CO)\}_2L\] fragments in 3–6 projected onto the C\(_2\)B\(_3\) carborane face.

As we have already noted,\(^ {10}\) for a conical metal fragment with dissimilar ligands bonded to a carbons-adjacent carborane the Expopolyhedral Ligand Orientation (ELO) is controlled by the carbon atoms in the carborane, with the weakest (in terms of structural trans effect) exopolyhedral ligand expected to lie over the cage C atoms. Thus from Table 3 it is apparent that the alkyne in HIZQIQ, the ylide in HIZQOW, the phosphines in HIZQUC and KISBIX, the MeCN in MEFNEQ and the Cl ligand in ZEPYIC all have weaker structural trans effects than CO since they all have low \(\theta_L\) values. This, in turn, means that the two \(\theta_{CO}\) values are necessarily rather similar, and this leads to very similar M–CO distances. The exception literature structure is TAKCIR. Here the weaker exopolyhedral ligand is CO (Sn\(_R_3\) is well-recognised as having a strong structural trans effect),\(^ {21}\) so one CO has a small \(\theta_{CO}\) and the other a much larger one. Because of the differing structural trans effects of
cage C and B the former CO ligand (opposite B) has a measurably longer M–CO bond.

In compound 3 the weaker exopolyhexaligand (C=CC) is constrained to have a low θL value because it is incorporated in the exopolyhexal C6 cycle; again this results in structurally-eqivalent CO ligands. The structure of 4, with θL123.7°, implies that, at least in this compound, PMe3 has a stronger structural trans effect than CO. As anticipated the CO ligand that is therefore forced to lie effectively over the cage C atoms has a significantly longer Ru–CO bond than the other one, 1.940(3) Å vs. 1.895(3) Å. P(OMe)3, a weaker donor but stronger acceptor ligand than PMe3, adopts a similar orientation in compound 5 although, as previously noted, there is an intramolecular H-bond in 5 that might be a factor in the ELO adopted. Again, in 5 the Ru–CO bonds are unequal, with that at high θCO significantly the shorter. In contrast, the orientation of the [Ru(CO)3]L set in the t-butylisocyanide compound 6 is quite different. Here the t-BuNC ligand clearly has the weaker structural trans effect since θL is only 11.1°, resulting in the two CO ligands occupying equivalent orientations with respect to the carborane cage and having similar Ru–CO distances.

Conclusions

Further evidence for an Enhanced Structural Carborane Effect has been found from comparisons of the molecular structures of the [Ru(CO)3] compounds 1 and 2. The dicarbonyl η1-ene compound 3 is afforded from 2 by thermolysis or reaction with Me3NO and is converted into 2 by treatment with CO. The η1-ene interaction is also displaced by PMe3, P(OMe)3, and t-BuNC, and structural studies of the products of these reactions (compounds 4–6, respectively) allow comment on the relative structural trans effects of the added ligand relative to CO. The first examples of transition-metal derivatives of biphenylcarborane, compounds 7 and 8, are reported and their structures discussed in relation to Clar’s rule for polycyclic aromatic hydrocarbons.

Experimental

Synthesis

Experiments were performed under dry, oxygen free, N2 using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. Diethylether, tetrahydrofuran (THF) and 40–60 petroleum ether (petrol) were freshly distilled under nitrogen from sodium wire immediately before use whilst CH2Cl2 (DCM) was distilled under nitrogen from CaH2. All solvents were degassed (3 × freeze–pump–thaw cycles) before use. Deuterated solvents were stored over 4 Å molecular sieves. Preparative TLC employed 20 × 20 cm Kieselgel F254 glass plates and column chromatography used 60 Å silica as the stationary phase. NMR spectra at 400.1 MHz (1H), 162.0 MHz (31P) or 128.4 MHz (11B) were recorded on a Bruker AVIII-400 spectrometer from CDCl3 at room temperature unless otherwise stated. IR spectra were recorded from DCM solutions using a PerkinElmer Spectrum 100 FTIR spectrophotometer. Electron impact mass spectrometry (EIMS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. Elemental analyses were conducted using an Exeter CE-440 elemental analyser. [HNMe3][7,8-μ-(C4H4)-7,8-nido-C2B9H10] was prepared by literature methods, and [HNMe3][7,8-μ-(C4H4)-7,8-nido-C2B9H10] was prepared analogously. All other reagents were supplied commercially.

1,2-μ-(C4H4)3-3,3,3-(CO)3-3,1,2-closo-RuC2B9H9 (1). n-BuLi (0.65 mL of 2.5 M solution in hexanes, 1.63 mmol) was added dropwise at 0 °C to a solution of [HNMe3][7,8-μ-(C4H4)-7,8-nido-C2B9H10] (0.180 g, 0.74 mmol) in THF (10 mL) to afford a bright yellow solution. This was added dropwise to a solution of [Ru(CO)3]Cl2 (0.200 g, 0.39 mmol) in THF (10 mL) at 0 °C. The cooling bath was removed and solvent immediately removed under vacuum from the orange reaction mixture. The residue was eluted through a short silica plug using 2 : 1 DCM : petrol. The yellow-orange eluent was collected, reduced in volume and purified by preparative TLC (DCM : petrol, 1 : 2) to afford [1,2-μ-(C4H4)3-3,3,3-(CO)3-3,1,2-closo-RuC2B9H9] (1).
(0.021 g, 8%) as a yellow solid at RT. C_{28}H_{33}B_{10}O_{18}Ru requires C 29.4, H 3.56. Found for C 28.5, H 3.67%. 11B{1H} NMR, δ 5.4 (1B), −2.4 (1B), −6.3 (6B), −10.6 (1B).

1H NMR, δ 6.99 (m, 2H, tether CH), 6.05 (m, 2H, tether CH). IR, δmax at 2557 (BH), 2109 (CO), 2054 (CO) cm⁻¹. EIMS, envelopes centred on m/z 367 (M⁺), 340 (M⁻ + CO), 312 (M⁻ + 2CO), 283 (M⁻ + 3CO).

[1,2-μ-(C₄H₆)-3,3-(CO)₂-3-PMe₃-3,1,2-closo-RuC₂B₉H₉] (2) and [η-[1,2-μ-(C₄H₆)]₃-3,3-(CO)₂-3,1,2-closo-RuC₂B₉H₉] (3).

A solution of [HNMe₃]₇[7,8-nido-C₄B₉H₁₀] (0.470 g, 1.91 mmol) in DCM (5 mL) was stirred under an atmosphere of CO. The solution decolourised within a few minutes. Stirring was continued overnight. Solvent was removed and the resulting colourless solid shown to be analytically pure 2 by 1H and 11B NMR spectroscopies.

[1,2-μ-(C₄H₆)-3,3-(CO)₂-3,1,2-closo-RuC₂B₉H₉] (2) and [η-[1,2-μ-(C₄H₆)]₃-3,3-(CO)₂-3,1,2-closo-RuC₂B₉H₉] (3).

A solution of [HNMe₃]₇[7,8-nido-C₄B₉H₁₀] (0.470 g, 1.91 mmol) in DCM (5 mL) was stirred under an atmosphere of CO. The solution decolourised within a few minutes. Stirring was continued overnight. Solvent was removed and the resulting colourless solid shown to be analytically pure 2 by 1H and 11B NMR spectroscopies.

Conversion of 2 → 3

(a) Chemical. Compound 2 (0.021 g, 0.054 mmol) was dissolved in DCM (10 mL) and frozen in liq. N₂. MeNO (0.004 g, 0.054 mmol) was added and the mixture warmed to room temperature and stirred for 10 min. The mixture was then passed through a short silica plug, eluting with DCM, and solvent removed to afford compound 3 (0.014 g, 73%), identified by IR and NMR spectroscopies.

(b) Thermal. Compound 2 (0.015 g, 0.31 mmol) was dissolved in THF (10 mL) and heated to reflux for 2 days, during which time the initially colourless solution turned yellow. Removal of solvent gave compound 3 (0.094 g, 89%), identified by IR and NMR spectroscopies.

Conversion of 3 → 2. A solution of compound 3 (0.014 g, 0.041 mmol) in DCM (5 mL) was stirred under an atmosphere of CO. The solution decolourised within a few minutes. Stirring was continued overnight. Solvent was removed and the resulting colourless solid shown to be analytically pure 2 by 1H and 11B NMR spectroscopies.

Compound 3 was dissolved in THF (5 mL) and the reaction mixture stirred overnight. Solvent and excess phosphine were removed in vacuo and the product purified by TLC (DCM: petrol, 1:1) to afford [1,2-μ-(C₄H₆)-3,3-(CO)₂-3-PMe₃-3,1,2-closo-RuC₂B₉H₉] (4) (0.021 g, 67%) as a colourless solid at RT. C_{28}H_{33}B_{10}O_{18}Ru requires C 28.1, H 4.43. 11B{1H} NMR, δ 5.7 (t, 2H, tether CH₂), 3.86 (d, 9H, C₆H₃CH₃), 3.07 (app. s, 4H, tether CH₂). IR, δmax at 2553 (BH), 2057 (CO), 2010 (CO) cm⁻¹. EIMS, envelopes centred on m/z 466 (M⁺), 438 (M⁻ - CO), 410 (M⁻ - 2CO).

[1,2-μ-(C₄H₆)-3,3-(CO)₂-3-P(OMe)₃-3,1,2-closo-RuC₂B₉H₉] (5)

To a solution of compound 3 (0.025 g, 0.073 mmol) in DCM (5 mL) was added, dropwise, P(OMe)₃ (0.1 mL, 0.85 mmol) and the reagents stirred for 45 min affording a pale-brown solution. Following removal of solvent in vacuo the product was purified by TLC (DCM: petrol, 1:2) to yield [1,2-μ-(C₄H₆)-3,3-(CO)₂-3-P(OMe)₃-3,1,2-closo-RuC₂B₉H₉] (5) (0.014 g, 41%) as a colourless solid at RT. C_{28}H_{33}B_{10}O_{18}Ru requires C 28.4, H 5.20. Found for C 28.9, H 5.43%. 11B{1H} NMR, δ 5.2 (1B), −4.5 (1B), −7.1 (4B), −11.0 (3B). IR, δmax at 2547 (BH), 2039 (CO), 1989 (CO) cm⁻¹. EIMS, envelopes centred on m/z 418 (M⁺), 390 (M⁻ - CO), 360 (M⁻ - 2CO).

[1,2-μ-(C₄H₆)-3,3-(CO)₂-3-P(OEt)₂-3,1,2-closo-RuC₂B₉H₉] (6)

Similarly compound 3 (0.025 g, 0.073 mmol) in DCM (5 mL) was treated with t-BuNC (0.1 mL, 0.85 mmol) resulting in immediate decolourisation. After stirring for 5 min solvent was removed in vacuo and the product was purified by TLC (DCM: petrol, 2:1) to afford [1,2-μ-(C₄H₆)-3,3-(CO)₂-3-P(OEt)₂-3,1,2-closo-RuC₂B₉H₉] (6) (0.010 g, 32%) as a colourless solid at RT. C_{30}H_{33}B₁₂O₁₀Ru requires C 36.8, H 5.70, N 3.30. Found for C 36.8, H 5.81, N 3.24%. 11B{1H} NMR, δ 4.2 (1B), −4.6 (1B), −5.9 (2B), −6.8 (2B), −10.1 (1B), −11.6 (2B). IR, δmax at 2554 (BH), 2192 (CN), 2062 (CO), 2020 (CO) cm⁻¹. EIMS, envelopes centred on m/z 424 (M⁺), 397 (M⁻ - CO), 367 (M⁻ - 2CO), 311 (M⁻ - CO - BuNC).

Improved synthesis of [1,2-μ-(C₄H₆)-1,2-closo-C₂B₁₀H₁₀] (III): [1,2-μ-(C₄H₆)-1,2-closo-C₂B₁₀H₁₀] (675 mg, 4.68 mmol) was dissolved in 35 mL of dry, degassed, 1,2-dimethoxyethane. The solution was cooled to 0 °C, n-BuLi (3.80 mL of 2.5 M solution in hexanes, 9.50 mmol) was added by syringe and the resulting white suspension stirred for 20 min. This was then frozen and CuCl (0.941 g, 9.50 mmol) added. Thawing and stirring at room temperature for 20 min afforded a dark brown suspension. Pyridine (2.7 mL) was added and the mixture stirred for a further 20 min. The green-brown mixture was frozen, 2,2-diiododiphenyl (1.90 g, 4.68 mmol) was added and a condenser fitted to the reaction vessel. After thawing, the mixture was heated at 100 °C for 70 h. The resulting maroon suspension
was cooled, diluted with 175 mL diethyl ether and stirred for 2 h. A dark solid was removed by filtration and the filtrate treated with 125 mL of 3 M hydrochloric acid. The orange organic layer was separated and washed with 2 × 150 mL H2O. Solvent was removed to give an orange solid. Column chromatography eluting with petrol gave a colourless solid. This was washed with cold petrol to remove unreacted [1,2-closo-C6B6H12] and 2,2'-diodobiphenyl, to leave [1,2-μ-(C6H4)2-1,2-closo-C6B6H10] (III) (0.772 g, 56.1%) identical to an authentic sample\(^b\) by \(^1\)H and \(^11\)B NMR spectroscopies.

\[
[\text{HNMe}_3]_2[7,8-\mu-(C_6H_4)_2-7,8-nido-C_6B_9H_9] \quad (\text{HNMe}_3)_2IV.
\]

Compound III (0.950 g, 3.22 mmol) and KOH (0.460 g, 8.15 mmol) in EtOH (60 mL) were heated to reflux for 20 h. After cooling to room temperature CO2 was bubbled through the solution to precipitate excess KOH as K2CO3, subsequently removed by filtration. The filtrate was evaporated to afford a yellow solid which was then dissolved in 10 mL H2O and filtered. To the filtrate was added [HNMe3]Cl (0.960 g, 10.00 mmol) in 10 mL H2O. The resulting precipitate was collected by filtration, washed with H2O then EtO and dried in vacuo to afford [HNMe3]2[7,8-μ-(C6H4)2-7,8-nido-C6B9H9] (HNMe3)IV as an off-white solid (0.690 g, 62%). C14H32B9N requires C 59.4, H 8.21, N 4.08. Found for [HNMe3]IV C 58.3, H 7.93, N 3.77%. \(^{11}\)B\(^{(1)}\)H NMR \([\text{CD}_3]_2\text{CO}\), \(\delta = -6.7\) (2B), -15.5 (1B), -17.0 (2B), -18.3 (2B), -31.9 (1B), -36.6 (1B). \(^1\)H NMR \([\text{CD}_3]_2\text{CO}\), \(\delta = 8.61\) (br. s, 1H, NH), 7.65 (m, 2H, tether CH), 7.41 (m, 2H, tether CH), 7.06 (m, 4H, tether CH). 3.04 (s, 9H, CH3).

[1,2-μ-(C6H4)2-3-Cp-3,1,2-closo-CoC6B9H9] (7). [HNMe3]IV (0.150 g, 0.44 mmol) in THF (15 mL) was treated with n-ButLi (0.35 mL of 2.5 M solution in hexanes, 0.88 mmol) and the resultant yellow solution stirred for 40 min then frozen in liq. N2. NaCp (0.65 mL of 2 M solution in THF, 1.30 mmol) and CoCl2 (0.200 g, 1.54 mmol) were added and the mixture allowed to warm to room temperature. Following overnight stirring the brown solution was aerobically oxidised for 30 min and then volatiles removed in vacuo. Column chromatography eluting with DCM : petrol 1 : 1 yielded a major yellow band at \(R_f\) 0.61, from which \([1,2-\mu-(C_6H_4)_2-3-Cp-3,1,2-closo-CoC_6B_9H_9]\) (7) was isolated as an orange-yellow solid (0.080 g, 45%). C13H27B9Co requires C 56.1, H 5.45. Found for 7 C 55.0, H 5.47%. \(^{11}\)B\(^{(1)}\)H NMR, \(\delta = 4.7\) (1B), 3.3 (1B), -2.5 (2B), -6.4 (2B), -11.5 (2B), -13.4 (1B). \(^1\)H NMR, \(\delta = 8.16\) (m, 2H, tether CH), 7.71 (m, 2H, tether CH), 7.43 (m, 4H, tether CH), 4.77 (s, 5H, C6H5). EIMS, envelope centred on \(m/z\) 407 (M\(^+\)).

\[\text{[1,2-\mu-(C_6H_4)_2-3,3,3-(CO)_3-3,1,2-closo-RuC_6B_9H_9]} \quad (8) \quad [\text{HNMe}_3]IV (0.094 g, 0.27 mmol) in THF (10 mL) was treated with n-ButLi (0.22 mL of 2.5 M solution in hexanes, 0.55 mmol) and stirred for 25 min. This solution was then droppedwise to a stirring solution of [Ru(CO)C12], 0.070 g, 0.14 mmol) in THF (10 mL) at 0 °C to afford an orange solution. This was allowed to warm to room temperature and the solvent removed in vacuo. The solid residue was dissolved in DCM and passed through a short silica plug. The filtrate was concentrated and finally purified by TLC (DCM : petrol, 1 : 4) to afford \([1,2-\mu-(C_6H_4)_2-3,3,3-(CO)_3-3,1,2-closo-RuC_6B_9H_9]} \quad (8) \quad (R_f, 0.35, trace) as a yellow solid. \(^{11}\)B\(^{(1)}\)H NMR, \(\delta = 8.2\) (1B), -1.2 (1B), 2.1 1.2 (2B), 4.8 (1B), 3.2 (1B), 7.62 (m, 2H, tether CH), 7.41 (m, 2H, tether CH), 4.77 (s, 5H, C6H5).

<table>
<thead>
<tr>
<th>Formula</th>
<th>(\text{C}<em>{95}H</em>{13}B_{9}O_{3}Ru)</th>
<th>(\text{C}<em>{95}H</em>{15}B_{9}O_{3}Ru)</th>
<th>(\text{C}<em>{85}H</em>{15}B_{9}O_{2}Ru)</th>
<th>(\text{C}<em>{115}H</em>{24}B_{9}O_{2}PRu)</th>
<th>(\text{C}<em>{115}H</em>{24}B_{9}O_{5}PRu)</th>
<th>(\text{C}<em>{135}H</em>{24}B_{9}O_{2}PRu)</th>
<th>(\text{C}<em>{195}H</em>{22}B_{9}Co)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>367.55</td>
<td>369.57</td>
<td>341.56</td>
<td>417.63</td>
<td>465.60</td>
<td>424.69</td>
<td>406.58</td>
</tr>
<tr>
<td>(a/Å)</td>
<td>8.9837(9)</td>
<td>10.829(7)</td>
<td>11.290(2)</td>
<td>13.332(10)</td>
<td>15.8356(7)</td>
<td>17.9446(7)</td>
<td>13.2284(8)</td>
</tr>
<tr>
<td>(b/Å)</td>
<td>27.262(3)</td>
<td>9.115(5)</td>
<td>8.5139(15)</td>
<td>9.525(8)</td>
<td>7.9871(4)</td>
<td>13.4065(7)</td>
<td>10.3136(10)</td>
</tr>
<tr>
<td>(c/Å)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>115.178(5)</td>
<td>102.484(2)</td>
<td>12.1827(5)</td>
<td>10.3514(10)</td>
</tr>
<tr>
<td>(α/°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(β/°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(γ/°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>(U/Å^3)</td>
<td>3013.0(6)</td>
<td>1533.6(17)</td>
<td>684.1(2)</td>
<td>947.5(13)</td>
<td>985.22(8)</td>
<td>2001.85(14)</td>
<td>3803.5(4)</td>
</tr>
<tr>
<td>(D)</td>
<td>0.63</td>
<td>0.52</td>
<td>0.74</td>
<td>2.64</td>
<td>2.09</td>
<td>0.38</td>
<td>0.35</td>
</tr>
<tr>
<td>(μ/\text{mm}^2/Å^2)</td>
<td>0.0546</td>
<td>0.0254</td>
<td>0.0236</td>
<td>0.0470</td>
<td>0.0433</td>
<td>0.0409</td>
<td>0.0778</td>
</tr>
<tr>
<td>Crystallographic data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
−4.7 (2B), −6.3 (2B), −6.9 (2B), −9.0 (1B). $^1$H NMR, δ 8.10 (m, 2H, tether CH$_2$), 7.55 (m, 2H, tether CH$_2$), 7.39 (m, 4H, tether CH). IR, $v_{max}$ at 2557 (BH), 2110 (CO), 2056 (CO) cm$^{-1}$. EIMS, envelopes centred on m/z 468 (M$^+$), 440 (M$^+$−CO), 412 (M$^+$−2CO), 384 (M$^+$−3CO).

**Crystallography**

Diffraction-quality crystals of all compounds studied were grown from slow diffusion of a concentrated DCM solution of the compound and petrol at −30 °C.

Intensity data were collected on a Bruker X8 APEXII diffractometer using Mo-K$_x$ X-radiation, with crystals mounted in inert oil on a cryoloop and cooled to 100 K (200 K in the case of 6) by an Oxford Cryosystems Cryostream. Indexing, data collection and absorption correction were performed using the APEXII suite of programs. Using OLEX2 structures were solved using the olex2.solve, SHELXS or SHELXT programmes and refined by full-matrix least-squares (SHELXL). All crystals were single and free of solvate, and all are fully ordered except for 1 (two rotational conformers of the [Ru(CO)$_3$] fragment) of equal effective population [SOF for CO ligands labelled A 0.5010(16), SOF for CO ligands labelled B 0.4990(16)] and 6 [two rotational conformers of the r-Bu unit, one major, SOF = 0.776(13), and one minor, SOF = 0.224(13)]. In 5 there is a large peak of residual electron density within 1 Å of the metal atom but this could not be sensibly modelled. In 7 the space group is noncentrosymmetric and the Flack parameter, 0.49(2), suggests a racemate, but this is fully consistent with the fact that both crystallographically independent molecules have effective $C_s$ symmetry. All other structures were free of complications.

For all structures H atoms bound to B atoms were allowed to refine positionally whilst H atoms bound to C atoms were constrained to idealised geometries; C$_{methyl}$−H = 0.95 Å, C$_{methylene}$−H = 0.98 Å, C$_{C}$ bonded to $M^+$−H = 1.00 Å. All H displacement parameters, $U_{iso}$, were constrained to be $1.2 \times U_{eq}$ (bound B or C) except Me H atoms [$U_{iso}(H) = 1.5 \times U_{eq}$ C(Me)]. Table 4 contains further experimental details.

**Acknowledgements**

We thank the EPSRC for a DTP Studentship supporting SLP.

**References**

18 D. Ellis, P. Jelliss and F. G. A. Stone, private communication to CSD, 2000 (CCDC 140550).