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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*

Abstract

Detailed comparison of the molecular structures of [1,2-µ-(C₆H₆)-3,3,3-(CO)₃-3,1,2-closo-
RuC₂B₄H₆] (1) and [1,2-µ-(C₆H₆)-3,3,3-(CO)₃-3,1,2-closo-RuC₂B₄H₆] (2) reveals evidence for an enhanced structural carborane effect in 1 arising from the involvement of the cage pz orbitals in the exopolyhedral ring to some degree. A minor co-product in the synthesis of 2 is
[1,2-µ-(C₆H₆)-3,3,3-(CO)₃-3,1,2-closo-RuC₂B₄H₆] (3). Compounds 2 and 3 are readily interconverted, since heating 2 to reflux in THF or reaction with Me₃NO affords 3 which readily reacts with CO to regenerate 2. The η-ene bonding in 3 is also displaced by PMe₃, P(OMe)₃ and t-BuNC to yield [1,2-µ-(C₆H₆)-3,3,3-(CO)₃-3-PMe₃-3,1,2-closo-RuC₂B₄H₆] (4), [1,2-µ-(C₆H₆)-3,3,3-(CO)₃-3-P(OMe)₃-3,1,2-closo-RuC₂B₄H₆] (5) and [1,2-µ-(C₆H₆)-3,3,3-(CO)₃-3-t-BuNC-3,1,2-closo-RuC₂B₄H₆] (6), respectively. Structural studies of 4-6, focussing on the exopolyhedral ligand orientation of the {Ru(CO)₃L} fragment relative to the C₂B₃ carborane face, are discussed in terms of the structural trans effects of PMe₃, P(OMe)₃, and t-BuNC relative to that of CO. An improved synthesis of [1,2-µ-(C₆H₆)-1,2-closo-C₂B₁₀H₁₀], “biphenylcarborane”, is reported following which the first transition-metal derivatives of this species, [1,2-µ-(C₆H₆)-3-Cp-3,1,2-closo-CoC₂B₄H₆] (7) and [1,2-µ-(C₆H₆)-3,3,3-(CO)₃-3,1,2-closo-RuC₂B₄H₆] (8), are prepared. Comparisons of the structures of 7 and 8 with the corresponding benzocarborane derivatives [1,2-µ-(C₆H₆)-3-Cp-3,1,2-closo-CoC₂B₄H₆] and 1, respectively, suggest that Clar’s rule for aromaticity can be applied to polycyclic aromatic hydrocarbons fused onto carborane cages.

† Electronic supplementary information (ESI) available: NMR spectra of all new compounds reported. CCDC 1479545-1479552. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/xxxxxxxxxx
**Introduction**

We recently named the phenomenon whereby cage C atoms in metallacarboranes of the type 3,1,2-closo-MC₂B₉H₁₁ 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).¹ This arises when an exopolyhedral \{C₄H₄\} diene tethers the two carborane C atoms allowing the \(p_\pi\) orbitals of the cage C atoms to participate in a pseudoaromatic C₆ 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 \(p_\pi\) 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, [1,2-\(\mu\)-(C₄H₄)-1,2-closo-C₂B₁₀H₁₀] (“benzocarborane”, I, Fig. 1) and [1,2-\(\mu\)-(C₄H₆)-1,2-closo-C₂B₁₀H₁₀] (“dihydrobenzocarborane”, II, Fig. 1) as one pair,³ and their \{CoCp\} derivatives [1,2-\(\mu\)-(C₄H₄)-3-Cp-3,1,2-closo-CoC₂B₉H₉] (I-Co) and [1,2-\(\mu\)-(C₄H₆)-3-Cp-3,1,2-closo-CoC₂B₉H₉] (II-Co) as the other.¹ Although the differences were small they were significant – in the compounds with the \{C₄H₄\} tether the C₆-C₆ distances were shorter, than those in the compounds with the \{C₄H₆\} tether, providing firm evidence for an ESCE.

Seeking to extend this work we herein describe the synthesis and complete characterisation, including structural studies, of \{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 \{C₄H₆\} tricarbonyl compound can be interconverted with an \(\eta_1\)-(C₄H₆)(CO)₂ species and we have explored substitution of the ene of the latter compound with various 2e donor ligands. Finally we have prepared and characterised the first examples of metal derivatives of [1,2-\(\mu\)-(C₆H₄)₂-1,2-closo-C₂B₁₀H₁₀], “biphenylcarborane”. Analysis of their structures in comparison with those of analogous metal complexes of benzocarborane provides evidence that the three fused C₆ rings in biphenylcarborane can be discussed in terms of the Clar structure of phenanthrene.


Results and Discussion

The [HNMe$_3$]$^+$ salt of [7,8-μ-(C$_4$H$_6$)-7,8-nido-C$_2$B$_9$H$_{10}$]$^-$ (deboronated I) was synthesised analogously to the [HNMe$_3$]$^+$ salt of [7,8-μ-(C$_4$H$_6$)-7,8-nido-C$_2$B$_9$H$_{10}$]$^-$ (deboronated II). Deprotonation of the former followed by reaction with [Ru(CO)$_3$Cl$_2$)$_2$ in THF and work-up involving thin-layer chromatography (TLC) afforded, in low yield, the yellow compound [1,2-μ-(C$_4$H$_6$)-3,3,3-(CO)$_3$-3,1,2-closo-RuC$_2$B$_9$H$_9$] (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 [NMe$_4$][1,2-μ-(C$_4$H$_6$)-3,3,3-(CO)$_3$-3,1,2-closo-MnC$_2$B$_9$H$_9$], a direct analogue of 1, has previously been reported but no structural study performed.

A perspective view of a single molecule of 1 is shown in Fig. 2. The molecule is partially disordered in that there are two different conformations of the {Ru(CO)$_3$} fragment leading to six effectively half-occupied CO ligands, only one set of three (the A set) being arbitrarily shown in Fig. 2. The molecule has effective C$_5$ symmetry about the plane passing through Ru3, B6, B10 and B8.

Key molecular parameters in compounds 1 and 2 are compared in Table 1. Both the $<$C$_{cage}$−Ru$>$ and $<$C$_{cage}$−B6$>$ distances are significantly shorter [differences 0.042(3) and 0.015(4) Å, respectively] and the C1−C2 distance significantly longer [difference 0.036(4) 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 $p_z$ 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 1-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 11B and 1H NMR spectra implied retention of C, symmetry, but in the 1H spectrum the resonance for the CH atoms had moved upfield, from δ 5.83 ppm in 2 to δ 4.09 ppm in 3. Collectively, these data were consistent with displacement of one CO ligand by an η1-co-ordinated {HC=CH} unit, and this was confirmed by a crystallographic study (Fig. 4).

Thus compound 3 is [η1-{1,2-µ3-(C6H5)}-3,3-(CO)2-3,1,2-closo-RuC2B9H8] in which, formally, the C4=C5 ene unit in the tether has displaced the C31O31 ligand of 2, and the ability of the exopolyhedral C3H6 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 η1-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-µ3-(C6H5)-7,8-nido-C2B9H8]2− is treated with a source of {Ru(CO)3}2+ 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 tricarbonyl 2 is readily converted into the dicarbonyl/ene 3 by reaction with Me2NO in CH2Cl2 or simply by heating to reflux in THF. In reverse, compound 3 is quantitatively converted into 2 by reaction with CO.

The η1-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-µ3-(C6H5)-3,3-(CO)2-3-PMe3-3,1,2-closo-RuC2B9H8] (4), [1,2-µ3-(C6H5)-3,3-(CO)2-3-P(OMe)3-3,1,2-closo-RuC2B9H8] (5) and [1,2-µ3-(C6H5)-3,3-(CO)2-3-t-
Compounds 4-6 were fully characterised by elemental analysis, mass spectrometry, and IR and $^1$H, $^{11}$B and (for 4 and 5) $^{31}$P 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)$_2$L] fragment with respect to the carborane cage so finally all three compounds were subjected to X-ray diffraction studies. Figs. 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 CH$_2$ 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).

An obvious extension of the chemistry of benzocarborane I would be to consider analogues in which the C$_6$ 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′-BrC$_6$H$_4$)$_2$-1,2-closo-C$_2$B$_{10}$H$_{10}$ to afford the compound [1,2-μ-(C$_6$H$_4$)$_2$-1,2-closo-C$_2$B$_{10}$H$_{10}$] (“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 $\pi$-sextets is a better description of the molecule than structure A with only one central $\pi$-sextet. 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 C$_{cage}$−B and C$_{cage}$−C$_{cage}$ 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 C$_6$ ring of III and consequently less of a ESCE (hence shorter C$_{cage}$−B) but more localised double-bond character in the C$_{cage}$−C$_{cage}$ link (hence shorter C$_{cage}$−C$_{cage}$).

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]⁺ salt. No metal derivatives are currently known. However, because the original synthesis of III is poor-yielding (ca. 7% based on B₁₀H₁₄), we have first developed an improved synthesis. Double deprotonation of 1,2-closo-C₃B₁₀H₁₂ followed by addition of CuCl/pyridine and then 2,2’-diiodobiphenyl, following the general procedure developed by Fox et al., 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] ([HNMe₃]IV). From this we have subsequently prepared the {CoCp} species [1,2-µ-(C₆H₄)₂-3-Cp-3,1,2-closo-CoC₂B₉H₆] (7) and the {Ru(CO)₃} species [1,2-µ-(C₆H₄)₂-3,3,3-(CO)₃-3,1,2-closo-RuC₂B₉H₆] (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 Figs. 10 and 11, respectively.

Key average molecular dimensions for 7 and 8 are given in Table 1. In comparison with I-Co compound 7 shows evidence of a reduced ESCE (shorter C₉-Co and C₉-B₆ distances) consistent with less aromaticity in the central C₆ 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 C₉-B₆ distances in the former, but this time the C₉-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 I-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 {RuL₃} fragment attached to a carbons-adjacent C₂B₉ carborane ligand. In 1, 2 and 8 the metal fragment is {Ru(CO)₃} whilst in 3-6 the metal fragment is {Ru(CO)₂L}. 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.
There are five examples of \( [3,3,3-(CO)_33,1,2-closo-MC_2B_9H_{11}] \) species in the Cambridge Structural Database (CSD),\(^{11} \) 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 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 \( \{\text{Ru}(CO)_3\} \) fragments in 1A, 1B, 2 and 8 projected onto the C_2B_3 carborane face.

The orientation of the \( \{\text{Ru}(CO)_3\} \) 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 \( \{\text{M}(CO)_2L\} \) fragment is bonded to a (C_2B_9H_{11}) carborane ligand as the 3,1,2-MC_2B_9 isomer, and selected data on these are collected in Table 4. 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 \( \{\text{M}(CO)_2L\} \) 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\_2B\_3 carborane face.

As we have already noted,\textsuperscript{10} for a conical metal fragment with dissimilar ligands bonded to a carbons-adjacent carborane the \textit{Expolyhedral 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 lidand is CO (SnR\_3 is well-recognised as having a strong structural trans effect),\textsuperscript{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 measureably longer M–CO bond.

In compound 3 the weaker exopolyhedral ligand (C=C) is constrained to have a low \(\theta_L\) value because it is incorporated in the exopolyhedral C\_6 cycle; again this results in structurally-equivalent CO ligands. The structure of 4, with \(\theta_L\) 123.7°, implies that, at least in this compound, PMe\_3 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) vs. 1.895(3) Å. P(OMe)\_3, a weaker donor but stronger acceptor ligand than PMe\_3, 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 \(\theta_{CO}\) significantly the shorter. In contrast, the orientation of the \{Ru(CO)\_2L\} set in the \(t\)-butylisocyanide compound 6 is quite different. Here the \(t\)-BuNC ligand clearly has the weaker structural trans effect since \(\theta_L\) 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 \(\eta\)-ene compound 3 is afforded from 2 by thermolysis or reaction with Me\_3NO and is converted into 2 by treatment with CO. The \(\eta\)-ene interaction is also displaced by PMe\_3, P(OMe)\_3 and \(t\)-BuNC, and structural studies of the products of these reactions (compound 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.

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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 (3xfreeze-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 (13P) 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-C₂B₆H₁₀] was prepared by literature methods, and [HNMe₃][7,8-µ-(C₄H₄)-7,8-nido-C₂B₆H₁₀] was prepared analogously. All other reagents were supplied commercially.

[1,2-µ-(C₄H₄)-3,3,3-(CO)₃]-3,1,2-closo-RuC₂B₆H₆] (1). n-BuLi (0.65 mL of 2.5M solution in hexanes, 1.63 mmol) was added dropwise at 0 °C to a solution of [HNMe₃][7,8-µ-(C₄H₄)-7,8-nido-C₂B₆H₁₀] (0.18 g, 0.74 mmol) in THF (10 mL) to afford a bright yellow solution. This was added dropwise to a solution of [Ru(CO)₂Cl₂] (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-(CO)₃]-3,1,2-closo-RuC₂B₆H₆] (1) (0.021 g, 8%) as a yellow solid at Rₜ 0.58. C₈H₃B₆O₃:Ru requires C 29.4, H 3.56. Found for 1 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 CH₂), 6.05 (m, 2H, tether CH₂). IR, ν_max 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-(C₄H₄)-3,3,3-(CO)₃]-3,1,2-closo-RuC₂B₆H₆] (2) and [η-(1,2-µ-(C₄H₄)-3,3-(CO)₂]-3,1,2-closo-RuC₂B₆H₆] (3). A solution of [HNMe₃][7,8-µ-(C₄H₄)-7,8-nido-C₂B₆H₁₀] (0.470 g, 1.91 mmol) in THF (25 mL) at 0 °C was treated with n-BuLi (1.55 mL of 2.5M solution in hexanes, 3.88 mmol) and then stirred for 40 min. at room temperature. The resulting orange solution was added dropwise to a solution of [Ru(CO)₂Cl₂] (0.490 g, 0.96 mmol) in THF (25
mL) at 0 °C. Immediately following addition the orange solution was removed from the cooling bath and the solvent removed in vacuo. The residue was dissolved in a 2:1 mixture of DCM and petrol and eluted through a short silica plug. The solution was reduced in volume and purified by preparative TLC (DCM:petrol, 1:2) to afford [1,2-µ-(C₅H₅)₃,3,3-(CO)₂,3,1,2-closo-RuC₂B₃H₆] (2) (Rf 0.52, 0.174 g, 25%) as a colourless solid and [η-{1,2-µ-(C₅H₅)}-3,3-(CO)₂,3,1,2-closo-RuC₂B₃H₆] (3) (Rf 0.31, 0.028 g, 4%) as a yellow solid.

2: C₅H₅B₉O₃Ru requires C 29.3, H 4.09. Found for 2 C 28.3, H 4.28%. ¹¹B{¹H} NMR, δ 8.3 (1B), -3.8 (1B), -5.1 (4B), -8.5 (1B), -9.9 (2B). ¹H NMR, δ 5.83 (app. s, 2H, tether CH), 3.18 (app. d, 2H, tether CH₂), 3.00 (app. d, 2H, tether CH₂). IR, νmax at 2575 (BH), 2102 (CO), 2051 (CO), 2044 (CO) cm⁻¹. EIMS, envelopes centred on m/z 369 (M⁺), 342 (M⁺-CO), 313 (M⁺-2CO), 283 (M⁺-3CO).

3: C₅H₅B₉O₃Ru requires C 28.1, H 4.43. Found for 3 C 27.4, H 4.36%. ¹¹B{¹H} NMR, δ 8.1 (1B), 0.9 (1B), -4.1 (2B), -7.1 (2B), -10.1 (1B), -17.7 (2B). ¹H NMR, δ 4.09 (m, 2H), 3.70 (d, 2H), 3.44 (m, 2H). IR, νmax at 2559 (BH), 2064 (CO), 2021 (CO) cm⁻¹. EIMS, envelopes centred on m/z 342 (M⁺), 313 (M⁺-CO), 283 (M⁺-2CO).

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. Me₃NO (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 (0.115 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.

[1,2-µ-(C₅H₅)-3,3-(CO)₂,3-PMe₃,3,1,2-closo-RuC₂B₃H₆] (4). PMe₃ (0.73 mL of 1.0M solution in THF, 0.73 mmol) was added dropwise to compound 3 (0.025 g, 0.073 mmol) in DCM (5 mL) and the reaction mixture stirred overnight. Solvent and excess phosphine was removed in vacuo and the product purified by TLC (DCM:petrol, 1:1) to afford [1,2-µ-(C₅H₅)-3,3-(CO)₂,3-PMe₃,3,1,2-closo-RuC₂B₃H₆] (4) (0.021 g, 67%) as a colourless solid at Rf 0.56. C₁₁H₁₂B₉O₃PRu requires C 31.6, H 5.79. Found for 4 C 31.2, H 5.88%. ¹¹B{¹H} NMR, δ 2.2 (1B), -5.2 (3B), -7.2 (2B), -9.4 (1B), -12.4 (2B). ¹H NMR, δ 5.73 (app. s, 2H, tether CH), 3.08 (d, 2H, tether CH₂), 2.93 (d, 2H, tether CH₂), 1.85 (d, 9H, CH₃). ³¹P{¹H} NMR, δ 11.08 (s)
IR, $\nu_{\text{max}}$ at 2547 (BH), 2039 (CO), 1989 (CO) cm$^{-1}$. EIMS, envelopes centred on $m/z$ 418 (M$^+$), 390 (M$^+$-CO), 360 (M$^+$-2CO).

$[\text{1,2-\mu-(C}_5\text{H}_4]-3,3,3,3\text{-}(\text{CO}-2\text{-P(OMe)}_3)-3,1,2\text{-closos-RuC}_2\text{B}_3\text{H}_6]$ (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 $[\text{1,2-\mu-(C}_5\text{H}_4]-3,3,3,3\text{-}(\text{CO}-2\text{-P(OMe)}_3)-3,1,2\text{-closos-RuC}_2\text{B}_3\text{H}_6]$ (5) (0.014 g, 41%) as a colourless solid at $R_f$ 0.35. $C_{11}H_{24}B_3O_3$PRu requires C 36.8, H 5.72, N 3.30. Found for 5 C 36.8, H 5.81, N 3.24$.  $^{11}$B $\{^1$H$\}$ NMR, $\delta$ 4.2 (1B), -4.6 (1B), -6.8 (2B), -10.1 (1B), -11.6 (2B). $^1$H NMR, $\delta$ 5.72 (t, 2H, tether CH), 3.86 (d, 9H, CH$_3$), 3.07 (app. s, 4H, tether CH$_2$). $^{31}$P $\{^1$H$\}$ NMR, $\delta$ 133.75 (s). IR, $\nu_{\text{max}}$ at 2553 (BH), 2057 (CO), 2010 (CO) cm$^{-1}$. EIMS, envelopes centred on $m/z$ 466 (M$^+$), 438 (M$^+$-CO), 410 (M$^+$-2CO).

$[\text{1,2-\mu-(C}_5\text{H}_4]-3,3,3,3\text{-}(\text{CO}-2\text{-t-BuNC}-3,1,2\text{-closos-RuC}_2\text{B}_3\text{H}_6]$ (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 $[\text{1,2-\mu-(C}_5\text{H}_4]-3,3,3,3\text{-}(\text{CO}-2\text{-t-BuNC}-3,1,2\text{-closos-RuC}_2\text{B}_3\text{H}_6]$ (6) (0.010 g, 32%) as a colourless solid at $R_f$ 0.32. $C_{13}H_{32}B_3O_3$PRu requires C 36.8, H 5.70, N 3.30. Found for 5 C 36.8, H 5.81, N 3.24$.  $^{11}$B $\{^1$H$\}$ NMR, $\delta$ 4.2 (1B), -4.6 (1B), -5.9 (2B), -6.8 (2B), -10.1 (1B), -11.6 (2B). $^1$H NMR, $\delta$ 5.72 (app. s, 2H, tether CH), 3.10 (app. d, 2H, tether CH$_2$), 2.97 (app. d, 2H, tether CH$_2$), 1.58 (s, 9H, CH$_3$). IR, $\nu_{\text{max}}$ at 2545 (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$^+$-3CO -BuNC).

**Improved synthesis of $[\text{1,2-\mu-(C}_5\text{H}_4]-2,1,2\text{-closos-C}_2\text{B}_{10}\text{H}_{10}]$ (III).** $[\text{1,2-closos-C}_2\text{B}_{10}\text{H}_{12}]$ (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 2.5M solution in hexanes, 9.50 mmol) was added by syringe and the resulting white suspension stirred for 20 min. This was then was 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’-diodobiphenyl (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 3M hydrochloric acid. The orange organic layer was separated and washed with 2×150 mL H$_2$O. 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 $[\text{1,2-closos-C}_2\text{B}_{10}\text{H}_{12}]$ and 2,2’-diodobiphenyl, to leave $[\text{1,2-\mu-(C}_5\text{H}_4]-2,1,2\text{-closos-}$
C₂B₁₀H₁₀ (III) (0.772 g, 56.1%) identical to an authentic sample by ¹H and ¹¹B NMR spectroscopies.

[HNMe₃][7,8-μ-(C₃H₄)₂-7,8-nido-C₂B₉H₁₀] ([HNMe₃]IV). 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 Et₂O and dried in vacuo to afford [HNMe₃][7,8-μ-(C₃H₄)₂-7,8-nido-C₂B₉H₁₀] ([HNMe₃]IV) as an off-white solid (0.690 g, 62%). C₁₇H₂₆B₉N requires C 59.4, H 8.21, N 4.08. Found for [HNMe₃]IV C 58.3, H 7.93, N 3.77%. ¹¹B{¹H} NMR [(CD₃)₂CO], δ -6.7 (2B), -15.5 (1B), -17.0 (2B), -18.3 (2B), -31.9 (1B), -36.6 (1B). ¹H NMR [(CD₃)₂CO], δ 8.61 (br. s, 1H, NH), 7.85 (m, 2H, tether CH), 7.41 (m, 2H, tether CH), 7.06 (m, 4H, tether CH), 3.04 (s, 9H, CH₃).

[1,2-μ-(C₃H₄)₂-3-Cp-3,1,2-closo-CoC₂B₉H₆] (7). [HNMe₃]IV (0.150 g, 0.44 mmol) in THF (15 mL) was treated with n-BuLi (0.35 mL of 2.5M 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 2M 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 aerily oxidised for 30 min. and then volatiles removed in vacuo. Column chromatography eluting with DCM:petrol 1:1 yielded a major yellow band at Rₜ 0.61, from which [1,2-μ-(C₃H₄)₂-3-Cp-3,1,2-closo-CoC₂B₉H₆] (7) was isolated as an orange-yellow solid (0.080 g, 45%). C₁₉H₂₅B₉Co requires C 56.1, H 5.45. Found for 7 C 55.0, H 5.47%. ¹¹B{¹H} NMR, δ 4.7 (1B), 3.3 (1B), -2.5 (2B), -6.4 (2B), -11.5 (2B), -13.4 (1B). ¹H NMR, δ 8.16 (m, 2H, tether CH), 7.71 (m, 2H, tether CH), 7.43 (m, 4H, tether CH), 4.77 (s, 5H, CpH₃). EIMS, envelope centred on m/z 407 (M⁺).

[1,2-μ-(C₃H₄)₂-3,3,3-(CO)₃-3,1,2-closo-RuC₂B₉H₆] (8). [HNMe₃]IV (0.094 g, 0.27 mmol) in THF (10 mL) was treated with n-BuLi (0.22 mL of 2.5M solution in hexanes, 0.55 mmol) and stirred for 25 min. This solution was then added dropwise to a stirring solution of [Ru(CO)₃Cl₂] (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-μ-(C₃H₄)₂-3,3,3-(CO)₃-3,1,2-closo-RuC₂B₉H₆] (8) (Rₜ 0.35, trace) as a yellow solid. ¹¹B{¹H} NMR, δ 8.2 (1B), -1.2 (1B), -4.7 (2B), -6.3 (2B), -6.9 (2B), -9.0 (1B). ¹H NMR, δ 8.10 (m, 2H, tether CH), 7.55 (m,
2H, tether CH), 7.39 (m, 4H, tether CH). IR, \( \nu_{\text{max}} \) 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\(_\alpha\) 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.\(^{22}\) Using OLEX2\(^\text{23}\) structures were solved using the olex2.solve,\(^\text{24}\) SHELXS\(^\text{25}\) or SHELXT\(^\text{26}\) programmes and refined by full-matrix least-squares (SHELXL).\(^\text{25}\)

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 effectively equal 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 \( t \)-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; \( C_{\text{aryl}} - H = 0.95 \, \text{Å} \), \( C_{\text{methyl}} - H = 0.98 \, \text{Å} \), \( C_{\text{methylene}} - H = 0.99 \, \text{Å} \), \( C_{\eta} \)-bonded to M - H = 1.00 Å. All H displacement parameters, \( U_{\text{iso}} \), were constrained to be 1.2×\( U_{\text{eq}} \) (bound B or C) except Me H atoms [\( U_{\text{iso}}(H) = 1.5 \times U_{\text{eq}}(\text{C(Me)}) \). Table 4 contains further experimental details.

<Table 4 near here>
Scheme 1  Synthesis of compound 1.
Scheme 2 Synthesis of compounds 2 and 3.
Scheme 3  Interconversion of compounds 2 and 3, and transformation of 3 into 4-6 (4, L = PMe$_3$; 5, L = P(OMe)$_3$; 6, L = t-BuNC).
Scheme 4  Synthesis of compounds 7 ([M] = CoCp) and 8 ([M] = Ru(CO)₃).
Fig. 1  Benzocarborane (I), dihydrobenzocarborane (II) and their \{\text{CoCp}\} derivatives I-Co and II-Co.
Fig. 2  Perspective view of compound 1 with atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level except for H atoms. Only one component of the disordered \{\text{Ru(CO)}_3\} fragment shown.
Fig. 3  Perspective view of compound 2 with atomic numbering scheme. The molecule has crystallographically-imposed $C_s$ symmetry. Displacement ellipsoids as in Fig. 2.
Fig. 4  Perspective view of compound 3 with atomic numbering scheme. Displacement ellipsoids as in Fig. 2.
**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.
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.
**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.
Fig. 12 Generalised representation of [3-L-3,1,2-closo-MC$_2$B$_9$H$_{11}$]. The θ value of the ligand L is defined by the torsion angle L−M−A−B, where A is the centroid of the metal-bound C$_2$B$_3$ face (green dot) and B is the centroid of the Cl−C2 connectivity (purple dot).
**Fig. 13** The orientations of the \( \{\text{Ru(CO)}_2\text{L}\} \) fragments of compounds 1, 2 and 8 projected onto the C\(_2\)B\(_3\) carborane ligand face, together with Ru–CO distances (Å). 1A and 1B are both compound 1 with alternative sets of (disordered) CO ligands.
The orientations of the \{Ru(CO)\_2L\} fragments of compounds 3-6 projected onto the C\_2B\_3 carborane ligand face, together with Ru–CO distances (Å).
Table 1  Selected molecular parameters \(^a\) (Å) in the \{CoCp\} compounds II-Co, I-Co and 7 and in the \{Ru(CO)\(_3\)\} compounds 2, 1 and 8

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<th>Compound</th>
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<th>&lt;C(_{\text{cage}})-B6&gt;</th>
<th>&lt;C(_1)-C(_2)&gt;</th>
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<td>1.6388(16)</td>
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<tr>
<td>7</td>
<td>2.042(14)</td>
<td>1.750(10)</td>
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<tr>
<td>2</td>
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<td>1.6627(19)</td>
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<tr>
<td>1</td>
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<tr>
<td>8</td>
<td>2.3538(13)</td>
<td>1.7452(20)</td>
<td>1.5963(12)</td>
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\(^a\) E.s.d.s of the mean of \(N\) independent observations given by the expression \(\sigma^2 = (\sigma_1^2+\sigma_2^2)\) for \(N = 2\), and \(\sigma^2 = \{\sum (\chi_i - \chi_N)^2\}/(N - 1)\) where \(\chi_i\) is the \(i^{th}\) and \(\chi_N\) the mean value for \(N > 2\).
Table 2  Dihedral angle $\theta$ (°) and M–CO distances (Å) for literature [3,3,3-(CO)$_3$-3,1,2-closo-MC$_2$B$_9$H$_{11}$]$^\text{v}$ structures and for compounds 1, 2 and 8

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<th>CSD code / Compound</th>
<th>M, x</th>
<th>$\theta$, M–CO</th>
<th>$\theta$, M–CO</th>
<th>$\theta$, M–CO</th>
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<td>62.8, 1.9804(10)</td>
<td>178.0, 1.8909(10)</td>
<td>this work</td>
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$^a$ no e.s.d.s on atomic coordinates. E.s.d.s on bond distances only estimated.

$^b$ 1A and 1B are both compound 1 with alternative sets of (disordered) CO ligands.

$^c$ by symmetry.
Table 3 Ligand $L$, dihedral angle $\theta_L$ (°), $\theta_{CO}$ (°) and M–CO distances (Å) for literature [3-L-3,3-(CO)$_2$-3,1,2-closo-MC$_2$B$_9$H$_{11}$] structures and for compounds 3-6

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<th>CSD code / Compound</th>
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<th>L</th>
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$a$ using the centre of the C≡C bond in the calculation of $\theta_L$.

$b$ two independent Ru centres.

$c$ using the centre of the C=C bond in the calculation of $\theta_L$. 
### Table 4  Crystallographic data.

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References