COMMUNICATION

Tethered N-heterocyclic carbene–carboranes: unique ligands that exhibit unprecedented and versatile coordination modes at rhodium†

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Four brand new hybrid ligands combining an N-heterocyclic carbene tethered with two isomeric *nido*-dicarbaundecaborane dianions, a neutral *closo*-dicarbadodecaborane or a *closo*-dicarbadodecaborane anion are described. Versatile coordination of the ligands to Rh^I is demonstrated, in which both NHC and carborane moieties covalently coordinate a metal centre.

Ligand design is central to the development of new organo-metallic and coordination compounds as they control the overall properties, the activities and the reactivities of a metal centre. This leads to potential new applications in materials, biomedicine and catalysis.[1–6] Whilst modifying current ligands may induce incremental changes in the chemical behaviour of a metal complex, novel ligand architectures can lead to more diverse variations. N-Heterocyclic carbenes (NHCs) are excellent two electron donor ligands, with their steric and electronic properties being controlled and tuned through alteration of the N-substituents and backbone substituents respectively (Fig. 1A. R^1–R^4).[7,8]

Carborane anions are also important classes of ligands, having very different properties to neutral NHCs. While there are many known classes of carboranes, the well-known *ortho*-carborane of type 1,2-R^5,R^6-1,2-C$_2$B$_{10}$H$_{10}$ (Fig. 1B) and the *nido*-carborane dianion of type [7,8-R^5,R^6-7,8-C$_2$B$_9$H$_9$]$^{2-}$ (Fig. 1D) are explored here. They can coordinate to a metal through either a boron atom or a carbon atom of a *closo*-carborane anion (*e.g.* Fig. 1C),[9] or through the open face of a *nido*-carborane dianion (*e.g.* Fig. 1D) to form a metallacarborane,[10] in analogy to the widely used cyclopentadienyl ligand. *Ortho*-carborane precursors can be easily modified by substituting the acidic cage hydrogen atom(s) at the cluster carbons with groups that have desirable electronic and steric effects. This includes the addition of tethering substituents such
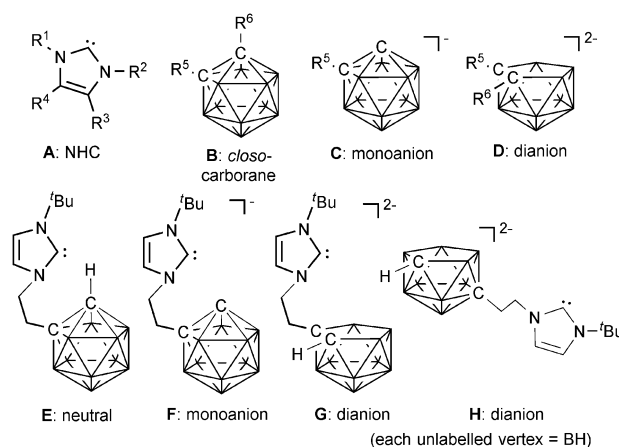

Fig. 1 Representation of an NHC (A), a neutral *ortho*-carborane (B), an *ortho*-carborane anion (C), a *nido*-carborane dianion (D) and novel hybrid ligands described in this study (E–H).

as amino[11–13] or cyclopentadienyl[14–16] groups. Herein, we report unprecedented tethered NHC–carborane ligands (Fig. 1E–H) in which both the carborane and the NHC moieties are available for metal binding.

Slow addition of one equivalent of ^{t}butylimidazole to bromoethyl-*ortho*-carborane in toluene was carried out at 75 °C for 18 hours (Scheme 1). The product, isolated in 72% yield, was characterised as an imidazolium salt linked to a *closo*-carborane *via* an ethylene tether (**1**). Addition of excess ^{t}butylimidazole to bromoethyl-*ortho*-carborane induced deboronation, with the ^{11}B NMR data for the resulting product exhibiting characteristic resonances for a *nido*-carborane monoanion of type [7,8-R^5,R^6-7,8-C$_2$B$_9$H$_{10}$]$^-$. The product, isolated in 65% yield, was identified as an unusual imidazolium *nido*-carborane zwitterion **2**. This compound could also be prepared from imidazolium **1** with two equivalents of ^{t}butylimidazole. Compounds **1** and **2** were characterised using multinuclear NMR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography (see ESI†).

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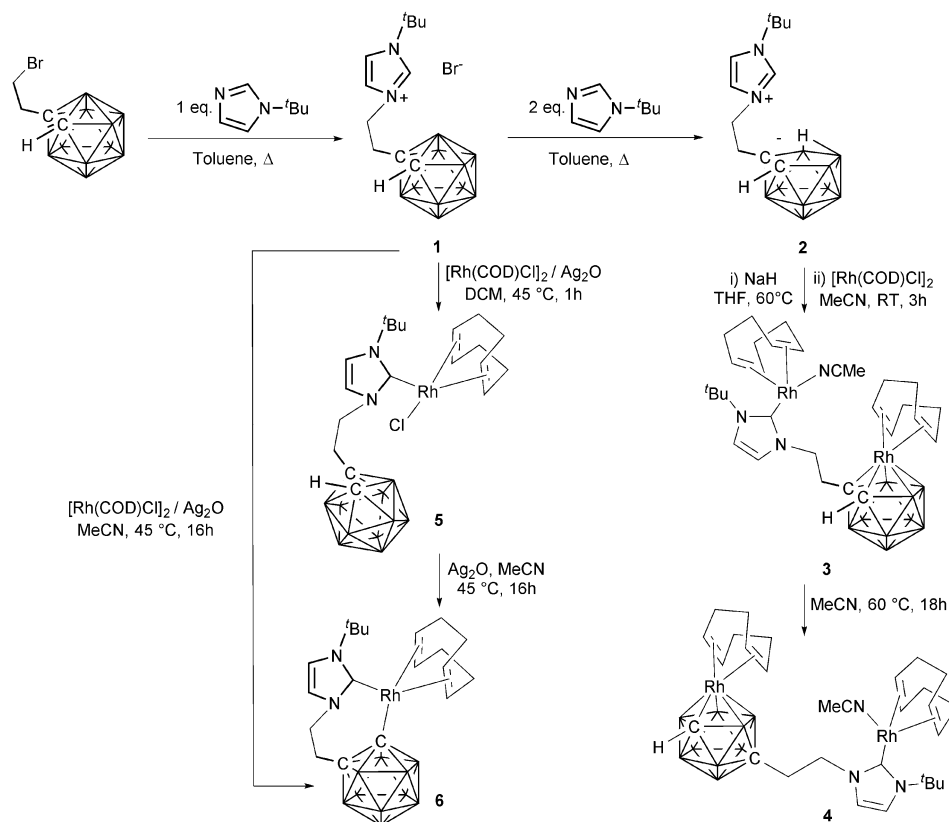
Scheme 1 Synthesis of new ligand precursors **1** and **2**. Deprotonation and variable coordination of the ligands to Rh^I (unlabelled vertices = BH).

A common method to prepare metallacarboranes involves deprotonation of the *nido*-carborane of type [7,8-R^5,R^6-7,8-C$_2$B$_9$H$_{10}$]$^-$ using NaH with subsequent coordination of the dianion of type [7,8-R^5,R^6-7,8-C$_2$B$_9$H$_9$]$^{2-}$ (Fig. 1D) to a metal. As NaH may also be used to generate free carbenes from imidazolium salts, zwitterion **2** was reacted with NaH to deprotonate both sites (Scheme 1). Subsequent treatment with [Rh(COD)Cl]$_2$ for 3 hours at room temperature resulted in the presence of two new Rh–NHC species, **3**·MeCN and **4**·MeCN, in the ^{1}H NMR spectrum (CD$_3$CN), with the ^{11}B{^{1}H} NMR spectrum showing resonances characteristic of *closo* MC$_2$B$_9$ metalladicarboranes. Crystals grown from the product mixture were identified as complex **3**·MeCN (Fig. 2), a bimetallic complex featuring two linked Rh^I centres in very different chemical environments, formally [Rh^I(NHC)(COD)(MeCN)]$^+$ and [Rh^I(carborane)(COD)]$^-$. While derivatives of the [Rh^I(carborane)(COD)]$^-$ anion have been known for decades,[17,18] this is the first solid-state structural elucidation of its kind.

Heating of the reaction mixture of **3**·MeCN and **4**·MeCN in MeCN for 18 hours gave only the thermodynamically stable product **4**·MeCN in 67% yield. Similarly to **3**·MeCN, crystals of **4**·MeCN revealed [Rh^I(NHC)(COD)(MeCN)]$^+$ and [Rh^I(carborane)(COD)]$^-$ moieties, but with the 2,1,8-MC$_2$B$_9$ metalladicarborane isomer present, where one cluster carbon atom is not bonded to Rh. The cluster carbon atoms in both **3**·MeCN and **4**·MeCN were identified using the vertex-to-centroid distance (VCD) method.[19] The observed 3,1,2 to 2,1,8 RhC$_2$B$_9$ cluster rearrangement is known,
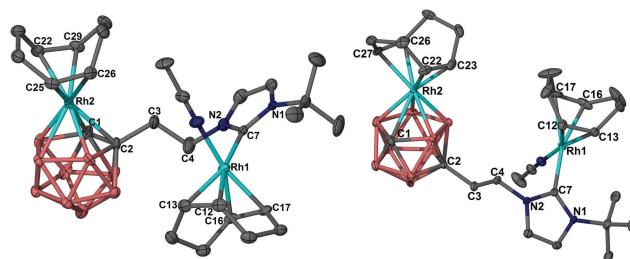

Fig. 2 Molecular structure of Rh^I complexes **3**·MeCN (left) and **4**·MeCN (right). H atoms are omitted for clarity and ellipsoids are plotted at 50% probability level. Selected bond lengths (Å): **3**·MeCN Rh1–C7, 2.061(4); C12–C13, 1.380(6); C16–C17, 1.389(6); Rh2–C1, 2.231(4); Rh2–C2, 2.306(4); C1–C2, 1.608(5); C25–C26, 1.410(5); C22–C29, 1.399(6). **4**·MeCN Rh1–C7, 2.048(3); C12–C13, 1.394(4); C16–C17, 1.371(5); Rh2–C1, 2.290(3); C22–C23, 1.404(5); C26–C27, 1.393(5).

and attributed to relief of steric crowding.[20] In addition, Stone and co-workers reported a series of Pd^{II}-metalladicarboranes, and found that polytopal rearrangement occurs readily in the presence of a COD co-ligand, thought to be promoted by dissociation of the COD.[21] Rearrangement of complex **3**·MeCN to **4**·MeCN occurs under relatively mild conditions, with both steric crowding and the presence of a COD co-ligand being contributing factors.

Recrystallisation of **4**·MeCN with a mixed solvent system (MeCN/Et$_2$O/hexane) resulted in the unexpected formation of a dimeric solid-state structure (**4**$_2$) with MeCN ligands absent
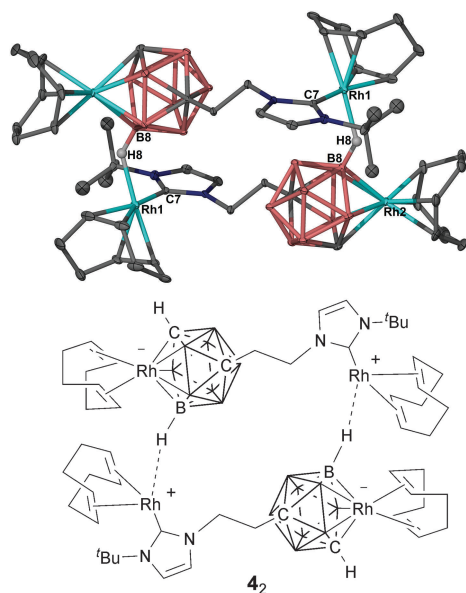
Fig. 3 Molecular structure of **4₂**. H atoms (except H8) are omitted for clarity and ellipsoids are plotted at 30% probability level. Selected bond lengths (Å): Rh1–C7, 2.043(4); Rh2–C1, 2.276(4); Rh2–B8, 2.229(5); Rh1–B8, 2.788.

Fig. 4 Molecular structure of [Rh^I(NHC)(COD)Cl] **5** (left) and Rh^I metalla-cycle **6** (right). H atoms are omitted for clarity and ellipsoids are plotted at 50% probability level. Selected bond lengths (Å): **5** Rh1–C7, 2.036(3); C15–C16, 1.407(6); C12–C19, 1.375(6); C1–C2, 1.653(5). **6** Rh1–C7, 2.028(3); Rh1–C1, 2.156(3); C12–C19, 1.405(4); C15–C16, 1.385(4); C1–C2, 1.738(4).

(Fig. 3). The cationic [Rh^I(NHC)(COD)]$^+$ moiety appears to be stabilised by the anionic [Rh^I(carborane)(COD)]$^-$ moiety of a second molecule via close Rh···H–B links and vice versa, resulting in the formation of a dimer. Rhodacarborane clusters containing Rh···H–B bridges have previously been reported,[22] with the complexes usually bimetallic. The dimer **4₂** does not appear to persist in solution, as the coordinated acetonitrile ligand is observed in the ^{1}H NMR spectrum (acetone-d₆). However, the demonstrated lability of the MeCN ligand and the contrasting Rh^I environments renders complex **4**·MeCN interesting for development in, for example, tandem catalysis without the need for a hetero-bimetallic system.[23,24]

Boron atoms in the closo-dicarbaborane cluster (Fig. 1B) are susceptible to attack by NaH in THF and by NHCs generated from imidazolium salts.[25,26] Thus, a milder route to NHC complexes, involving transmetallation from Ag, is successfully applied here without affecting the closo-carbaborane boron atoms. Reaction of imidazolium bromide **1** with [Rh(COD)Cl]₂ in the presence of Ag₂O in DCM resulted in a Rh^I–NHC complex (**5**) in 74% yield (Scheme 1). The carboranyl C–H proton resonates as a broad singlet at 4.17 ppm in the ^{1}H NMR spectrum, and the unsubstituted carborane carbon is at 63.6 ppm in the ^{13}C{^{1}H} NMR spectrum (500 MHz, CDCl₃). The solid state structure of **5** displays a square planar Rh^I centre, coordinating an NHC, a chloride and the two alkenes of a COD ligand (Fig. 4).

A surprising result was observed upon further reaction of complex **5** with Ag₂O in MeCN to yield complex **6** (Scheme 1). In this case, the ligand chelates the Rh^I centre, coordinating through the carbenic carbon of the NHC and through a carbon atom of the closo-carborane to form a 7-membered metallacycle. The carboranyl C–H resonance is absent in the ^{1}H NMR spectrum of complex **6**, with the ^{13}C{^{1}H} NMR spectrum exhibiting a doublet

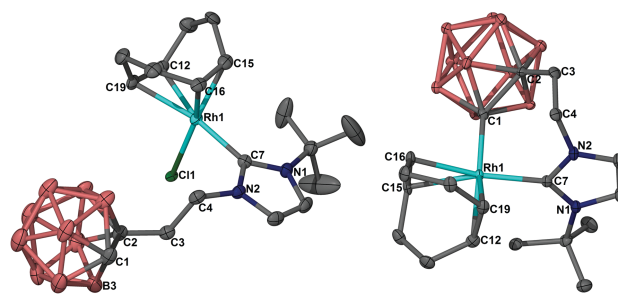at 70.6 ppm attributable to the Rh-coordinated carboranyl carbon, with a C–Rh coupling constant of 52.9 Hz. The metallacycle **6** could be formed in 79% yield directly from the imidazolium precursor **1** by conducting the initial [Rh(COD)Cl]₂/Ag₂O reaction step in MeCN. The solid-state structure of **6** shows a distorted square planar Rh^I centre, bearing a chelating NHC-closo-carborane ligand coordinating in a cis fashion through the carbenic carbon and through the carbon atom of the carborane cage (Fig. 4). C-cyclometallation of a carborane anion at Rh^I is rare, with only one other reported example found in the literature.[27]

While we may expect silver salts such as AgOTf to abstract the chloride anion in **5**, leading to a highly reactive Rh^I cation, the use of Ag₂O along with MeCN to generate **6** is more unusual. It is possible that the carborane C–H bond is cleaved to form a Ag–C bond followed by transmetallation with Rh. However, the possibility of an oxidative addition pathway with subsequent reductive elimination of HCl promoted by Ag₂O cannot be ruled out.

In conclusion, we have developed new ligand systems which combine soft and hard ligands, namely NHCs and carborane anions. Examination of the ligands has revealed unique and versatile coordination to Rh^I through both the NHC and either a nido-dicarbaundecaborane dianion or a closo-dicarbadodecaborane anion. The nido-carborane ligands form homo-bimetallic complexes, with two Rh^I centres in considerably different chemical environments. The closo-carborane ligand forms a remarkable 7-membered metallacycle coordinating through both the NHC and the carbon atom of the carborane. Expansion of these highly tailorable ligand classes through substituent modifications, varying tethers and different metals is currently underway in our laboratory, with the possibilities of extending to pincer ligands[28] and introducing chiral centres into the ligand architectures.[29] Our novel ligands will be of broad interest for development in catalytic, materials and biomedical applications, with the NHC and carborane moieties working synergistically to tune a particular system.

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