Unprecedented flexibility of the 1,1′-bis(*o*-carborane) ligand: catalytically-active species stabilised by B-agostic B–H→Ru interactions †‡

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Abstract

Doubly-deprotonated 1,1′-bis(*o*-carborane) reacts with $[RuCl_2(p\text{-cymene})]_2$ to afford [Ru(κ^3-2,2′,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(*p*-cymene)] (**1**) in which 1,1′-bis(*o*-carborane) acts as an $X_2(C,C')L$ ligand where "L" is a B3′–H3′→Ru B-agostic interaction, fluctional over four BH units (3′, 6′, 3 and 6) at 298 K but partially arrested at 203 K (B3′ and B6′). This interaction is readily cleaved by CO affording [Ru(κ^2-2,2′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(*p*-cymene)(CO)] (**2**) with the 1,1′-bis(*o*-carborane) simply an $X_2(C,C')$ ligand. With PPh_3 or dppe **1** yields [Ru(κ^3-2,3′,3-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(PPh_3)_2$] (**3**) or [Ru(κ^3-2,3′,3-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(dppe)] (**4**) via unusually facile loss of the η-(*p*-cymene) ligand. In **3** and **4** the 1,1′-bis(*o*-carborane) has unexpectedly transformed into an $X_2(C,B')L$ ligand with "L" now a B3–H3→Ru B-agostic bond. Unlike in **1** the B-agostic bonding in **3** and **4** appears non-fluctional at 298 K. With CO the B-agostic interaction of **3** is cleaved and a PPh_3 ligand is lost to afford [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(CO)_3(PPh_3)$] (**5**), which exists as a 1:1 mixture of isomers, one having PPh_3 trans to C2, the other trans to B3′. With MeCN the analogous product [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(MeCN)_3(PPh_3)$] (**6**) is formed as only the former isomer. With CO **4** affords [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(CO)_2$(dppe)] (**7**), whilst with MeCN **4** yields [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(MeCN)_2$(dppe)] (**8**). In **5** and **6** the three common ligands (CO or MeCN) are meridional, whilst in **7** and **8** the two monodentate ligands are mutually trans. Compound **1** is an 18-e, 6-co-ordinate, species but with a labile B-agostic interaction and **3** and **4** are 16-e, formally 5-co-ordinate, species also including a B-agostic interaction, and thus all three have the potential to act as Lewis acid catalysts. A 1% loading of **1** catalyses the Diels-Alder cycloaddition of cyclopentadiene and methacrolein in CH_2Cl_2 with full conversion after 6 hrs at 298 K, affording the product with exo diastereoselectivity (de >77%). Compounds **1**-**8** are fully characterised spectroscopically and crystallographically.

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‡ Details of 3-channel NMR experiments on compound **4**. Perspective views of single molecules of compounds **3**, **6** and **8**. Line diagrams of both structural isomers of compound **5**. CCDC 1418090-1418096 and 1431560. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

Introduction

Carboranes are a little over 50 years old,[1] and over those five decades a substantial amount of research has been devoted to them to the point where they are now regarded as an established part of inorganic, bordering on organic, chemistry.[2] It is particularly pleasing to note that, especially in the last 10-15 years, in parallel with the growing maturity of carborane chemistry there has been an increasing appreciation of the applications of carboranes and their derivatives in a truly diverse range of fields,[3] in large measure due to the unique nature and structure of these compounds.

1,1′-Bis(*o*-carborane) is the trivial name for [1-(1′-1′,2′-*closo*-$C_2B_{10}H_{11}$)-1,2-*closo*-$C_2B_{10}H_{11}$] (Figure 1), the simplest bis(carborane) species comprising two *ortho*-carborane units connected by a C–C bond.[4] It was first prepared by insertion of diacetylene into B_{10} frameworks [5] but it is now most conveniently synthesised from two C_2B_{10} units by copper-coupling reactions.[6,7] Compared to the extensive chemistry of *ortho*-carborane, 1,2-*closo*-$C_2B_{10}H_{12}$,[2] that of 1,1′-bis(*o*-carborane) remains considerably underdeveloped. Early studies reported both 2-e and 4-e reduction [8,9] and a limited amount of deboronation [8] and deboronation-metallation chemistry.[10-13] More recently we have expanded the deboronation-metallation chemistry [14] and exploited the 4-e reduction and metallation of 1,1′-bis(*o*-carborane), the latter leading in one case to racemic and meso diastereoisomers of 13-vertex metallacarborane/13-vertex metallacarborane species [15] and in another to a unique 13-vertex metallacarborane/12-vertex carborane species whose formation involves cleavage of an aromatic C–C bond under ambient conditions.[16]

<Figure 1 near here>

Of particular relevance to the present work is the fact that double deprotonation of 1,1′-bis(*o*-carborane) affords a chelating (*C*,*C*′), dianionic, ligand which has been used to complex a variety of transition-metal [17-19] and main-group [20] fragments. In the majority of these cases the 1,1′-bis(*o*-carborane) unit functions simply as a X_2(*C*,*C*′) ligand with the metal or main-group element bound to it via two σ-bonds to C2 and C2′.

In this contribution we report the interaction of doubly-deprotonated 1,1′-bis(*o*-carborane) with the {Ru(*p*-cymene)} fragment (*p*-cymene = η-$C_{10}H_{14}$, 1-^{i}Pr,4-MeC_6H_4) to afford an 18-e complex in which 1,1′-bis(*o*-carborane) displays its co-ordinative flexibility, acting as an X_2(*C*,*C*′)L ligand with, in addition to σ-bonds from C2 and C2′, a B–H⇀Ru B-agostic interaction providing an additional pair of electrons to the metal centre. This B-agostic bond is readily cleaved by CO with the 1,1′-bis(*o*-carborane) reverting to a simple X_2(*C*,*C*′) ligand. With PPh_3 and dppe [dppe = 1,2-bis(diphenylphosphino)ethane] however, it is the η-(*p*-cymene) ligand which is surprisingly displaced affording 5-co-ordinate 16-e bis(phosphine) species in which the 1,1′-bis(*o*-carborane) has undergone a remarkable transformation into an

$X_2(C,B')$L ligand. With either CO or MeCN these 5-co-ordinate compounds are converted into fully electronically and co-ordinatively saturated species with the 1,1′-bis(*o*-carborane) an $X_2(C,B')$ ligand. Finally, we demonstrate the potential of some of these compounds to act as homogeneous Lewis acid catalysts or catalyst precursors for the cycloaddition of cyclopentadiene and methacrolein.

Results and Discussion

The reaction between doubly-deprotonated 1,1′-bis(*o*-carborane) and $[RuCl_2(p\text{-cymene})]_2$ affords, after work-up involving column chromatography, an orange product **1** in modest yield, identified by microanalysis and mass spectrometry as $C_{14}H_{34}B_{20}Ru$. See Scheme 1. The room temperature $^{11}B\{^1H\}$ NMR spectrum of **1** reveals five resonances with relative integrals 2:2:4:8:4 from high frequency to low frequency and in the ^1H NMR spectrum are two integral-2 doublets assigned to aromatic protons, an integral-3 singlet at δ 2.35 ppm assigned to the 4-Me group, and a linked 1-H septet at δ 2.81 and 6-H doublet at δ 1.39 ppm arising from the 1-^{i}Pr group. Both spectra are consistent with the molecule $[Ru(C_2B_{10}H_{10}–C_2B_{10}H_{10})(p\text{-cymene})]$ having time-averaged C_s molecular symmetry.

<Scheme 1 near here>

A crystallographic study of **1** (Figure 2) revealed that, unlike in the recently-reported [18] 16-e species $[M(\kappa^2\text{-}2,2'\text{-}\{1\text{-}(1'\text{-}1',2'\text{-}closo\text{-}C_2B_{10}H_{10})\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}\})Cp^*]$ ($Cp^* = \eta\text{-}C_5Me_5$, *M* = Rh, Ir) the 1,1′-bis(*o*-carborane) ligand in **1** is κ^3-bonded to the Ru atom *via* not only the expected σ-bonds from C2 and C2′ but also an additional interaction involving the {B3′H3′} fragment, Ru1–B3′ 2.430(3) Å, Ru1–H3′ 1.89(3) Å. This last interaction could be alternatively described as a 3c-2e Ru–H–B bridge or as a B–H→Ru agostic interaction.[21] To fully emphasise the organometallic nature of **1**, we prefer the latter although we shall refer to it as B-agostic to differentiate it from the classic C–H→M for which the term agostic was formally intended.[22] Thus the deprotonated 1,1′-bis(*o*-carborane) is now an $X_2(C,C')$L ligand and the metal centre has an 18-e configuration. Compound **1** is therefore formulated as $[Ru(\kappa^3\text{-}2,2',3'\text{-}\{1\text{-}(1'\text{-}1',2'\text{-}closo\text{-}C_2B_{10}H_{10})\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}\})(p\text{-cymene})]$.[23] Note that whilst B–H→*M* agostic interactions are well-known (and generally involve *nido* heteroboranes),[24] those involving B3 are relatively rare,[25] particulary when the heteroborane is *closo*.[23]

<Figure 2 near here>

Seeking to establish if this B-agostic bonding is retained in solution we recorded the $^1H\{^{11}B\}$ NMR spectrum of **1**. At room temperature, in addition to the resonances due to the *p*-cymene ligand, are observed five resonances between δ 2.58 and 2.11 ppm, integrating for 16H, and a low frequency resonance at δ -0.02 ppm integrating for 4H. This implies that at

room temperature there is a fluctional process operating by which four {BH} units (presumably BH3, BH3′, BH6 and BH6′) alternatively act as the B-agostic BH in rapid exchange with each other. Cooling the sample causes the signal at δ -0.02 to slowly collapse into the baseline at 233 K, re-emerging as two integral-2 resonances at lower temperatures, δ 0.78 and -1.03 ppm at the lowest temperature achieved, 203 K. Assuming that the lower frequency resonance arises from the B-agostic BH [22,26] we conclude that even at 203 K the fluctional nature of the B-agostic interaction is only partially arrested. At 203 K the resonances arising from the *p*-cymene ligand still show time-averaged C_s symmetry. However, the BH resonances which were never involved in B-agostic bonding now appear as a 2:2:3:3:3:3 pattern (between δ 2.52 and 1.96 ppm, from high frequency to low frequency). The presence of odd-numbered integrals suggests that at 203 K the *p*-cymene ligand is no longer rapidly rotating about the Ru-arene axis, but is aligned such that its mirror plane is aligned with that containing C2C1C1′C2′, i.e. the low-temperature C_s conformation of the molecule is that shown in Figure 3a rather than Figure 3b. The B-agostic bonding is still fluctional between two sites on the same cage, i.e. B3′ and B6′ (numbering as in Figure 2) or alternatively B3 and B6.

<Figure 3 near here>

Compound **1** reacts readily with CO to afford [Ru(κ^2-2,2′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(*p*-cymene)(CO)] (**2**), isolated as a yellow crystalline material in modest yield. Microanalysis, mass spectrometry and IR spectroscopy (ν_{CO} at 2007 cm^{-1}) all support carbonyl bonding. The $^{11}B\{^1H\}$ and ^1H NMR spectra of **2** are relatively uninformative (but are consistent with time-averaged C_s molecular symmetry), however crucially the $^1H\{^{11}B\}$ spectrum yields no evidence of B-agostic bonding with resonances from all 20 BH units appearing between δ 2.88 and 2.12 ppm. A crystallographic study (Figure 4) confirms that the CO ligand has displaced the B-agostic interaction and thus demonstrates the flexibility of the 1,1′-bis(*o*-carborane) ligand, now a simple $X_2(C,C')$ ligand. There are slight increases in the Ru–C2, Ru–C2′ and Ru–arene distances on moving from **1** to **2**, but essentially the two structures are very similar except for replacement of the B-agostic link by the CO ligand.

<Figure 4 near here>

A much more profound change happens on reaction of **1** with PPh_3. Initially this reaction was performed with one equivalent of phosphine yielding a small amount of a yellow-orange product, **3**, after chromatography. Microanalysis and mass spectrometry suggested a product of formula $C_{40}H_{50}B_{20}P_2Ru$, i.e. containing two PPh_3 ligands but no *p*-cymene, a conclusion also supported by ^1H NMR spectroscopy. Accordingly the reaction was repeated using two equivalents of phosphine affording **3** in somewhat better yield.

Similarly compound **4** is afforded when **1** is treated with dppe, and spectroscopically compounds **3** and **4** are fully analogous. Their $^{11}B\{^{1}H\}$ NMR spectra are relatively uninformative with multiple overlapping resonances between δ 3 and -20 ppm (compound **3**) and δ 1 and -17 ppm (compound **4**). The ^{31}P spectra consist of two doublets, one broad at higher frequency and the other sharp one at lower frequency. In the ^{1}H NMR spectra is one broad resonance characteristic of a $C_{cage}H$ signal (δ 1.94 ppm in **3** and 2.17 ppm in **4**) which integrates for 1 H atom assuming there are 30 aromatic protons (compound **3**) or 20 aromatic protons (compound **4**). On ^{11}B decoupling there appears, in addition to a set of resonances assigned to BH_{exo} nuclei, a low-frequency doublet resonance in the B-agostic region, δ -4.23 ppm in **3** and δ -2.25 ppm in **4**. That this doublet arises from coupling to a P atom was only established by a $^{1}H\{^{11}B, ^{31}P\}$ NMR experiment on compound **4** (see ESI).

The structures of **3** and **4** were established by diffraction studies. Unfortunately that of **3** suffers from disorder modelled in terms of major and minor components of the Ru atom, with site occupancy factors of 0.803(2) and 0.197(2) respectively, and although it must be the case that more of the molecule than simply the Ru atom is disordered it was not possible to account for this. Because of this disorder the crystallographic determination is relatively imprecise but nevertheless accurately defines the molecular structure (see ESI). Fortunately the structure of **4** (Figure 5) suffers no such disorder and is of high precision so the following discussion focuses on this structure. The *p*-cymene ligand of **1** has indeed been lost and the Ru atom is coordinated by dppe and the 1,1′-bis(*o*-carborane). The primed cage is now bound to the Ru atom by a 2c-2e B–Ru σ bond and not a C–Ru σ bond. The unprimed cage is still connected to the metal by a C–Ru σ bond but this is now complemented by a B–H⇀Ru B-agostic bond from the {B3H3} unit. Overall, the 1,1′-bis(*o*-carborane) unit has changed from an $X_2(C,C')L$ ligand in **1** to an $X_2(C,B')L$ ligand in **3** and **4**, now established as $[Ru(\kappa^3\text{-}2,3',3\text{-}\{1\text{-}(1'\text{-}1',2'\text{-}closo\text{-}C_2B_{10}H_{10})\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}\})(PPh_3)_2]$ and $[Ru(\kappa^3\text{-}2,3',3\text{-}\{1\text{-}(1'\text{-}1',2'\text{-}closo\text{-}C_2B_{10}H_{10})\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}\})(dppe)]$, respectively, 16-e, 5-coordinate Ru^{II} species formally related to classic co-ordination compounds such as $[RuCl_2(PPh_3)_3]$.[27] The metal geometry is approximately square-pyramidal (B3′ apical) and, as was also the case in the structure of $[RuCl_2(PPh_3)_3]$,[28] there is a long Ru…H anagostic [29] interaction to a phenyl α-H atom [H212 in **4**, Ru1…H212 2.724(5) Å, Ru1…H212–C126 122.6(2)°] blocking the sixth octahedral site.

<Figure 5 near here>

Having identified the nature of **3** a more obvious route to its synthesis was apparent; the reaction of doubly-deprotonated 1,1′-bis(*o*-carborane) with either $[RuCl_2(PPh_3)_4]$ or $[RuCl_2(PPh_3)_3]$ affords **3** in somewhat better yield than going *via* the *p*-cymene compound **1**.

The formation of compounds **3** and **4** by the room-temperature arene displacement from **1** was unexpected. Although not unknown under ambient conditions,[30] arene substitution in Ru^{II} species usually involves either heating or UV irradiation.[31] Indeed, the kinetic stability of the {(η-arene)Ru} moiety is one of the key factors in the use of arene-Ru species in both medicine [32] and catalysis.[33]

Compound **2** does not react with triphenylphosphine suggesting that in the reaction between **1** and PPh_3 the initial stage is displacement of the weak B-agostic interaction in **1** by phosphine. This would afford a presumably very sterically-crowded species which might then facilitate slippage of the *p*-cymene ligand from η^6- to η^4- to η^2-bonding and eventually complete dissociation, accompanied by bonding of the second PPh_3 to Ru at some point. An analogous process for the reaction between **1** and dppe would involve initial κ^1-co-ordination by dppe.

In forming **3** and **4**, either from the reaction between **1** and the appropriate phosphine or (for **3**) by the reaction between doubly-deprotonated 1,1′-bis(*o*-carborane) and either $[RuCl_2(PPh_3)_4]$ or $[RuCl_2(PPh_3)_3]$, 1,1′-bis(*o*-carborane) further displays its flexibility by becoming an $X_2(C,B')L$ ligand. Transition-metal metallacarboranes with B–*M* σ bonds are comparatively rare [34] and cases in which a carborane previously bound to metal through C is converted to B-bound are even rarer.[34c] In the present case it is likely that the initial products of these reactions are the species [Ru(κ^3-2,2′,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})P_2], in which the 1,1′-bis(*o*-carborane) acts as an $X_2(C,C')L$ ligand with a B-agostic bond from the {B3′H3′} fragment to Ru. However, even with this B-agostic interaction the metal centre is only in a 16-e configuration. Since a carborane is expected to be a stronger σ-donor when bonded to metal through B as opposed to C (clear evidence for this is presented subsequently) and the B3′–H3′ bond is already activated by the agostic bonding, we suggest that the B3′–H3′ bond is cleaved and the primed cage changes from C2′–Ru σ-bonded to B3′–Ru σ-bonded by a ca. 72° rotation about the C1–C1′ axis. Whether the H atom lost by B3′ is transferred to C2′ or whether C2′ picks up H from solvent during work-up is unknown at this stage. The final stage in the process is the formation of a B-agostic bond from the {B3H3} unit to Ru to restore the 16-e configurations in **3** and **4**.

Since compounds **3** and **4** are both electronically and co-ordinatively unsaturated their reactions with 2-e donor ligands were explored. A freshly-prepared (not isolated) sample of **3** in THF was allowed to react with CO to afford the colourless product **5**. Microanalysis of crystals of **5** corresponds to $[Ru(C_2B_{10}H_{10}–C_2B_{10}H_{10})(CO)_3(PPh_3)]$ plus one molecule of DCM of crystallisation. Although there is only one triphenylphosphine ligand, two singlets are observed in the ^{31}P NMR spectrum (the lower-frequency one being very broad) and in the ^1H

spectrum are two broad singlets in the region associated with carborane C*H* resonances, each of which integrates for 0.5 protons against an assumed total of 15 aromatic protons.

Collectively, these data suggest that **5** is afforded as a mixture of isomers, and this is fully supported by the crystallographic structure (Figure 6). One PPh_3 ligand from **3** has been replaced by three CO ligands and the B-agostic interaction has been broken. Thus compound **5** is [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(CO)_3(PPh_3)$]. The geometry of the Ru centre is octahedral and the three CO ligands are in a meridional arrangement. However, crystallographically there is 1:1 disorder between C2 and B3′, meaning that the compound exists as two isomers, one with PPh_3 trans to C2 (shown in Figure 6) and the other with PPh_3 trans to B3′ (see ESI). We attribute the broad ^{31}P resonance to this latter phosphine.

<Figure 6 near here>

A fully analogous reaction occurs upon dissolving **3** in MeCN, resulting in immediate decolourisation and the isolation, following work-up, of a new compound [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(MeCN)_3(PPh_3)$] (**6**). In **6** there is only one (narrow) signal in the ^{31}P NMR spectrum and in the ^1H spectrum are observed a single C*H* resonance and three resonances assigned to MeCN. The $^{11}B\{^1H\}$ spectrum features a high-frequency (δ 12.8 ppm), integral-1, resonance that does not show ^1H coupling in the ^{11}B spectrum. These spectroscopic data are fully consistent with the structure established for **6** by a crystallographic study (see ESI). Relative to the precursor compound **3** a PPh_3 ligand has been lost and the B-agostic interaction broken, to be replaced by three meridional MeCN ligands. Compound **6** exists in a single isomeric form, with no disorder between C2 and B3′ and with the PPh_3 ligand trans to C and an MeCN ligand trans to B. This arrangement is fully consistent with the concept of a carborane being a stronger σ-donor ligand when bonded to metal through B rather than through C and the stronger trans influence of triphenylphosphine compared to MeCN.[35] Thus in existing as a single isomer compound **6** differs from compound **5**, where the broadly similar trans influences of PPh_3 and CO result in two isomers and partial crystallographic disorder.

The reaction of compound **4** with CO affords a pale-yellow product, **7**, which features a broad, high-frequency, resonance in its $^{11}B\{^1H\}$ NMR spectrum (δ 8.5 ppm) which integrates for 1 B out of a total of 20 and remains a singlet in the ^{11}B spectrum. In the ^{31}P NMR spectrum are two resonances indicating inequivalent P environments with the lower-frequency one being very broad, and in the ^1H spectrum is a single resonance typical of carborane C*H* of integral 1. Collectively these data suggest that **7** is [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(CO)_2$(dppe)], a conclusion confirmed by a crystallographic study (Figure 7). In the octahedral geometry at the metal centre the carbonyl

ligands are mutually trans and the Ru–P distance trans to B3′, 2.4328(6) Å, is significantly longer than that trans to C2, 2.3964(6) Å, confirming that carborane is a stronger σ-donor when bound to a metal through B compared to through C.

<Figure 7 near here>

Finally, treating compound **4** with MeCN also results in partial decolourisation and the isolation of compound **8**, [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(MeCN)_2$(dppe)], which spectroscopically is closely related to **7**. A crystallographic study (as the tri-MeCN solvate, see ESI) confirms the structural analogy between **8** and **7**. In compound **8** the Ru–P bond trans to B3′, 2.4256(5) Å, is again significantly longer than that trans to C2, 2.3473(5) Å.

In compounds **5**-**8** the 1,1′-bis(*o*-carborane) is now an X_2(*C*,*B*′) ligand, the fourth different ligating mode observed in this series of compounds. It is important to note that although the nature of the B- or C-ligation of 1,1′-bis(*o*-carborane) was inferred from NMR spectroscopic studies, the positions of the cage C atoms in the crystallographic structures were independently and unambiguously established by both the *Vertex-to-Centroid Distance* (VCD) [36] and *Boron-Hydrogen Distance* (BHD) [37] methods in every case.

Compounds **3** and **4** contain electronically and co-ordinatively unsaturated metal centres and in compound **1** the metal atom is only electronically and co-ordinatively saturated by virtue of the B-agostic interaction which is easily broken. Hence compounds **1**, **3** and **4** all have the potential to act as Lewis acid catalysts or catalyst precursors. In a preliminary sighting study, a 1 mol % loading of compound **1** was found to catalyse the cycloaddition reaction between methacrolein and cyclopentadiene to afford 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde, according to Scheme 2. The product was obtained with exo diastereoselectivity (de = 77%) with full conversion after 6 hrs at room temperature in CH_2Cl_2. Without catalyst the reaction still favours the exo diastereoisomer [38] (de = 67%) but proceeds with only 19% conversion after 6 hrs under the same conditions.

<Scheme 2 near here>

Conclusions

This work has demonstrated the remarkable (and previously unrecognised) ligating flexibility of 1,1′-bis(*o*-carborane). In compound **1** 1,1′-bis(*o*-carborane) acts as a X_2(*C*,*C*′)L ligand (where L here refers to a B–H→Ru agostic interaction which affords the otherwise co-ordinatively and electronically unsaturated metal centre an additional pair of electrons) but this is easily modified to X_2(*C*,*C*′) in compound **2**. In compounds **3** and **4** we see a switch to X_2(*C*,*B*′)L ligation accompanying a most unusual displacement of the *p*-cymene ligand of compound **1** by PPh_3 or dppe under ambient conditions. Compounds **3** and **4** react with either

CO or MeCN to co-ordinatively and electronically saturate the metal centre, with the 1,1′-bis(*o*-carborane) becoming an $X_2(C,B')$ ligand in compounds **5**-**8**. The $X_2(C,C')L$ ligating mode for 1,1′-bis(*o*-carborane) has only been reported once previously and the $X_2(C,B')L$ and $X_2(C,B')$ ligating modes are reported for the first time here. Compounds **1**, **3** and **4** have the potential to act as Lewis acid catalysts or catalyst precursors, and this is demonstrated for **1** by its catalysis of the Diels-Alder cycloaddition of cyclopentadiene and methacrolein.

Experimental

Synthetic and spectroscopic details

Experiments were performed under dry, oxygen free N_2, using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. Solvents were freshly distilled under nitrogen from the appropriate drying agent immediately before use (THF and 40-60 petroleum ether; sodium wire) or were purified in an MBRAUN SPS-800 [CH_2Cl_2 (DCM), MeCN] and were degassed (3×freeze-pump-thaw cycles) before use. Deuterated solvents ($CDCl_3$, CD_2Cl_2) were stored over 4 Å molecular sieves. Preparative TLC employed 20×20 cm Kieselgel F_{254} glass plates and for column chromatography we used 60 Å silica as the stationary phase. IR spectra were obtained from DCM solutions using a PerkinElmer Spectrum 100 FT-IR spectrometer. NMR spectra at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B) or 162.0 MHz (^{31}P) were recorded on a Bruker AVIII-400 spectrometer from $CDCl_3$ solutions at 298 K unless otherwise stated. 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. The starting materials 1,1′-bis(*o*-carborane),[7] $[RuCl_2(p\text{-cymene})]_2$,[39] $[RuCl_2(PPh_3)_3]$ [40] and $[RuCl_2(PPh_3)_4]$ [40] were prepared by literature methods or slight variations thereof. All other reagents were supplied commercially.

[Ru(κ^3-2,2′,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(*p*-cymene)] (1). *n*-BuLi (2.80 mL of 2.5 M solution, 6.982 mmol) was added dropwise to a cooled (0°C) solution of 1,1'-bis(*o*-carborane) (1.000 g, 3.491 mmol) in THF (20 mL) and the products stirred for 1 hr. The pale yellow solution was frozen at -196 °C then $[RuCl_2(p\text{-cymene})]_2$ (1.069 g, 1.746 mmol) was added and the reaction mixture stirred overnight at room temperature to give a green solution. The THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered. Following spot TLC (DCM:petroleum ether, 50:50, R_f = 0.71) purification by column chromatography using the same eluent gave, on removal of solvent, an orange solid (0.678 g, 37%), subsequently identified as **[**Ru**(**κ^3-2,2′,3′-**{**1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}**)**(*p*-cymene)] (**1**). $C_{14}H_{34}B_{20}Ru$ requires C 32.3, H 6.59. Found for **1**: C 32.6, H 6.76%. $^{11}B\{^1H\}$ NMR (CD_2Cl_2), δ -1.4 (2B), -4.8 (2B), -7.1 (4B), -9.5 plus shoulder (8B),

-10.6 (4B). ^{1}H NMR (CD_2Cl_2), δ 5.48 [d, J = 6.0 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 5.30 [d, J = 6.0 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 2.81 [sept, J = 6.8 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$], 2.35 [s, 3H, $CH_3C_6H_4CH(CH_3)_2$], 1.39 [d, J = 6.8 Hz, 6H, $CH_3C_6H_4CH(CH_3)_2$]. ^{1}H{^{11}B} NMR (CD_2Cl_2), δ 5.48 [d, J = 6.0 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 5.31[d, J = 6.0 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 2.81 [sept, J = 6.8 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$], 2.58 [s, 4B*H*, 2.36 (s, 3H, $CH_3C_6H_4CH(CH_3)_2$], 2.25 (s, 4B*H*), 2.21 (s, 2B*H*), 2.15 (s, 4B*H*), 2.11 (s, 2B*H*), 1.40 [d, J = 6.8 Hz, 6H, $CH_3C_6H_4CH(CH_3)_2$], -0.02 (s, 4H, B$H_{agostic}$). ^{1}H{^{11}B} NMR (CD_2Cl_2, 203 K), δ 5.44 [d, J = 6.0 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 5.24 [d, J =6.0 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 2.74 [sept, J = 6.8 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$], 2.52 (s, 2B*H*), 2.47 (s, 2B*H*), 2.29 [s, 3H, $CH_3C_6H_4CH(CH_3)_2$], 2.12 (s, 3B*H*), 2.06 (s, 3B*H*), 2.02 (s, 3B*H*), 1.96 (s, 3B*H*), 1.30 [d, J = 6.8 Hz, 6H, $CH_3C_6H_4CH(CH_3)_2$], 0.78 (s, 2B*H*), -1.03 (s, 2H, B$H_{agostic}$). EIMS: *m/z* 520.4 (M^+).

[Ru(κ^2-2,2′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(*p*-cymene)(CO)] (2). Compound **1** (0.100 g, 0.192 mmol) was dissolved in THF (10 mL), frozen at -196 °C and the Schlenk tube was then charged with carbon monoxide (0.3 bar)**.** The orange solution was left to warm to room temperature and stirred vigorously overnight to yield a yellow-green solution. The THF was removed *in vacuo* and the product isolated by preparative TLC (DCM:petroleum ether, 50:50), affording a yellow band (R_f = 0.34) subsequently identified as **[**Ru**(**κ^2-2,2′-**{**1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}**)**(*p*-cymene)(CO)] (**2**) (0.037 g, 35%). $C_{15}H_{34}B_{20}ORu$ requires C 32.9, H 6.26. Found for **2**: C 32.4, H 6.27%. IR: ν_{max} 2570 (BH), 2007 (CO) cm^{-1}. ^{11}B{^{1}H} NMR, δ -2.6 (4B), -5 to -11 (overlapping resonances with maxima at -6.6, -7.8, -8.5, 16B). ^{1}H NMR, δ 6.02 [d, J = 6.6 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 5.92 [d, J = 6.6 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 2.89 [sept, J = 6.8 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$], 2.40 [s, 3H, $CH_3C_6H_4CH(CH_3)_2$], 1.35 [d, J = 6.8 Hz, 6H, $CH_3C_6H_4CH(CH_3)_2$]. ^{1}H{^{11}B} NMR, δ 6.03 [d, J = 6.6 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 5.94 [d, J = 6.6 Hz, 2H, $CH_3C_6H_4CH(CH_3)_2$], 2.88 (s, 2B*H*), 2.87 [sept, J = 6.8 Hz, 1H, $CH_3C_6H_4CH(CH_3)_2$], 2.72 (s, 2B*H*), 2.41-2.12 (multiple overlapping resonances, 16B*H*), 2.36 [s, 3H, $CH_3C_6H_4CH(CH_3)_2$], 1.31 [d, J = 6.8 Hz, 6H, $CH_3C_6H_4CH(CH_3)_2$]. EIMS: *m/z* 520.4 (M^+-CO), 548.4 (M^+).

[Ru(κ^3-2,3′,3-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(PPh_3)$_2$] (3)

Method A: Displacement of (p-cymene). Compound **1** (0.100 g, 0.192 mmol) was dissolved in THF (10 mL), frozen at -196 °C then triphenylphosphine (0.111 g, 0.423 mmol) was added. The orange solution was allowed to warm to room temperature and stirred for 2 hrs to yield a dark red solution. The THF was removed *in vacuo* and the product purified by preparative TLC (DCM:petroleum ether, 20:80) affording a yellow-orange band (R_f = 0.19)

subsequently identified as **[**Ru**(**κ^3-2,3′,3-**{**1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$**})**$(PPh_3)_2$] (**3**) (0.027 g, 15%).

Method B1: Reaction between [$RuCl_2(PPh_3)_4$] and dilithiated 1,1'-bis(o-carborane). *n*-BuLi (0.30 mL of 2.3 M solution, 0.698 mmol) was added dropwise to a cooled (0°C) solution of 1,1'-bis(*o*-carborane) (0.100 g, 0.349 mmol) in THF (10 mL) and the products stirred for 1 hr. The pale yellow solution was frozen at -196 °C then [$RuCl_2(PPh_3)_4$] (0.426 g, 0.349 mmol) was added and the reaction mixture was stirred for 4 hrs at room temperature to give a dark red solution. The THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered. The product was purified using preparative TLC (DCM:petroleum ether, 30:70) affording an orange band (R_f = 0.24, trace) and a yellow band (R_f = 0.42) subsequently identified as **3** (0.073 g, 23%).

Method B2: Reaction between [$RuCl_2(PPh_3)_3$] and dilithiated bis(o-carborane). *n*-BuLi (0.30 mL of 2.3 M solution, 0.698 mmol) was added dropwise to a cooled (0°C) solution of 1,1'-bis(*o*-carborane) (0.100 g, 0.349 mmol) in THF (10 mL) and the products stirred for 1 hr. The pale yellow solution was frozen at -196 °C, [$RuCl_2(PPh_3)_3$] (0.335 g, 0.349 mmol) was added and the reaction mixture was stirred for 4 hrs at room temperature to give a dark red solution. THF was removed *in vacuo* and the crude mixture dissolved in DCM. Purification by preparative TLC (DCM:petroleum ether, 30:70) yielded a yellow-orange band (R_f = 0.51) subsequently identified as **3** (0.078 g, 25%).

$C_{40}H_{50}B_{20}P_2Ru$ requires C 52.8, H 5.54. Found for **3**: C 52.5, H 5.53%. $^{11}B\{^1H\}$ NMR, δ 3 to -20 (overlapping resonances with maxima at 0.1, -4.8, -7.9, -9.2, -10.1, -12.5, -14.6, -17.4 , assume 20B). ^1H NMR, δ 7.47-7.12 (m, 30H, C_6H_5), 1.94 (br. s, 1H, $C_{cage}H$). $^1H\{^{11}B\}$ NMR, δ 7.47-7.12 (m, 30H, C_6H_5), 1.94 (br. s, 1H, $C_{cage}H$), [2.56, 2.47, 2.34, 2.30, 2.24, 2.19, 2.14, 2.10, 2.04, 1.87, 1.79, 1.58, 1.47 (total 19 H, B*H*)], -4.23 (d, 32.0 Hz, 1H, $BH_{agostic}$). $^{31}P\{^1H\}$ NMR, δ 57.98 (br. d, 25.1 Hz, 1P), 40.25 (d, 25.1 Hz, 1P). EIMS: *m/z* 910.5 (M^+).

[Ru(κ^3**-2,3′,3-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(dppe)] (4).** Compound **1** (0.140 g, 0.269 mmol) was dissolved in THF (10 mL), frozen at -196 °C then 1,2-bis(diphenylphosphino)ethane (0.107 g, 0.269 mmol) was added. The orange solution was allowed to warm to room temperature and stirred for 2 hrs to yield a dark red solution. The THF was removed *in vacuo* and the product was purified by preparative TLC (DCM:petroleum ether, 50:50) affording a yellow band (R_f = 0.69) subsequently identified as **[**Ru**(**κ^3-2,3′,3-**{**1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$**})**(dppe)] (**4**) (0.085 g, 28%). $C_{30}H_{44}B_{20}P_2Ru$ requires C 46.0, H 5.66. Found for **4**: C 44.8, H 6.25%. $^{11}B\{^1H\}$ NMR, δ 3 to -19 (overlapping resonances with maxima at 0.5, -4.3, -7.0, -7.9, -9.2, -10.4, -14.5, -16.1, assume 20 B). ^1H NMR, δ 7.92-7.01 (m, 20H, C_6H_5), 3.08-2.75 (m, 4H, CH_2), 2.17 (br. s, 1H,

$C_{cage}H$). $^{1}H\{^{11}B\}$ NMR, δ 7.90-7.01 (m, 20H, C_6H_5), 3.07-2.75 (m, 4H, CH_2), 2.17 (br. s, 1H, $C_{cage}H$), [2.74, 2.63, 2.57, 2.42, 2.23, 2.13, 2.09, 1.78, 1.75, 1.70, 1.30, 0.66 (total 19H, B*H*)], -2.25 (d, 28.0 Hz, 1H, $BH_{agostic}$). $^{31}P\{^{1}H\}$ NMR, δ 90.74 (br. unresolved d, 1P), 78.70 (d, 11.3 Hz, 1P). EIMS: *m/z* 286.3 [M^+-Ru(dppe)], 510.3, 783.3 (M^+).

[Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(CO)$_3$(PPh$_3$)] (5). Compound **3** was synthesised using Method **B1** (0.200 g, 0.698 mmol of 1,1′-bis(*o*-carborane)) and the compound was removed from the silica using THF (30 mL). The THF solution was reduced in volume to 10 mL, frozen at -196 °C and the Schlenk tube was then charged with carbon monoxide (0.3 bar). The orange solution was left to warm to room temperature and stirred vigorously overnight to yield a pale yellow solution. The THF was removed *in vacuo* and the product was purified by preparative TLC (DCM:petroleum ether, 50:50) affording a colourless band (R_f = 0.76) subsequently identified as **[**Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}**)**$(CO)_3(PPh_3)$] (**5**) (0.036 g, 7% based on 1,1′-bis(*o*-carborane)). $C_{25}H_{35}B_{20}O_3PRu$ requires C 41.0, H 4.82. $C_{25}H_{35}B_{20}O_3PRu{\cdot}CH_2Cl_2$ requires C 38.2, H 4.57. Found for **5**·CH_2Cl_2 (crystals submitted): C 38.5, H 4.62%. IR: ν_{max} 2570 (BH), 2042 (CO), 2034 (CO), 2028 (CO) cm^{-1}. NMR spectra consistent with a 1:1 mixture of two isomers. $^{11}B\{^{1}H\}$ NMR, δ 4.2 (br. 2B, B3′?), 1 to -14 (overlapping resonances with maxima at -2.2, -6.8, -8.9, 38B). ^{1}H NMR, δ 7.58-7.47 (m, 30H, C_6H_5), 4.18 (br. s, 1H, $C_{cage}H$), 3.94 (br. s, 1H, $C_{cage}H$). $^{31}P\{^{1}H\}$ NMR, δ 27.74 (s, 1P), 17.12 (v. br s, 1P). EIMS: *m/z* 647.1 (M^+-3×CO), 675.1 (M^+-2×CO), 703.1 (M^+-CO), 731.8 (M^+).

[Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(MeCN)$_3$(PPh$_3$)] (6). Compound **3** was synthesised using Method **B1** (0.200 g, 0.698 mmol of 1,1′-bis(*o*-carborane)) and the compound was removed from the silica using MeCN (30 mL). The orange compound instantly became colourless on contact with MeCN. The solution was left to stir for 2 hrs then the MeCN was removed *in vacuo*. The compound was separated by preparative TLC (DCM:petroleum ether, 50:50) affording an unidentified yellow band (R_f = 0.60, trace) and a colourless band (R_f = 0.14) which was subsequently identified as [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}**)**$(MeCN)_3(PPh_3)$] (**6**) (0.035 g, 7% based on 1,1′-bis(*o*-carborane)). $C_{28}H_{44}B_{20}N_3PRu$ requires C 43.6, H 5.75. N 5.45. Found for **6**: C 44.3, H 5.81, N 4.32%. $^{11}B\{^{1}H\}$ NMR, δ 12.8 (1B, B3′), 0 to -17 (overlapping resonances with maxima at -3.8, -8.4, -13.9, 19B). ^{1}H NMR, δ 7.48-7.38 (m, 15H, C_6H_5), 3.43 (br. s, 1H, $C_{cage}H$), 2.11 (d, 1 Hz, 3H, CH_3CN), 2.04 (d, 1 Hz, 3H, CH_3CN), 2.00 (br. s, 3H, CH_3CN). $^{31}P\{^{1}H\}$ NMR, δ 40.44 (s, 1P). EIMS: *m/z* 647.2 (M^+-3×MeCN), 688.1 (M^+-2×MeCN).

[Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})(CO)$_2$(dppe)] (7). Compound **4** (0.037 g, 0.047 mmol) was dissolved in THF (10 mL), frozen at -196 °C and the

Schlenk tube was then charged with carbon monoxide (0.3 bar). The yellow solution was left to warm to room temperature and stirred vigorously overnight to yield a pale yellow solution. The THF was removed *in vacuo* and the product was purified by preparative TLC (DCM:petroleum ether, 50:50) affording a yellow band (R_f = 0.50) subsequently identified as [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(CO)_2$(dppe)] (**7**) (0.020 g, 50%). Microanalysis unreliable due to air-instability of compound. IR: ν_{max} 2566 (BH), 1983 (CO) cm^{-1}. $^{11}B\{^1H\}$ NMR, δ 8.5 (1B, B3′), 0 to -15 (overlapping resonances with maxima at -2.7, -7.1, -9.8, 19B). ^1H NMR, δ 7.98-6.99 (m, 20H, C_6H_5), 3.90 (br. s, 1H, $C_{cage}H$), 3.06-2.86 (m, 4H, CH_2). $^{31}P\{^1H\}$ NMR, δ 49.15 (s, 1P), 40.56 (v. br. s, 1P) . EIMS: *m/z* 510.3, 783.3 (M^+-2×CO), 811.3 (M^+-CO).

[Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(MeCN)_2$(dppe)] (8). Compound **4** (0.052 g, 0.066 mmol) was dissolved in MeCN (10 mL) and stirred for 2 hrs to give a pale yellow solution. The solvent was removed *in vacuo* and the product was purified by preparative TLC (DCM:petroleum ether, 50:50) affording a pale yellow band (R_f = 0.32) subsequently identified as [Ru(κ^2-2,3′-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$})$(MeCN)_2$(dppe)] (**8**) (0.004 g, 7%). $C_{34}H_{50}B_{20}P_2N_2P_2Ru$ requires C 47.2, H 5.82, N 3.23. Found for **8**: C 46.1, H 5.97, N 3.47%. $^{11}B\{^1H\}$ NMR (CD_2Cl_2), δ 19.4 (1B, B3′), -1 to -15 (overlapping resonances with maxima at -2.9, -3.6, -6.0, -8.5, -12.4, 19B). ^1H NMR (CD_2Cl_2), δ 7.97-6.91 (m, 20H, C_6H_5), 3.47 (br. s, 1H, $C_{cage}H$), 3.00-2.75 (m, 4H, CH_2), 2.07 (dd, 3 Hz, 1 Hz, 3H, CH_3CN), 2.04 (app. t, 3H, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ 55.89 (s, 1P), 30.49 (v. br. s, 1P). EIMS: *m/z* 783.3 (M^+-2×MeCN).

Lewis Acid Catalysed Diels-Alder Cycloaddition.[41] A solution of **1** (0.011 g, 0.021 mmol) in DCM (2 mL) was added to a solution of methacrolein (0.18 mL, 2.175 mmol) in DCM (1 mL) to produce a yellow solution. An aliquot of freshly cracked CpH (2.17 mL, 25.719 mmol) was added to the reaction mixture and the resultant yellow solution stirred under N_2. Samples of the reaction mixture (0.20 mL) were taken at regular intervals for solution NMR study to determine conversion. Integration of the exo and endo aldehyde ^1H NMR resonances [($CDCl_3$, 298 K) δ 9.69 *exo*-C*H*O; 9.39 *endo*-C*H*O] [37] was used to calculate diastereomeric excess.

Crystallographic details

Single crystals of compound **1** were obtained by the slow evaporation of a DCM solution at room temperature, and crystals of **6** and **8** were similarly obtained by evaporation of MeCN solutions. Crystals of all other compounds (**2**, **3**, **4**, **5** and **7**) were afforded by diffusion of a DCM solution of the compound and a 5-fold excess of petroleum ether at -30ºC. Note that **4**

and **5** crystallise with one molecule of DCM of solvation and **8** crystallises with three molecules of MeCN of solvation.

Intensity data from single crystal 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 by an Oxford Cryosystems Cryostream. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.[42] Structures were solved by direct methods (SHELXS [43] or OLEX2 [44]) and refined by full-matrix least-squares (SHELXL).[43]

In all cases cage C or B atoms were initially all treated as B and the structures refined with cage H atoms allowed positional variation, leading to a *Prostructure* which was then analysed by both the VCD [36] and BHD [37] methods to identify the cage C atoms.

The structures of compounds **1**, **2**, **4** and **6-8** are free of disorder, except that in **8** there are three molecules of MeCN of solvation per asymmetric unit, two of which are disordered. In **3** there is evidence of considerable disorder, but the only part that could be modelled was a fractional Ru atom [Ru1A, SOF 0.197(2)] located 0.884(3) Å from Ru1 [SOF 0.803(2)]. In **5** atoms at cage vertices 2 and 3′ are each 0.5C+0.5B and there is one disordered molecule of CH_2Cl_2 of solvation per asymmetric unit.

Non-cage atoms were constrained to idealised geometries with $C_{aromatic}$–H (*p*-cymene ring) = 1.00 Å, C_{phenyl}–H = 0.95 Å, C_{methyl}–H = 0.98 Å, $C_{secondary}$–H = 0.99 Å, $C_{tertiary}$–H = 1.00 Å. All H displacement parameters, U_{iso}, were constrained to be 1.2×U_{eq} (bound B or C) except Me H atoms [U_{iso}(H) = 1.5×U_{eq} C(Me)]. Table 1 contains further experimental details.

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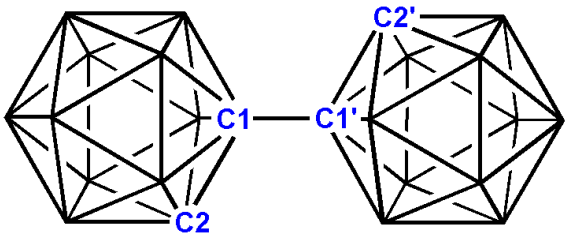
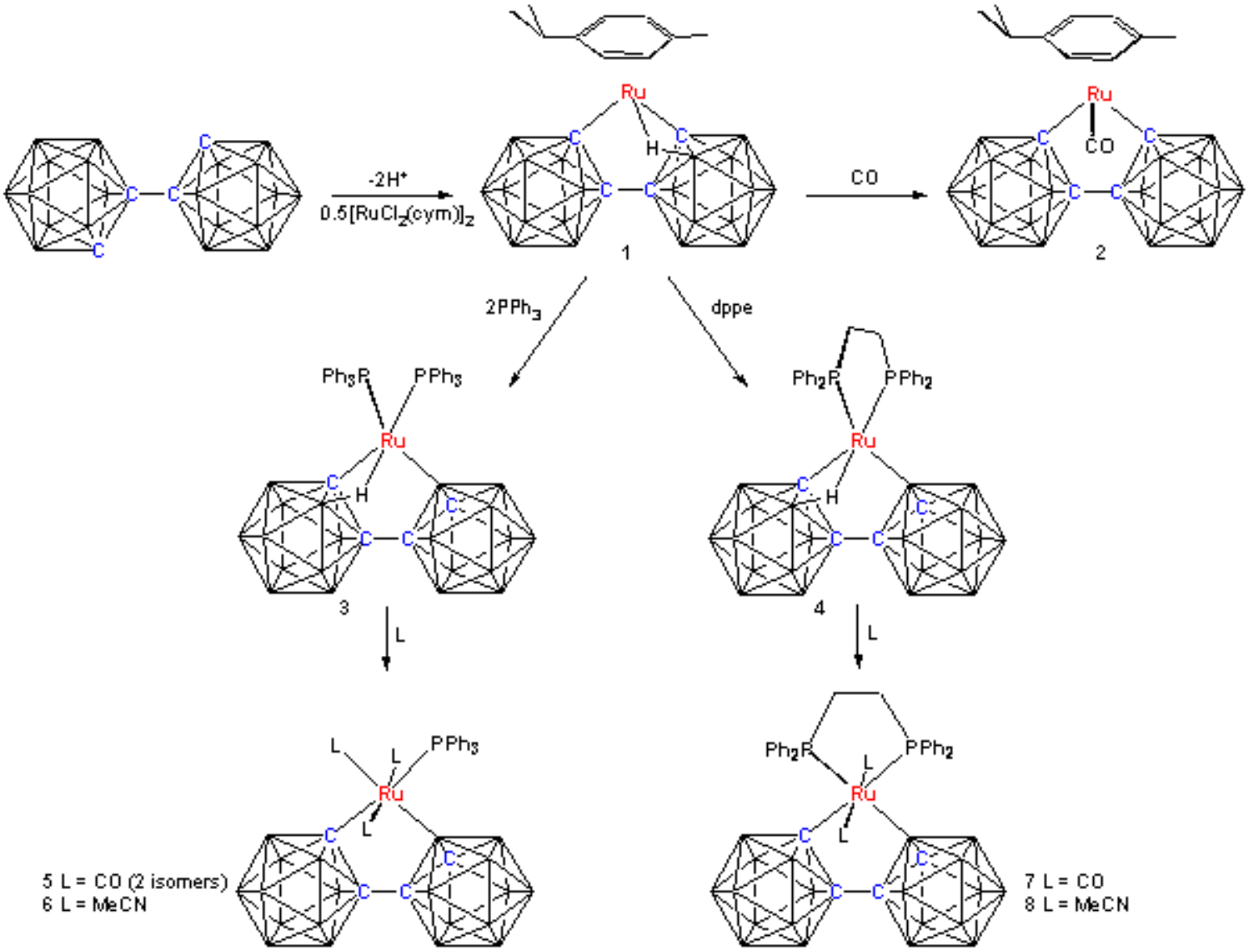


Fig. 1. 1,1′-bis(o-carborane)



Scheme 1. General reaction scheme for compounds **1**-**8**.

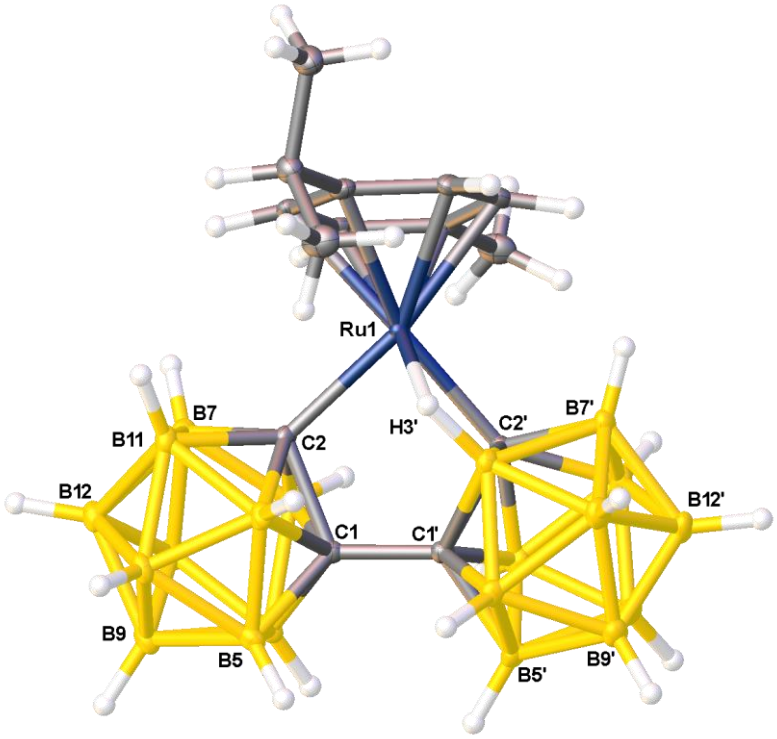


Fig. 2. Perspective view of compound **1** and part of the atom numbering scheme. Selected interatomic distances (Å): Ru1–C2 2.103(2), Ru1–C2′ 2.124(2), Ru1–H3′ 1.89(3), Ru1–B3′ 2.430(3), B3′–H3′ 1.18(3), Ru1–arene 2.163(2)-2.250(2), C1–C1′ 1.514(3).

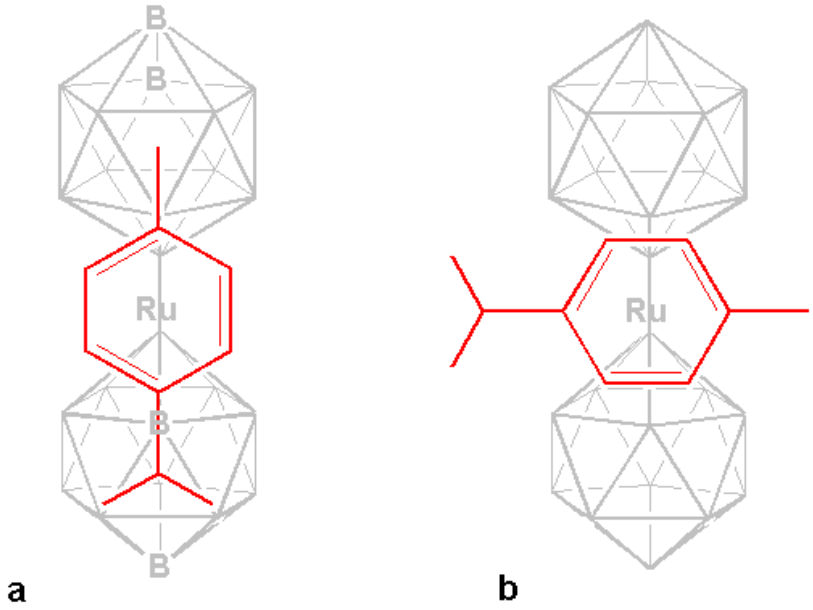


Fig. 3. Possible orientations of the *p*-cymene ligand above the Ru{κ^2-2,2′-[1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$]} unit in compound **1** such that the molecular symmetry is C_s. The observation of four BH resonances of integral 3 in the $^1H\{^{11}B\}$ NMR spectrum is only consistent with conformation **a**, not conformation **b**.

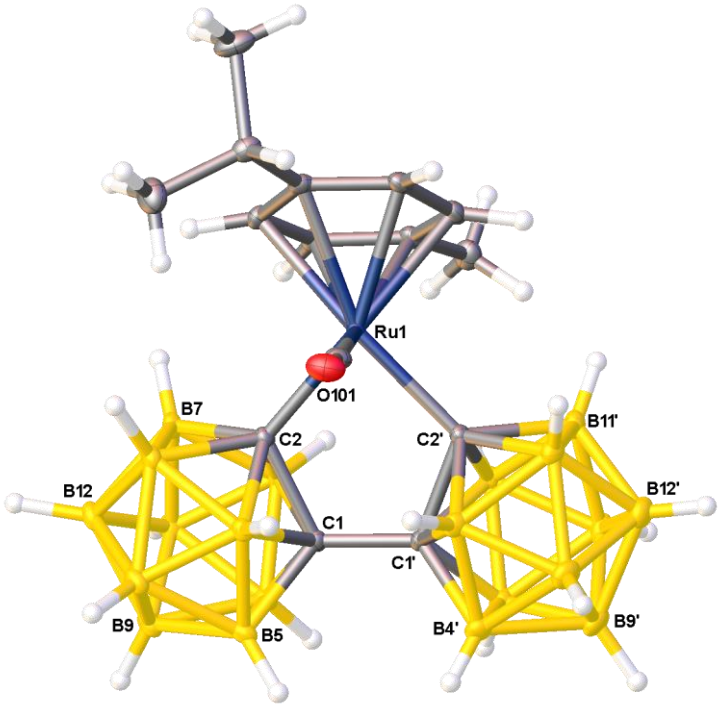


Fig. 4. Perspective view of compound **2** and part of the atom numbering scheme. Selected interatomic distances (Å) and angles (°): Ru1–C2 2.115(2), Ru1–C2′ 2.134(3), Ru1–C101 1.861(3), Ru1–arene 2.271(2)-2.398(2), C1–C1′ 1.526(2), Ru1–C101–O101 174.26(15)

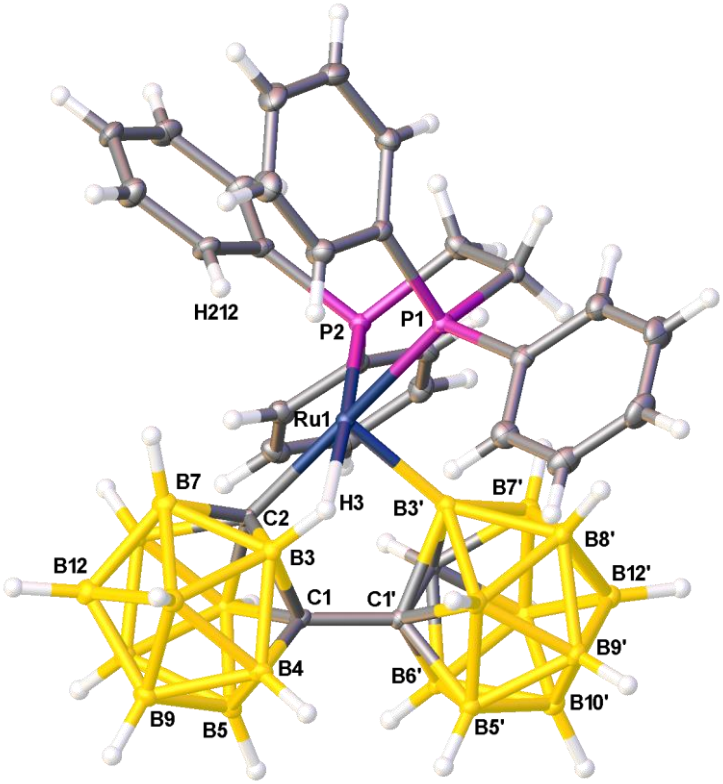


Fig. 5. Perspective view of compound **4** and part of the atom numbering scheme. Selected interatomic distances (Å): Ru1–C2 2.1479(19), Ru1–B3′ 2.034(2), Ru1–H3 1.955(19), Ru1–B3 2.413(2), B3–H3 1.15(2), Ru1–P1 2.2952(6), Ru1–P2 2.2423(6), C1–C1′ 1.520(3).

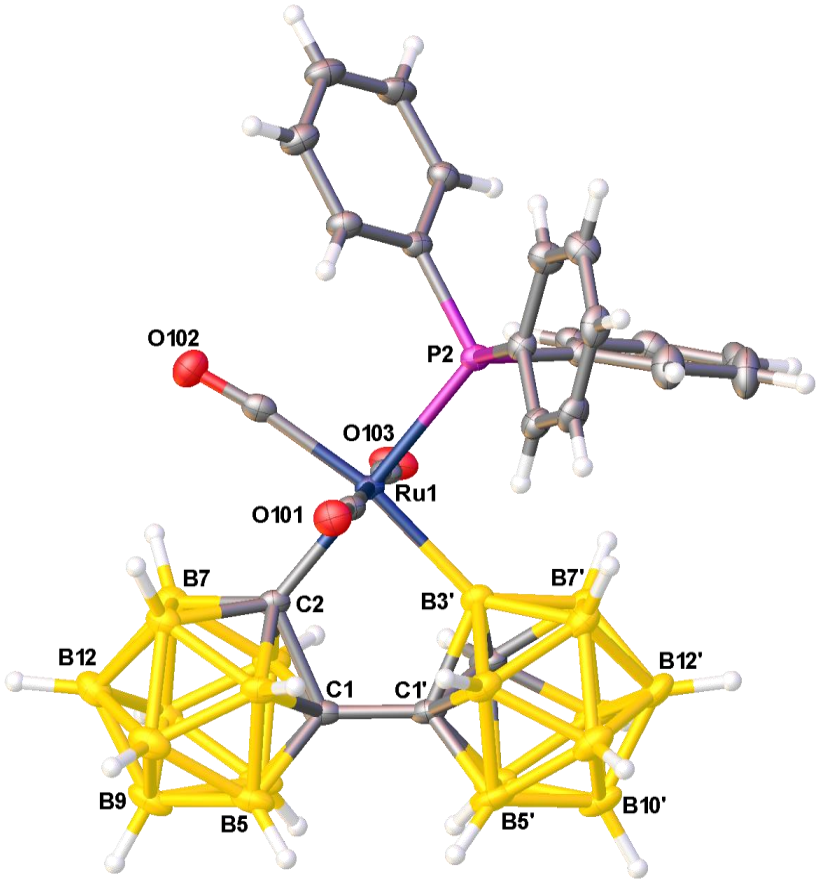


Fig. 6. Perspective view of compound **5** and part of the atom numbering scheme. Note that compound **5** is a mixture of two isomers only one of which is shown, and that crystallographically there is a 1:1 disorder between tatoms C2 and B3′. Selected interatomic distances (Å) and angles (°): Ru1–C/B2 2.188(2), Ru1–B/C3′ 2.243(2), Ru1–P2 2.4623(7), Ru1–C101 1.960(2), Ru1–C102 1.963(2), Ru1–C103 1.957(2), C1–C1′ 1.534(3), Ru1–C101–O101 174.67(19), Ru1–C102–O102 173.74(19), Ru1–C103–O103 178.28(19).

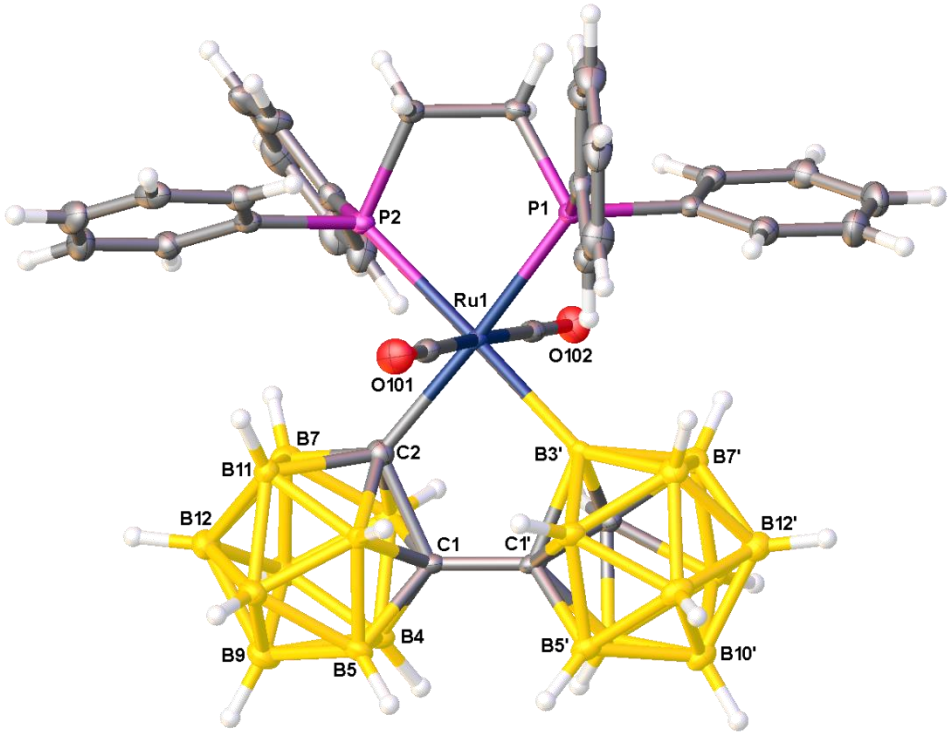
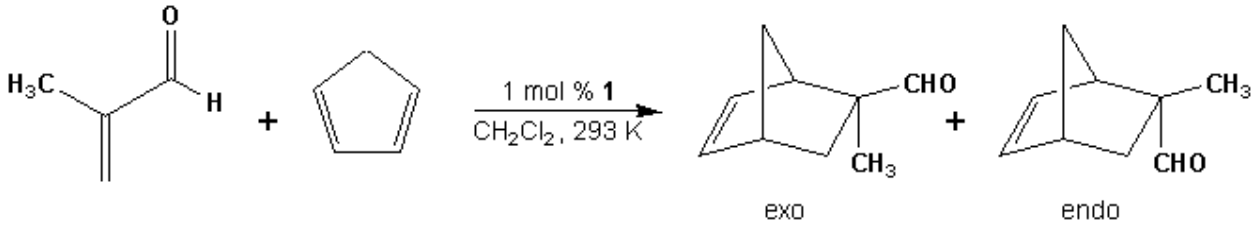


Fig. 7. Perspective view of compound **7** and part of the atom numbering scheme. Selected interatomic distances (Å) and angles (°): Ru1–C2 2.2078(19), Ru1–B3′ 2.242(2), Ru1–P1 2.3964(6), Ru1–P2 2.4328(6), Ru1–C101 1.9737(19), Ru1–C102 1.9615(19), C1–C1′ 1.537(3), Ru1–C101–O101 177.46(16), Ru1–C102–O102 173.76(15).



Scheme 2. The cycloaddition of methacrolein and cyclopentadiene catalysed by compound **1**.

Table 1 Crystallographic data.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{14}H_{34}B_{20}Ru$	$C_{15}H_{34}B_{20}ORu$	$C_{40}H_{50}B_{20}P_2Ru$	$C_{30}H_{44}B_{20}P_2Ru{\cdot}CH_2Cl_2$	$C_{25}H_{35}B_{20}O_3PRu{\cdot}CH_2Cl_2$	$C_{28}H_{44}B_{20}N_3PRu$	$C_{32}H_{44}B_{20}O_2P_2Ru$	$C_{34}H_{50}B_{20}N_2P_2Ru{\cdot}3CH_4N$
M	519.68	547.69	910.01	868.79	816.67	770.90	839.88	989.13
Crystal system	triclinic	orthorhombic	triclinic	Triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	*Pbar1*	$Pna2_1$	*Pbar1*	*Pbar1*	*Pbar1*	*P*bar1	*Pbar1*	*C*2/*c*
a/Å	9.9651(8)	17.7285(10)	11.2062(9)	10.6783(14)	10.774(2)	10.4838(14)	11.704(3)	21.5530(9)
b/Å	10.4007(8)	15.1002(8)	11.5418(10)	12.1648(17)	14.223(3)	10.6487(16)	12.184(3)	19.6096(8)
c/Å	13.6240(11)	9.8309(5)	17.9159(17)	17.624(2)	14.245(3)	18.114(3)	16.339(4)	23.5945(10)
α (º)	85.831(4)	90	81.178(5)	79.065(7)	63.017(11)	87.152(8)	104.475(7)	90
β (º)	70.460(4)	90	80.736(5)	74.204(7)	79.932(10)	75.088(7)	106.328(6)	94.465(2)
γ (º)	72.262(4)	90	85.546(5)	71.267(7)	80.026(10)	82.148(7)	98.443(7)	90
U / Å^3	1266.79(18)	2631.8(2)	2256.6(3)	2073.0(5)	1904.4(7)	1935.6(5)	2105.1(9)	9941.8(7)
Z, *Z′*	2, 1	4, 1	2, 1	2, 1	2, 1	2, 1	2, 1	8, 1
F(000)/e	524	1104	928	880	820	784	852	4064
D_{calc}/Mg m^{-3}	1.362	1.382	1.339	1.392	1.424	1.323	1.325	1.322
μ(Mo-K$_\alpha$)/mm^{-1}	0.624	0.608	0.451	0.611	0.626	0.474	0.480	0.417
θ_{max} (º)	27.28	36.13	27.78	30.93	31.36	34.18	30.63	30.20
Data measured	19182	70842	39226	46792	46419	40047	47883	107261
Unique data, *n*	5545	11988	10414	12793	12119	15552	12386	14488
R_{int}	0.0320	0.0370	0.0753	0.0661	0.0609	0.0399	0.0448	0.0429
Data with $I>2\sigma(I)$	5204	10594	8961	10032	8834	13111	9985	11576
R (obs. data)	0.0338	0.0250	0.0927	0.0382	0.0427	0.0368	0.0346	0.0351
wR_2 (obs. data)	0.0720	0.0513	0.1532	0.0771	0.0825	0.0740	0.0770	0.0917
S (all data)	1.085	1.014	1.229	1.059	1.052	1.022	1.031	1.057
Variables	379	397	639	562	567	541	574	714
E_{max}, E_{min}/e Å^{-3}	1.78, –0.82	0.74, –0.52	1.75, –1.31	0.62, –0.68	0.71, –0.71	0.56, –0.69	0.49, –0.79	0.53, –0.95
Flack parameter		-0.032(9)						

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