

# Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## ARTICLE

*In memory of Ken Wade -- a stellar scientist, original thinker, and good friend.* PERSPECTIVE

## Carboranes in the Chemist's Toolbox

Cite this: DOI: 10.1039/x0xx00000x

Russell N. Grimes

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Once seldom encountered outside of a few laboratories, carboranes are now everywhere, playing a role in the development of a broad range of technologies encompassing organic synthesis, radionuclide handling, drug design, heat-resistant polymers, cancer therapy, nanomaterials, catalysis, metal-organic frameworks, molecular machines, batteries, electronic devices, and more. This *perspective* highlights selected examples in which the special attributes of carboranes and metallocarboranes are being exploited for targeted purposes in the laboratory and in the wider world.

### Introduction

Some years ago, during a presentation on carboranes at an international symposium on inorganic chemistry, a member of the audience was heard to remark “This is fascinating stuff but it has no connection to anything I’m doing” — a view likely shared by others in that assembly. And these were *inorganic* chemists. At that time, carboranes and other polyhedral boron clusters were terra incognita to most organic and physical chemists, and certainly to biochemists. What possible relevance could these strange molecules with their bizarre structures and peculiar bonding have to biological systems, solid-state electronic devices, or organic synthesis? Well, times have changed, to a degree almost unimaginable a few decades ago. Today, of the hundreds of papers published annually dealing with carborane studies and applications, many are authored by workers whose scientific backgrounds are outside boron (or even inorganic) chemistry, but who have discovered that carborane-based science offers a way forward in their areas of interest. A significant mark of the times is that the mention of carboranes in most journals no longer requires a definition of the term — a sign of assimilation into the general body of knowledge of their readers.

Department of Chemistry, University of Virginia, Charlottesville VA 22901, USA.

Russ Grimes is a B.S. Chemistry graduate of Lafayette College and received his Ph.D. training with William N. Lipscomb at the University of Minnesota and at Harvard University, where his thesis research on boron hydride chemistry was conducted. After a postdoctoral year with Fred Hawthorne at UCR, in 1963 he began a 40-year career on the faculty at the University of Virginia with a term as Chemistry Department chair in 1981-84. He has been an Emeritus Professor since 2003.



This article highlights a few of the developing areas of basic and applied science in which carboranes are playing an expanding role, with selected examples including a number from recently published work. Others, not cited, are equally relevant and could have served just as well. My intention is to convey a general impression of the myriad ways in which carboranes are being used to advantage in science and technology.

### Carboranes in organic chemistry

#### Stabilization of highly reactive cations

The *closo*-1-CB<sub>11</sub>H<sub>12</sub><sup>-</sup> icosahedral anion, a 3-dimensional σ-aromatic system, is well known for its extremely low nucleophilicity.<sup>1-4</sup> This property is further enhanced in its polyhalo and polyalkyl derivatives, whose conjugate acids H<sup>+</sup>CB<sub>11</sub>X<sub>11</sub><sup>-</sup>, where X is F, Cl, Br, Me, or CF<sub>3</sub>, are extremely powerful proton donors, as is the diprotic acid (H<sup>+</sup>)<sub>2</sub>B<sub>12</sub>Cl<sub>12</sub><sup>2-</sup>. These are the least-coordinating anions yet found, not only surpassing the triflate ion in that respect but offering the additional advantage of being nonoxidizing and hence unreactive toward cationic species. As such, they have enabled the successful isolation and full structural characterization of some long-sought salts of a number of carbocations and other elusive species, including R<sub>3</sub>Si<sup>+</sup>, C<sub>60</sub><sup>•+</sup>, and H<sub>3</sub>O<sup>+</sup>. In recent work Reed and his coworkers, who have forged major advances in this area, have established H<sup>+</sup>HCB<sub>11</sub>F<sub>11</sub><sup>-</sup> as the strongest known Brønsted acid, a reagent capable of protonating hydrocarbons *at room temperature without oxidation*.<sup>5,6</sup> By this means, isolable C<sub>6</sub>H<sub>7</sub><sup>+</sup>, *n*-C<sub>6</sub>H<sub>13</sub><sup>+</sup>, and CMe<sub>3</sub><sup>+</sup> salts of HCB<sub>11</sub>F<sub>11</sub><sup>-</sup> have been generated from benzene, *n*-hexane, and (remarkably) *n*-butane, respectively. In a separate study, Jalilov et al. employed HCB<sub>11</sub>Me<sub>11</sub><sup>-</sup> as a counter ion to stabilize paracyclophane radical cations.<sup>7</sup> The capability of protonating hydrocarbons under ambient conditions affords a powerful tool for investigation in several areas such as hydrocarbon reformation on

zeolites, a process which normally occurs at high temperature and has been difficult to study.

The protonating power of the  $H^+CB_{11}X_{11}^-$  acids is not limited to hydrocarbons, and has enabled the stabilization and, in some cases structural characterization, of a range of elusive cationic species that were previously inaccessible or whose structures previously had been poorly defined. Among these are (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Sn<sup>+</sup>,<sup>8</sup> protonated porphyrins,<sup>9</sup> imidazolium salts,<sup>10,11</sup> C<sub>59</sub>N<sup>+</sup> (azafullerene),<sup>12,13</sup> silyl-stabilized allyl cations,<sup>14</sup> chloroalkanes,<sup>15</sup> ClR<sub>2</sub><sup>+</sup> (chloronium ions, R = Me or Et),<sup>16</sup> oxonium ions,<sup>17</sup> R<sub>3</sub>E<sup>+</sup> ions where E is Ge, Sn, or Pb,<sup>18</sup> and hydrated protons which have been isolated in benzene solvent as H<sub>3</sub>O<sup>+</sup>, H<sub>5</sub>O<sub>2</sub><sup>+</sup>, H<sub>7</sub>O<sub>3</sub><sup>+</sup>, and H<sub>9</sub>O<sub>4</sub><sup>+</sup>.<sup>19-21</sup> Also noteworthy is the protonation of fullerenes, with the isolation of HC<sub>60</sub><sup>+</sup>CB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub><sup>-</sup> as a stable salt and its structural characterization via <sup>13</sup>C CPMAS spectroscopy, revealing rapid movement of the proton that renders all 60 carbon atoms equivalent on the NMR time scale.<sup>22,23</sup>

Recently, Ozerov and his colleagues prepared and structurally characterized a silylium zwitterion stabilized by incorporation of a CB<sub>11</sub>Cl<sub>11</sub><sup>-</sup> unit (Fig. 1). This species, a strong Lewis acid, in turn generates other sought-after cationic species such as Ph<sub>4</sub>P<sup>+</sup>Me<sub>2</sub>SiCl-CH<sub>2</sub>-CB<sub>11</sub>Cl<sub>11</sub><sup>-</sup> and CMe<sub>3</sub><sup>+</sup>Me<sub>2</sub>SiClCH<sub>2</sub>CB<sub>11</sub>Cl<sub>11</sub><sup>-</sup> which are obtained on treatment with Ph<sub>4</sub>PCl and Me<sub>3</sub>CCl in liquid SO<sub>2</sub>, respectively.<sup>24</sup>

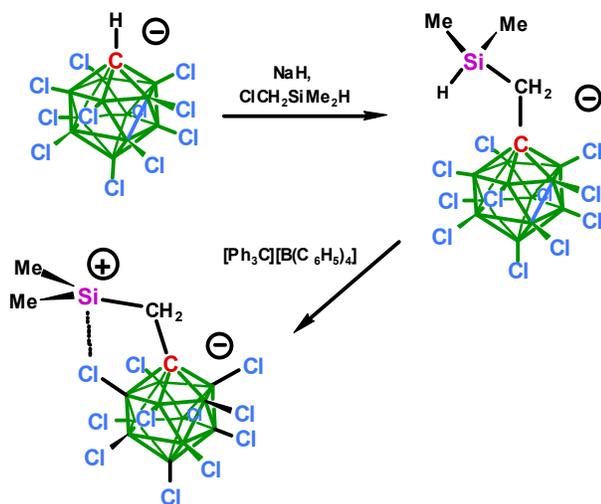


Fig. 1 Synthesis of Me<sub>2</sub>Si<sup>+</sup>CH<sub>2</sub>-CB<sub>11</sub>Cl<sub>11</sub><sup>-</sup>

Examples of the versatility afforded by monocarbon carborane anions are found throughout organic and organometallic chemistry. Mirkin's group has employed the unsubstituted CB<sub>11</sub>H<sub>11</sub><sup>-</sup> ion as a ligand in a novel type of weak-link approach (WLA) metal complexes, a genre that is currently of interest in the construction of supramolecular systems for potential biological and other applications.<sup>25</sup> In this work, a hemilabile (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>S)-1-CB<sub>11</sub>H<sub>11</sub><sup>-</sup> anion was used to prepare a series of Pt(II), Pd(II), and Rh(I) WLA complexes, in one of which the nearly noncoordinating carborane anion was combined with an isostructural and isoelectronic cation containing neutral 1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> (*m*-carboranyl) units to form the remarkable salt shown in Fig. 2. This compound, the first to incorporate both cationic and anionic WLA complexes,

demonstrates how the selection of appropriate carborane ligands can be used in the designed synthesis of novel reagents and materials.

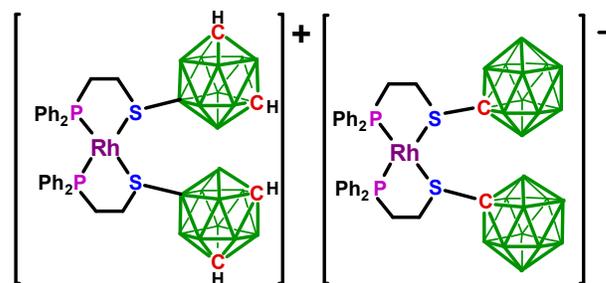


Fig. 2 Structure of Rh[PhP(CH<sub>2</sub>)<sub>2</sub>S-9-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]<sub>2</sub><sup>+</sup> Rh[Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>S-CB<sub>11</sub>H<sub>11</sub>]<sub>2</sub><sup>-</sup>

Strauss and coworkers have isolated and characterized the zwitterionic compound illustrated in Fig. 3 which contains AlMe<sub>2</sub><sup>+</sup> cations coordinated to MeCB<sub>11</sub>F<sub>11</sub><sup>-</sup> anions via Al-F bonds. The unusually long Al-F distances (ca. 1.92 Å) and large Me-Al-Me angles (147°) are consistent with large positive charge on the dimethylaluminum entities and hence support their designation as true cations.<sup>26</sup>

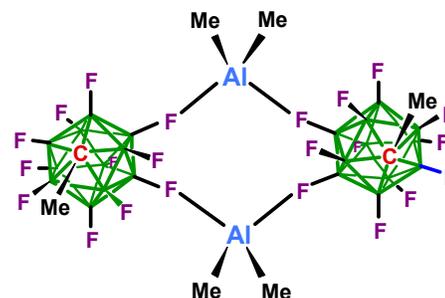


Fig. 3 Structure of [MeCB<sub>11</sub>F<sub>11</sub>]<sup>-2</sup> [AlMe<sub>2</sub>]<sup>+2</sup>

In another application, complexation with CB<sub>11</sub>H<sub>12</sub><sup>-</sup> ions enables the stabilization of N-heterocyclic carbenes (NHCs), as in the NHC-bridged species depicted in Fig. 4.<sup>27</sup>

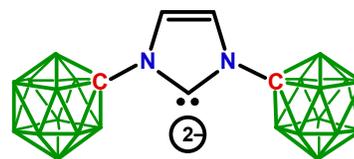
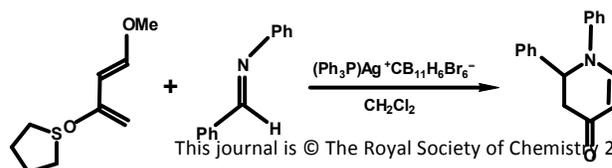


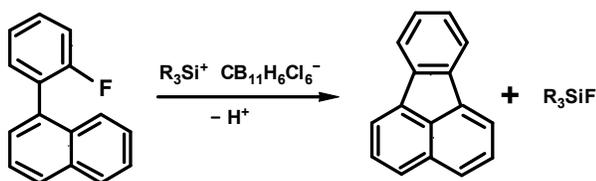
Fig. 4 Structure of the anion in (Li<sup>+</sup>)<sub>2</sub>H<sub>11</sub>B<sub>11</sub>C-N<sub>2</sub>C<sub>3</sub>H<sub>2</sub>Li-CB<sub>11</sub>H<sub>11</sub><sup>-2-</sup>

### Monocarbon carboranes in catalysis

The special properties of the CB<sub>11</sub> anions are used to advantage in a variety of ways. The hetero-Diels-Alder reaction between N-benzylidene and Danishefsky's diene is catalyzed by (Ph<sub>3</sub>P)Ag<sup>+</sup>CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub><sup>-</sup>, affording quantitative yields at room temperature.<sup>28</sup>



Friedel-Crafts proton-catalyzed coupling of fluoroarenes in high yield is promoted by  $R_3Si^+$  in the presence of a  $CB_{11}H_6Cl_6^-$  counterion:<sup>29</sup>

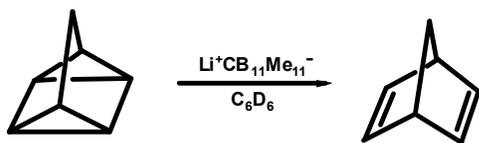


The highest known activity for the hydroamination of alkynes with amines, with a turnover rate of 95,000, has been observed in catalysis by the zwitterionic gold (I) complex  $C_4H_4S-Au-P(Me_2CH)_2CB_{11}H_{11}$ .<sup>30</sup>

The catalytic asymmetric synthesis of alkyl fluorides – a synthetic challenge – has been advanced via development of a planar-chiral Fe(II) nucleophilic catalyst employing a monocarborane counterion,  $Cp^*Fe(\eta^5-RNC_8H_5-NC_5H_{10})^+ CB_{11}H_{12}^-$  [ $R = C(O)C(CH_2Ph)PhF$ ], that promotes the formation of tertiary  $\alpha$ -fluoroesters from aryl alkyl ketenes.<sup>31</sup>

A special class of monocarbon carborane anions that is advantageous in some catalytic applications consists of the peralkylated derivatives such as  $CB_{11}Me_{12}^-$ . Like their counterpart  $B_{12}Me_{12}^{2-}$ ,<sup>32</sup> these ions function as spherical hydrocarbons whose  $CB_{11}$  core is protected, limiting interactions with external agents to the peripheral alkyl groups. Salts of  $CB_{11}Me_{12}^-$  are soluble even in organic solvents of low polarity, and solutions of the lithium salt in benzene are electrically conductive. Its methyl groups and those of  $HCB_{11}Me_{11}^-$  are calculated to have considerable  $CH_3$  (methide) character<sup>33</sup> and form strong bonds to transition metal and main-group metal cations. With some metal-containing cations, the metal-methyl group interaction is sufficiently strong to cleave a  $B-CH_3$  bond<sup>34</sup> and leave a neutral  $CB_{11}Me_{11}$  cluster having a “naked” boron atom lacking a substituent. Such boronium ylides can be generated from the neutral  $CB_{11}Me_{12}^{\bullet}$  radical obtained via oxidation of  $CB_{11}Me_{12}^-$ , as shown by Michl and his associates<sup>35</sup> who have extensively developed the chemistry of peralkylated  $CB_{11}$  clusters. This radical, a solid that is soluble in nonpolar solvents and sublimates at 150 °C, is quite reactive, extracting electrons from arenes, amines, and other species.<sup>5,35,36</sup>

The utility of the  $CB_{11}Me_{12}^-$  anion in various catalytic applications has been demonstrated, as in pericyclic rearrangements such as the conversion of quadricyclane to norbornadiene.<sup>37</sup>



Cubane is similarly converted to cuneane, and diademane to triquinacene, in all of which the catalytic effectiveness of the  $Li^+$  cation is considerably enhanced by the essentially nonbinding carborane anion.

Related lithium salts of 1,12-dialkylated anions, e.g.,  $Li^+RCB_{11}Me_{11}^-$  ( $R = Me, Et, i-C_4H_9, n-C_8H_{17}$ ), are effective Lewis acid catalysts.<sup>38</sup> In a somewhat different  $Li^+$ -catalyzed process, radical polymerization of alkenyl-carborane salts of the type

$Li^+[CH_2=CH(CH_2)_{n-2}]CB_{11}Me_{11}^-$  is initiated by  $O_2$ , azoisobutylnitrile, or di-*tert*-butylperoxide, and occurs in solution or in the solid state.<sup>39,40</sup> Polymerization of isobutylene in the presence of  $CB_{11}Me_{12}^-$ , in air at 25 °C or with di-*tert*-butyl peroxide at 80 °C, yields linear and highly branched polyisobutylene having molecular weights up to 50,000 and 26,000 respectively.<sup>41,42</sup> While the branched polymer is identical with that obtained under nonoxidizing conditions, the linear polymer has a  $CB_{11}Me_{12}^-$  unit appended at the end of the chain. The process is proposed to involve transfer of a methyl radical from a neutral  $CB_{11}Me_{12}^{\bullet}$  radical to isobutylene, thereby initiating radical polymerization, while the remaining  $CB_{11}Me_{11}$  boronium ylide, a strong Lewis acid, induces formation of the linear polymer by a cationic mechanism.<sup>41</sup>

### Exo-metallated carboranes and metallacarboranes in catalysis

Transition metal complexes of neutral carboranes, especially those of icosahedral 1,2-, 1,7-, and 1,12- $C_2B_{10}H_{12}$  (*o*-, *m*-, and *p*-carborane) have been intensively investigated as catalytic agents in a wide variety of organic syntheses, a topic on which a substantial literature has accumulated.<sup>43</sup> For present purposes, a few examples will serve to illustrate a small part of what has already been accomplished, as well as the enormous potential in this area. The incorporation of carborane cages in constrained-geometry catalysts affords significant advantages, including the ability to stabilize high and low metal oxidation states (as in reaction intermediates) as well as the unique steric properties and functional versatility of the carborane unit, which makes it possible to tailor catalysts for specific applications.<sup>44-46</sup> Among other advances, this has led to the development of improved constrained-geometry ruthenium catalysts for C-C coupling reactions.<sup>46</sup> Metal-carboranyl olefin polymerization precatalysts that outperform commercial cyclopentadienyl-bridged constrained-geometry complexes have been developed, such as (a) and (b) in Fig. 5, which are effective catalysts for the polymerization of ethylene in the presence of MAO (methylalumoxane).<sup>44-45</sup>

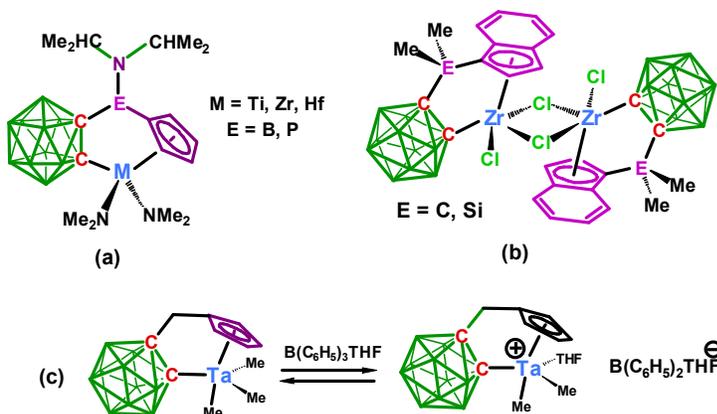
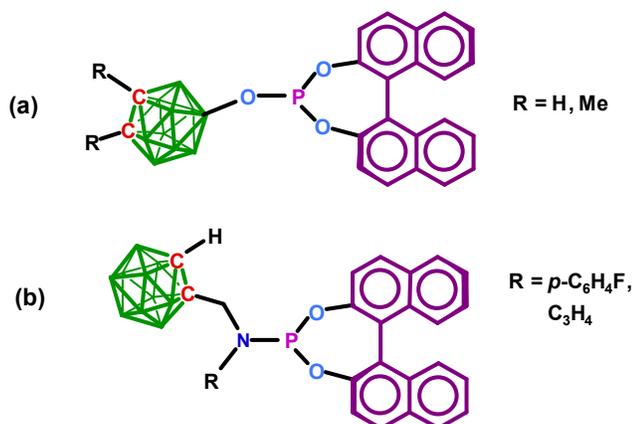


Fig. 5 o-Carboranyl constrained-geometry precatalysts

Other o-carboranyl zirconium complexes are effective in the catalytic conversion of  $CH_2=CHCN$  to poly(acrylonitrile), the trimerization of  $PhNCO$ ,<sup>47</sup> and the synthesis of syndiotactic poly(methylmethacrylate) from methyl methacrylate.<sup>48</sup> New architectures of constrained-geometry early transition metal

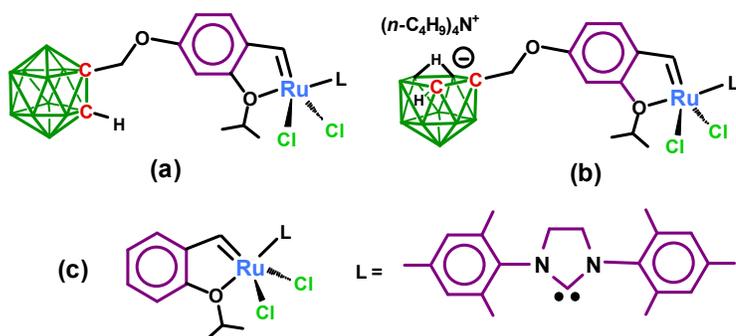
complexes have appeared, typified by the species in Fig. 5 (c) which is converted to a cationic form in the presence of  $B(C_6H_5)_3(THF)$ .<sup>49</sup>

In the important area of asymmetric catalysis, several classes of chiral carboranes have proved effective; recent examples include the BINOL (2,2'-dihydroxy-1,1'-binaphthyl) derivatives depicted in Fig. 6. In the presence of  $[Rh(COD)_2]BF_4$  in  $CH_2Cl_2$ , compounds of type (a) effect the hydrogenation of prochiral olefins in up to 99.5% ee,<sup>50</sup> while those of the (b) type promote the Rh-catalyzed asymmetric hydrogenation of enamides in supercritical carbon dioxide.<sup>51</sup> Other carboranyl phosphites have been employed in Rh-catalyzed hydroformylation of alkenes,<sup>52</sup> Pd-catalyzed allyl substitution,<sup>53</sup> and Suzuki-Miyaura Pd-catalyzed cross-coupling.<sup>54</sup>



**Fig. 6** Examples of BINOL-substituted chiral carboranes used in Rh-catalyzed asymmetric hydrogenation.

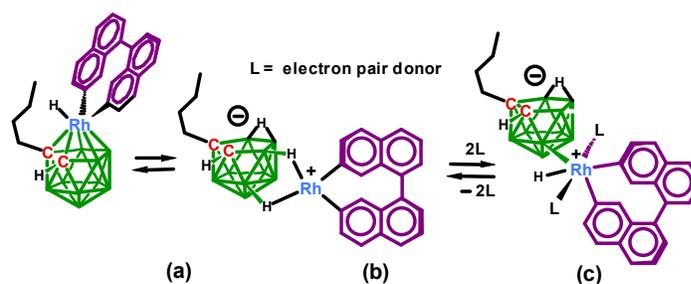
Carborane-based catalysts are often designed for specific applications, as in the ruthenium carbene in Fig. 7(a), which on deboronation with Lewis bases forms the *nido*- $C_2B_9$  anion (b), both of which are similar to the conventional catalysts (c). The closed-cage (a) and open-cage (b) types are both highly effective in promoting ring-closing metathesis, but are designed for different solvent systems, (a) and (b) being soluble in nonpolar and polar media, respectively. Salts of (b) are recyclable from ionic liquids and bind to cationic resins.<sup>55</sup>



**Fig. 7** Closo- and nido-carborane-based catalysts for ring-closing metathesis.

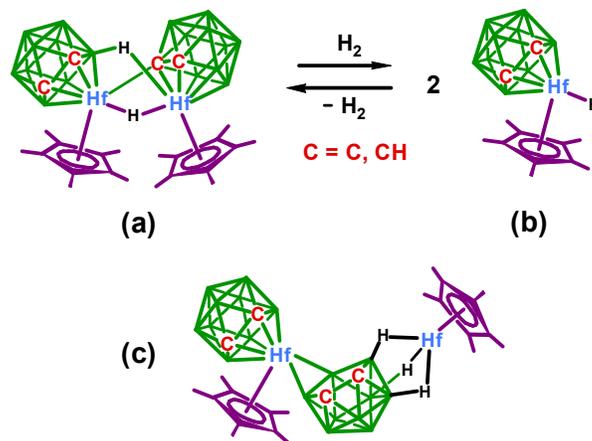
Metallacarboranes, in contrast to the exo-metal complexes in which the metal resides outside the cage, have their metal center(s)

incorporated into the cluster framework.<sup>†</sup> The role of metallacarboranes in catalysis has a long history extending back decades to the pioneering work of Hawthorne and his coworkers, who have done much to develop and extend this area over the years. Again, just a few examples can be cited. In a notable designed catalytic system, the asymmetric (R)-BINAP complex [(a) in Fig. 8] in ionic liquid media quantitatively hydrogenates prochiral ketones at 50 °C and 12 atm of  $H_2$  with very high ee.<sup>56</sup> Reversible oxidative addition of Rh(I) to the B–H bonds in (a) generates the Rh(III) complex (b), which is the active catalyst. The highest efficiency found for this reaction is obtained with the ionic liquid (N-*n*-butylpyridinium)<sup>+</sup> $CB_{11}H_{12}^-$  whose closo-carborane anion is proposed to interact with the rhodium center in (b) to generate catalytically active Rh(I) species.<sup>56</sup>



**Fig 8** A rhodacarborane-based hydrogenation catalyst.

In studies on early transition metal systems, Jordan and associates found that hydrogenation of the hafnium dimer in Fig. 9 (a) affords the monomer (b) which promotes the efficient hydrogenation of internal alkynes to *cis*-alkenes;<sup>57</sup> Another hafnium complex (c) catalyzes the regioselective dimerization of terminal alkynes, at the same time blocking the formation of trimers or higher oligomers via the intramolecular cyclization of a mononuclear intermediate.<sup>58</sup>



**Fig 9** Catalytically active *o*-carboranyl hafnium complexes.

## Stabilization of neutral species

Useful roles in organic synthesis have also been discovered for non-icosahedral carborane systems, such as the 7-vertex  $MC_2B_4$  clusters (where M is a transition metal) that are analogues of metallocenes in which two  $Cp^-$  ( $C_5H_5^-$ ) ligands are formally replaced by a single *nido*- $R_2C_2B_4H_4^{2-}$  ligand. These small metallacarboranes are characterized by high resistance to oxidation, solubility in organic solvents, and an ability to stabilize both high and low metal oxidation states owing to a substantial degree of covalence in the metal-ligand binding.<sup>4</sup> As one example, the hydridotantalum dimer  $[CpHTa(Et_2C_2B_4H_4)]_2(\mu-Cl)_2$  [Fig. 10 (a)] readily hydrometalates unsaturated hydrocarbons to afford different products from those typically obtained with  $Cp_2Zr(H)Cl$  (Schwartz's reagent).<sup>59</sup>

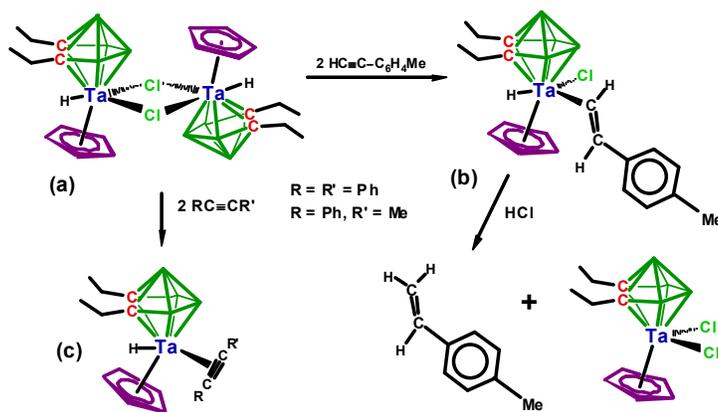


Fig. 10 Hydrometalation of alkynes by a tantalum-carborane complex.

Whereas insertion of alkenes and alkynes into the Zr–H bond of Schwartz's reagent produces alkenyl- or alkynylzirconium(IV) species that release the organic product on treatment with electrophilic reagents,<sup>60</sup> reaction of the tantalum-carborane complex with *p*-tolylacetylene and subsequent treatment with HCl affords only *trans-p*-tolylethylene.<sup>59</sup> Reactions of the same tantalum-carborane with alkynes yield stable hydridotantalum-alkyne monomers [Fig. 10 (c)] which are the first reported alkyne  $\pi$ -complexes of a formal  $d^0$  transition metal.<sup>59</sup>

The capacity of *nido*- $R_2C_2B_4H_4^{2-}$  ligands to stabilize highly reactive organic entities is demonstrated by the isolation and X-ray structural characterization of an air-stable metal-benzynes complex, a very rare genre (Fig. 11, upper right).<sup>61</sup> In contrast to the extreme reactivity of nearly all known metal-benzynes complexes, the phosphine-benzynes-tantalum(V) carborane is unreactive toward methanol, alkynes, and acetone, and the phosphine group is non-labile. As shown in the Figure, in the absence of the phosphine ligand Ta-benzynes intermediates are quite reactive, combining with alkynes to generate metallaindenes from which organic products can be released on further treatment.<sup>62</sup>

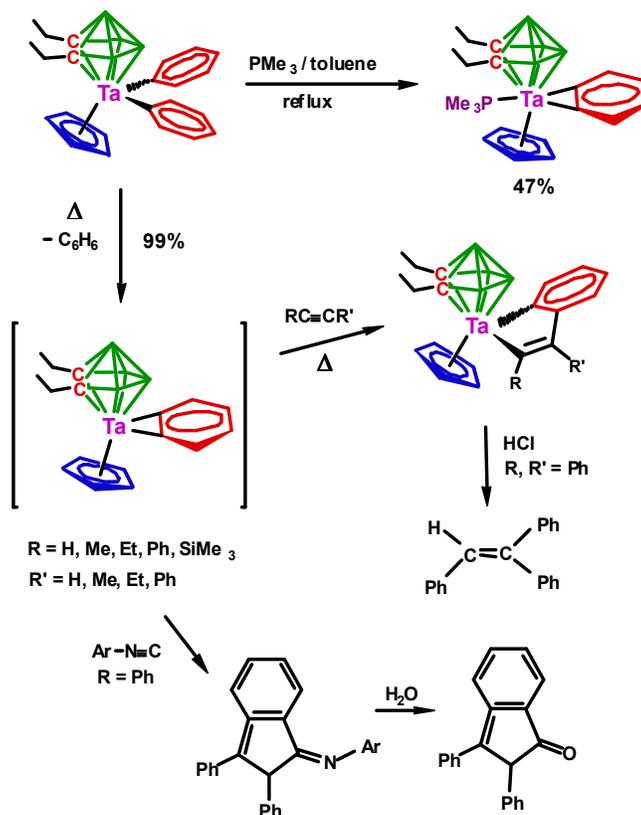


Fig. 11 Synthesis and activity of tantalum-benzynes complexes.

## Carboranes in drug design and delivery

The application of boron cluster science to medicine began decades ago with boron neutron capture therapy (BNCT), a technique that employs a nuclear reaction between low-energy neutrons and the  $^{10}B$  isotope to selectively destroy boron-enriched tumor cells, and has been in clinical trial on brain cancer patients in the U.S. and other countries.<sup>63</sup> This treatment exploits the high boron content of carboranes and other boron clusters for the purpose of delivering  $^{10}B$  to tumors via compounds that are essentially chemically inert toward biological systems.

In recent years, interest has also grown in the design and testing of carborane-based anticancer and anti-arthritis pharmaceutical agents.<sup>63-66</sup> This activity centers on several attributes of  $C_2B_{10}$  clusters and their  $CB_{11}$  and  $B_{12}$  analogues, i.e., their near-inertness in biological systems; their lipophilic and hydrophobic character (owing to the hydridic B–H bonds); their size and shape, which approximates the volume occupied by a rotating phenyl ring; and their non-participation in  $\pi$ - $\pi$  stacking interactions (a characteristic of phenyl groups that can cause unwanted side effects). Consequently, replacement of selected aryl rings in drugs with carborane units is a useful strategy for improving their pharmaceutical effectiveness, for example by exploiting the ability of the cage to occupy hydrophobic pockets on a protein. With appropriate selection of the carborane and introduction of substituents on the cage, the way is open to almost unlimited possibilities for drug design – actually, to a much greater extent than can be achieved with conventional organic chemistry – a concept

that has sparked considerable research activity and generated hundreds of publications within just the past few years. Here we cite a few illustrative examples of current work in this area.

### Quantum dots

Carborane-based metal complexes are of interest as potentially effective antitumor agents, and both exo-metallated clusters and metallacarboranes (which contain metal centers in the cage skeleton) are cytotoxic toward tumor cells, as summarized in recent reviews.<sup>65,66</sup> For example, water-soluble copper complexes of the type  $\text{Cs}^+\text{Cu}(\text{porphyrin})\text{Ph}_4[\text{CH}(\text{OH})\text{CB}_{11}\text{H}_{11}]^-$  are lethal toward K562 leukemia and MCF-7 breast carcinoma, which are resistant to conventional drugs.<sup>67</sup> In an extension of this idea, the conjugation of *o*-carborane-1,2-dicarboxylic acid to green-emitting CdTe quantum dots (QDs) quenches their fluorescence intensity and induces a red shift in the emission peak, which improves the efficiency of inhibition of target cancer cells relative to that observed with CdTe QDs in the absence of carboranes.<sup>68</sup> Specifically, the carborane QDs are reportedly much more efficient toward SMMC-7221 hepatocellular carcinoma cells than are cysteamine-CdTe QDs.<sup>69</sup>

### Dendritic gold nanoparticles

Another strategy for introducing carborane-functionalized drugs or BNCT agents into biological systems employs macromolecular systems such as dendrimers or nanoparticles, which can be synthesized efficiently through Cu(I)-catalyzed azide-alkyne cycloaddition CuAAC (“click”) reactions, or via direct reactions on gold nanoparticles. An example of the latter type is a polyethylene glycol-based (PEGylated) assembly anchored to a gold cluster, shown in Fig. 12.<sup>70</sup>

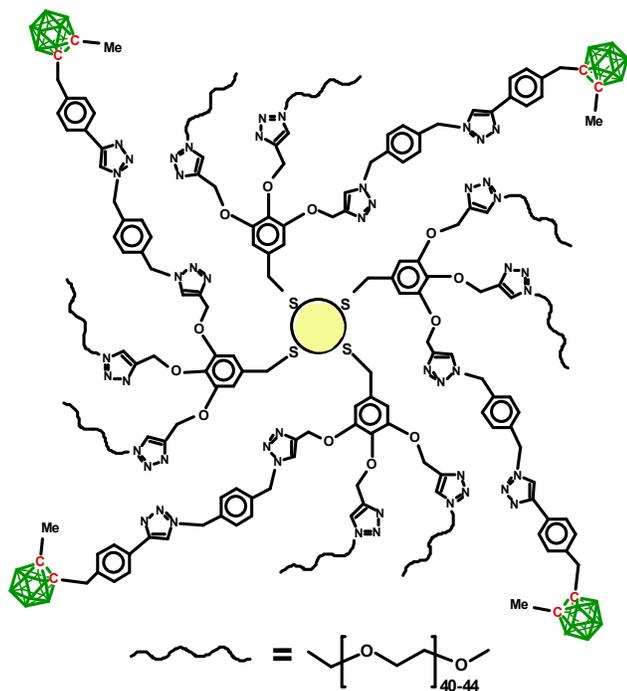


Fig 12 A carborane-functionalized PEGylated gold nanoparticle

Other types of multi-branched systems, in which the central core is a benzene ring or other arene system, have been prepared via designed synthesis. An example is a class of photoluminescent star-shaped dendrimers such as  $1,3,5\text{-}[\text{RCB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3\text{OC}_6\text{H}_4]_3\text{C}_6\text{H}_3$  ( $\text{R} = \text{Me}, \text{Ph}$ ); removal of one boron from each carborane cage (deboronation) affords negatively charged water soluble *nido*- $\text{C}_2\text{B}_9$ -based dendrimers.<sup>71</sup> A structurally similar compound, a star-shaped dendrimer with a 1,3,5-triphenylbenzene core and *o*-carborane units on its periphery, exhibits high accumulation in SK-Hep1 cancer cells and thus may be a viable candidate for BNCT application.<sup>72</sup>

### Carboranes in micelles and vesicles

The concept of loading carboranes into micelles as delivery vehicles for BNCT is under exploration by several groups. Micelles are typically spherical aggregates of surfactant molecules in a liquid colloid which feature hydrophilic “heads” that are directed outward toward the surrounding aqueous medium, while the other ends are hydrophobic and point inward. A problem with this approach as a boron-delivery system – leakage of the carborane from the micelle during blood circulation – has been circumvented by effecting radical polymerization between 1-*p*-vinylbenzyl-*o*-carborane and a polyethylene glycol-*block*-polylactide copolymer bearing an acetal group at one end and a methacrylyl group at the other (acetal-PEG-*b*-PLA-MA), effectively locking the carborane into the micelle (Fig. 13). *In vivo* studies in mice confirmed the absence of leakage in this system.<sup>73</sup>

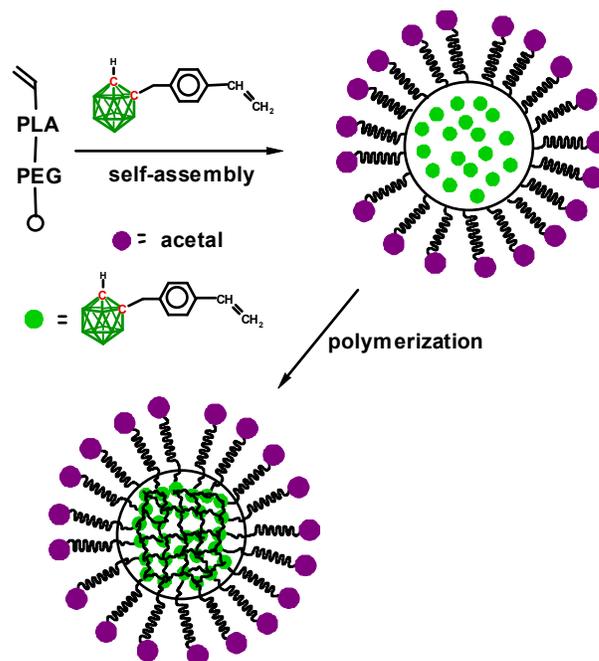


Fig 13 Preparation of a carborane-loaded micelle

In a different approach, the self-assembly of the 3-Co(1,2- $\text{C}_2\text{B}_9\text{H}_{11}$ ) $_2^-$  [bis(dicarbollyl)cobaltate] monoanion (Fig. 14) in water at low concentration has been shown to create monolayer vesicles, which at higher concentration rearrange to micelles, a behavior which is potentially applicable as an HIV-protease inhibitor, as well

as in nonmedical areas such as ion-selective electrodes or the extraction of radioisotopes from nuclear waste (see below).<sup>74</sup>

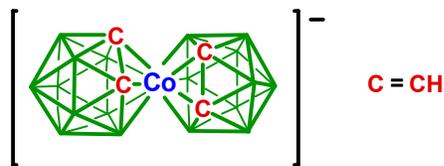


Fig 14 Structure of the 3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> anion.

Chen and coworkers have employed a multifunctional strategy in which a polyethylene glycol conjugate linear polymer ( $M_n = 2,000$  g/mol) labeled with a fluorescence rhodamine dye undergoes self-assembly in aqueous media to form narrowly distributed spherical vesicles that can function as a hydrophilic drug carrier or as a fluorescent probe for diagnostic imaging, as well as a boron delivery agent for BNCT.<sup>75</sup>

### Antibacterial agents

The distinctly abiological nature of carboranes and other boron clusters suggests a role for them in the development of resistance-suppressing antibiotics. In a recent biomedical application of carborane chemistry, the ruthenium-*o*-carboranyl-ferrocene complex in Fig. 15 has been demonstrated to have antimicrobial properties, countering the resistance of multidrug-resistant clinical isolates of certain MDR pathogens toward antibiotics in biofilms. This behavior apparently reflects a decrease in the expression of extracellular matrix proteins in these strains induced by the complex.<sup>76</sup>

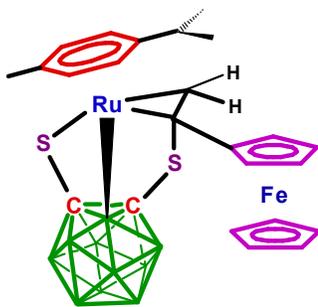


Fig 15 Structure of 1,2,3-tricyclo- $\{S\text{-Ru}(\text{MeC}_6\text{H}_4\text{CHMe}_2)(\mu\text{-CH}_2)\text{C}[(\text{C}_5\text{H}_4)\text{FeCp}]\}$

### Carboranes in electronic devices

Given their inherent robustness in a wide range of conditions, electron-delocalized skeletal bonding, ability to accommodate metal atoms in the cage framework, tailorability via attachment of functional groups, and power to stabilize both high and low metal oxidation states, carboranes and metallacarboranes are obvious candidates for electronic applications in microelectronic and logic devices, electropolymer, biosensors, microencapsulators, and other technologies. Again, space permits just a few cases in point to illustrate recent progress in this rapidly expanding area of research.

### Metallacarboranes

It was shown by Hawthorne et al. a decade ago that the bis(dicarbollyl)nickel(III) anion 3-Ni<sup>III</sup>(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> undergoes facile, reversible oxidation to the neutral 3-Ni<sup>IV</sup>(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>0</sup> species (Fig. 16) with an accompanying change in ligand conformation that in principle could be harnessed to create a redox-driven molecular machine (see below).<sup>77</sup>

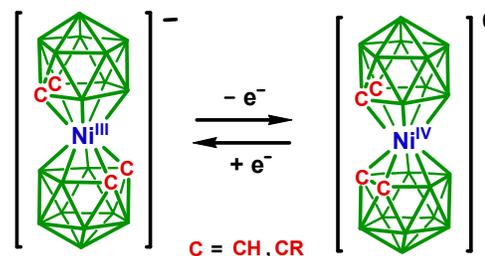


Fig 16 The 3-Ni(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> / 3-Ni(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>0</sup> couple

This system has been adapted, in a collaborative effort by several groups,<sup>78</sup> as an improved redox shuttle for dye-sensitized solar cells (DSCs), which in contrast to the widely employed  $\Gamma/I_3^-$  couple does not lead to adsorption on TiO<sub>2</sub> photoanodes. Moreover, its power conversion efficiency exceeds that of the ferrocene-ferrocenium (Fc/Fc<sup>+</sup>) couple by a factor of 90, and avoids the problem of electron interception by ferrocenium ion, thereby increasing the survival time of the electron in the photoelectrode. The utility of this system has been further enhanced by the introduction of functional groups at the B(9,12) cage vertices, which permit tuning of the redox shuttle potential over a 200 mV range.<sup>78</sup> A later modification, employing silica aerogels coated by atomic-layer-deposited TiO<sub>2</sub> in place of nanoparticles as a DSC platform, has led to greatly increased performance with photocurrent densities more than twice those of nanoparticle-based photoanodes.<sup>79</sup>

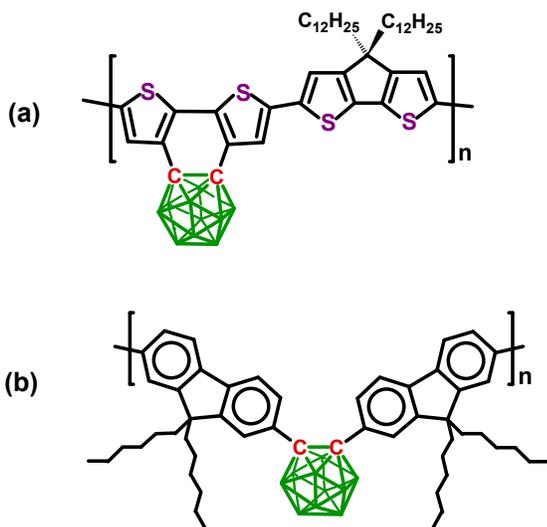
Derivatives of the well-known bis(dicarbollyl)cobaltate anion (Fig. 14) are also drawing attention in the design of new electronic materials and devices. Salts of the type L<sup>+</sup>Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> where L is a planar radical cation such as tetrathiafulvalene (TTF), bis-(methylenedilithio)tetrathiofulvalene (BMDT-TTF), or tetramethyl-tetraselenafulvalenium (TMTSF) are semiconductors with room temperature conductivities ranging between 10<sup>-4</sup> and 15 ohm<sup>-1</sup> cm<sup>-1</sup> that crystallize in layered structures which can be tailored via introduction of substituents on the cages.<sup>80</sup> Polypyrrole films doped with Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> show increased resistance to overoxidation (a degradative process that reduces electrical conductivity) by 300-500 mV; remarkably, even if the overoxidation limit is exceeded, the doped films regain their electroactivity within hours.<sup>81,82</sup> In a direct application of this work to the fabrication of electronic devices, Teixidor and coworkers have constructed a 3D array of highly conducting polypyrrole microrings doped with Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> anions via surface patterning and electropolymerization.<sup>83</sup>

In related work, polypyrrole microelectrodes doped with Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> have been developed as hydrogen sensors,<sup>84,85</sup> polymer membranes impregnated with Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Cl<sub>3</sub>)<sub>2</sub><sup>-</sup> function as electrochemical sensors for Pb<sup>2+</sup><sup>86</sup> or lanthanides,<sup>87</sup> and a poly(3,4-

ethylenedioxy-thiophene) polymer incorporating non-extradable  $\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2^-$  has been prepared.<sup>88</sup>

### Carborane derivatives

Also intensively studied as electroactive materials are non-metallated carboranes, in most of which the cages are covalently bound into a chain or network. As one example, conducting films based on thiophene polymers that incorporate *o*-, *m*-, or *p*-carborane units are typically superior to conventional polythiophenes in electrochemical and thermal stability.<sup>89</sup> In this category, the polythiophene shown in Fig. 17(a), and analogous materials incorporating *m*- and *p*-carboranyl units, exhibit optoelectronic, photovoltaic and charge-transporting properties of interest in the development of transistors, including ambipolar charge transport.<sup>90,91</sup> Arylene-linked polymers such as the fluorene-connected chain in Fig. 17(b)<sup>92</sup> are also of interest, as aromatic rings not only stabilize the system but can also be tailored by introduction of substituents to provide desired optoelectronic properties; *e.g.*, linear  $\pi$ -conjugated aryl-ethynyl-carborane polymers typically are intensely luminescent (the compound in Fig. 17(b) is a deep green emitter).

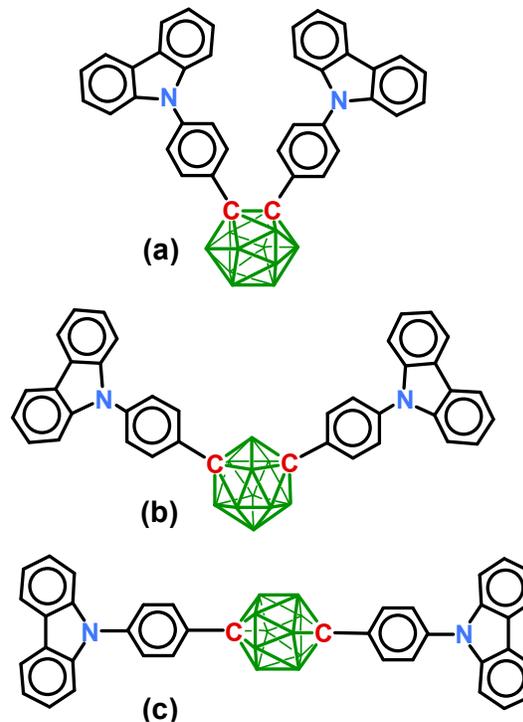


**Fig 17** (a)  $[-\text{cyclo-C}_8\text{S}_2\text{H}_2(\text{C}_2\text{B}_{10}\text{H}_{10})\text{-Ar}]_n$  dithiophene polymer. (b)  $\{1,2\text{-}[2'-(9',9''\text{-dihexylfluorenyl})\text{C}_2\text{B}_{10}\text{H}_{10}]\}_n$  polymer.

Carter and associates have demonstrated the ability of fluorene-*o*-carborane polymers to function as light-emitting diodes and transistors and as vapochromatic photoluminescent sensors toward volatile organics.<sup>93</sup> Although the carboranes in this case do not participate in the  $\pi$ -conjugation, they induce a major red shift in electroluminescence in devices and thin films. In field effect transistors their presence results in an order of magnitude increase in charge carrier mobility.<sup>94</sup>

Studies in Kang's laboratory have established that *o*-, *m*-, and *p*-carborane derivatives bearing attached photoactive carbazolyphenyl groups (Fig 18) localize triplet energy at one end of the aromatic substituents.<sup>95</sup> Unlike their bis(carbazolyphenyl)benzene counterparts, the carbazoly units in the *m*- and *p*-carboranyl

compounds are not conjugated, and exhibit blue phosphorescence. Particularly notable performance is observed when the *p*-carboranyl system [Fig. 18 (c)] is employed as a host in the emission layer for deep blue phosphorescent organic light-emitting diodes, exhibiting high external quantum efficiency (15.3%) and other desirable properties. Experimental and theoretical studies show that the photoinduced electron-transfer process occurs intramolecularly.<sup>96</sup>



**Fig 18** Carbazolyphenyl-carborane dyads

Complexes similar to those in Fig. 18 have other interesting properties. For example, a tunable coordination polymer composed of 1,2-[terpyridyl- $\text{C}_6\text{H}_4\text{-C}\equiv\text{C-p-C}_6\text{H}_4$ ] $\text{C}_2\text{B}_{10}\text{H}_{10}$  units (analogous to Fig. 18(a)) linked by zinc atoms exhibits strong luminescence arising from intraligand charge transfer.<sup>97</sup>

Two-photon-absorbing fluorophores, consisting of conjugated chains having a *p*-carborane unit at one end and an organic electron donor at the other, *e.g.*, 1- $\text{CH}=\text{CH-p-C}_6\text{H}_4\text{-C}\equiv\text{C-p-C}_6\text{H}_4\text{-CH}=\text{CH-C}_6\text{H}_2\text{-4-R-3',5'-R'}$  (where R and R' are, for example,  $\text{NPh}_2$  or  $\text{OC}_{12}\text{H}_{25}$ ), are strongly fluorescent in aqueous and nonaqueous media and may be suitable for two-photon excited microscopy as well as BNCT.<sup>98</sup>

The consequences of introducing carboranes as connecting units between large chromophores (as in some biological systems in which protein-bound reactants, separated by 30 Å or more, interact only very weakly) have been explored by Harriman and coworkers. Studies of molecular dyads linked by *o*- or *p*-carboranyl units, such as the bodipy-dpp system in Fig. 19 (dpp = diketopyrrolopyrrole, bodipy = boron dipyrromethene) reveal that energy transfer across the dyad involves both through-space and through-bond mechanisms.<sup>99</sup>

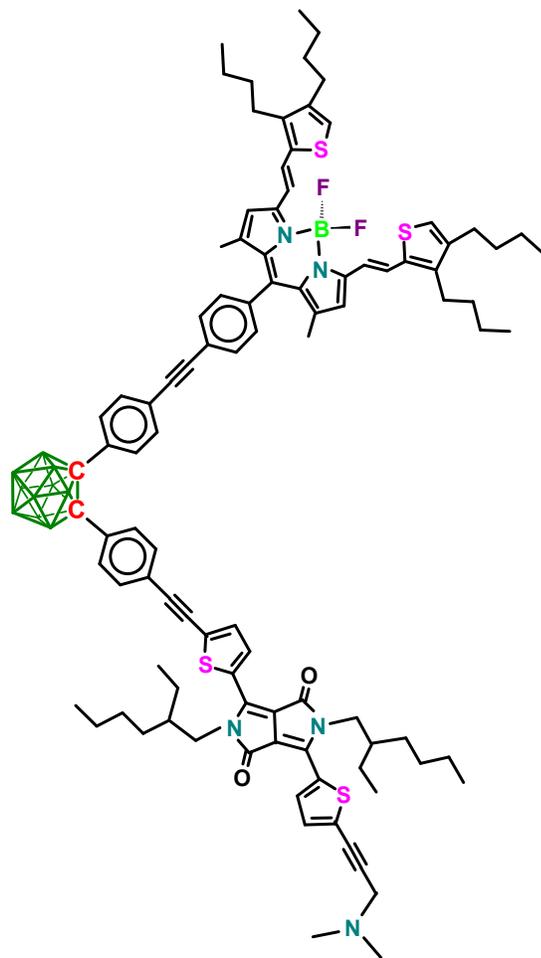


Fig 19 A carborane-bridged bodipy-dpp dyad.

Fullerene-carborane systems are also under investigation computationally and experimentally. The possibility of encapsulating icosahedral  $C_2B_{10}H_{12}$  or  $B_{12}H_{12}^{2-}$  units within fullerene cages to create novel nanoclusters has been explored theoretically,<sup>100</sup> although no such species has been synthesized as yet; however, a 1:1 *o*-carborane- $C_{60}$  adduct has been observed in an electron-impact mass spectrometer.<sup>101</sup> Dyads combining *o*-carborane and fullerene cages that exhibit remarkable electron mobility, such as that depicted in Fig. 20, have been fabricated into solution-processed organic field-effect transistors.<sup>102</sup>

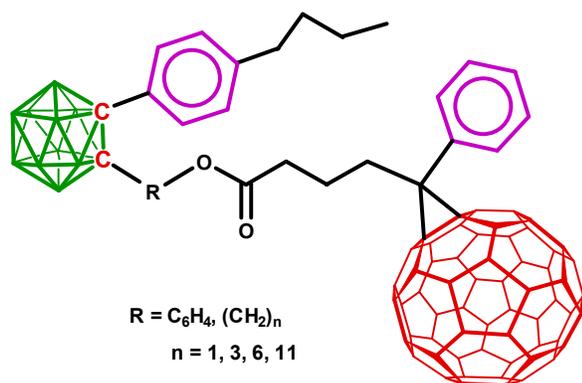


Fig 20 An *o*-carborane-fullerene dyad.

The implementation of carboranes in working electronic devices is proceeding. Li et al. have integrated parent *o*-carborane into a p-type field-effect transistor in a 28 nm state-of-the-art logic flow, whose performance was optimized via enhanced surface activation, reduced leakage, and control of boron lateral diffusion.<sup>103</sup>

### Thiol-carborane layers and films

Many developing applications employ monomolecular layers or thin films containing carboranes that are attached to metal or other surfaces. *o*-Carborane thiols such as 1,2- and 9,12-(HS) $_2$ C $_2$ B $_{10}$ H $_{10}$  serve as building-blocks in the self-assembly of monolayers on copper,<sup>104</sup> silver,<sup>105,106</sup> and gold.<sup>107,108</sup> Both isomers modify the surface potential of flat metal surfaces, but the 1,2 isomer increases the surface potential of modified Ag film more effectively than does the 9,12 compound, a finding attributed to the higher inductive electron withdrawal by the carboranyl carbon atoms in the 1,2-dithiol.<sup>105</sup> On the other hand, the 9,12-isomer affords excellent protection for silver surfaces against corrosion by H $_2$ S.<sup>106</sup>

A study of the deposition of 1-[HS(CH $_2$ ) $_3$ -tricyclo-(CH $_2$ ) $_3$ ]-*p*-carborane polycrystalline monolayers on a Au(111) surface revealed a major shift in the highest occupied molecular orbital (HOMO) to a level 2.2 eV below that of oligophenylene derivatives, a potentially useful observation in the design of carborane-based molecular electronic devices.<sup>107</sup> In other work, mixed self-assembled monolayers of 1- and 9-HS-*m*-carboranes on gold and silver were found to modulate the work functions in a controllable way, furnishing another potentially useful strategy for developing organic field-effect transistors.<sup>109</sup>

Mercaptocarborane-coated 2 nm gold nanoparticles with the composition Au $_n$ (HSC $_2$ B $_{10}$ H $_{11}$ ) $_m^{n-}$  are soluble and redox-tunable, and can be transferred between aqueous and nonpolar phases by altering the electronic charges in the metal cluster and the carborane shell.<sup>110</sup> These monolayer-protected clusters (MPCs) are taken up by HeLa cells with demonstrated toxicity and ability to reside within membranes, a finding that opens the way to biomedical application.

### Other supports

In a merger of newly evolving technologies, chemists have begun to explore the attachment of carboranes to graphene<sup>111</sup> and graphene oxide<sup>112</sup> surfaces. Electrochemical data together with transmission, atomic force, and electron force microscopies, along with scanning electron microscopy, suggest that carborane-functionalized graphene oxide is a good candidate for developing conductive self-assembled monolayers.<sup>112</sup> Other current frontier areas include the deposition of self-assembled metallocarboranes onto silicon wafers,<sup>113</sup> the grafting of ferracarboranes onto chitosan and multi-walled carbon nanotubes for biomedical application,<sup>114</sup> and the use of hydrogels as carriers. In the last case, luminescent hydrogel particles that exhibit high quantum yield. were obtained via self-assembly of a  $\beta$ -cyclodextrin polymer with hexacarboranyl-hexamolybdenum cluster complexes of the composition Na $_2$ [Mo $_6$ I $_8$ [OC(O)-C $_2$ B $_{10}$ H $_{11}$ ] $_6$ ] whose carborane units are *o*-, *m*-, or *p*-carborane, and function as efficient singlet oxygen sensitizers that may be useful as dual agents for

photodynamic therapy/BNCT agents.<sup>115</sup> The carborane cages in the hydrogel are protected from hydrolysis, and the clusters function as efficient singlet oxygen sensitizers. Given these properties, combined with the high boron content, the hydrogel particles may be useful as dual agents for photodynamic therapy/BNCT agents.

In a different application, p-type semiconducting  $C_2B_{10}H_x$  boron carbide films have been obtained by bombarding condensed *o*-carborane monolayers on polycrystalline copper with 200 eV electrons under high vacuum. The electron bombardment induces site-specific linkage of adjacent carborane units via B–B bonds.<sup>116</sup>

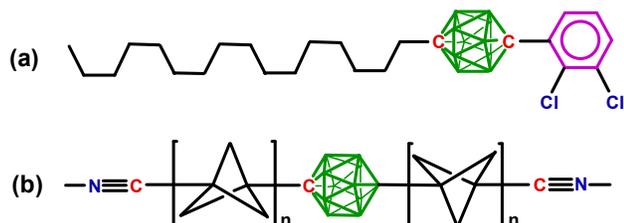
### Carboranes in molecular machines

Most developing applications for carboranes are centered principally on their electronic properties and tailorability, as reflected in this article; a frequent theme is the replacement of phenyl or other organic groups with carborane cages in order to achieve desired spectroscopic properties or reactivity. Less common, but receiving increasing attention, is the exploitation of their cluster architectures and three-dimensional aromaticity to create molecular systems that are beyond the reach of conventional organic chemistry. One such area, the utilization of carboranes in nanoscale mechanical devices,<sup>117,118</sup> has inspired a number of different applications of which a small sample is featured here.

#### Rotors

Molecular rotors of various types have been explored for use as ultrafast dielectric materials, an example of which is the dipolar molecule shown in Fig. 21(a) which forms a surface inclusion compound in a tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP) host. The *p*-carborane cage and *n*-hexadecyl chain reside in the channel and the 2,3-dichlorophenyl rotator protrudes above the surface of the crystal, as determined from solid-state NMR spectroscopy, DSC, and other evidence.<sup>119</sup> With other *p*-carborane-based rotors, bulk inclusion in TPP is observed.<sup>120</sup>

The feasibility and performance of several possible rotors have been investigated in molecular dynamics studies, including polyhedral  $CB_{11}$ ,  $C_2B_8$ , or supra-icosahedral  $CB_{13}$  or  $C_2B_{12}$  clusters that have [*n*]staffane “axes” and condensed aromatic ring “blades” and are mounted on a square grid and driven by flowing gas or an electric field. Figure 21(b) illustrates one such system containing a  $CB_{11}$  cluster.<sup>121</sup>



**Fig 21** (a) A hexadecyl-12-(2,3-dichlorophenyl)-*p*-carborane dipolar rotor. (b) A projected [*n*]staffane-*p*-carborane rotor.

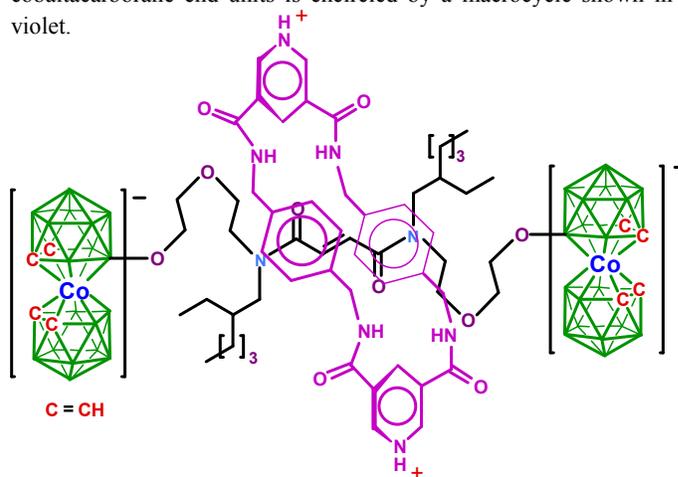
The controlled self-assembly of  $Na^+Co(C_2B_9H_{11})_2^-$  nanorotors via copolymerization of the cobaltacarborane tetrahydrate with

polyethylene oxide or polyvinylpyridyl isomers has been examined by Brus and Matějček and their colleagues.<sup>117</sup> Solid-state NMR spectra show that the metallacarborane anions rotate relatively freely in a rigid polymer matrix. By combining systems of this type with appropriate copolymers, amphidynamic nanocomposites having specific desired properties might be synthesized.

To reiterate a point made earlier, bis(dicarbollide) metal complexes such as those in Figs. 14 and 16 undergo changes in ligand conformation and metal radius upon metal oxidation or reduction, raising the possibility that they could be adapted as redox-driven molecular machines.<sup>77, 122</sup>

#### Rotaxanes

Rotaxanes (mechanically-interlocked systems in which dumbbell-shaped molecules are threaded through macrocycles) are of considerable current interest as molecular machines, because their various modes of behavior including linear, rotational, and pendular motion are controllable.<sup>123</sup> Once again, an obvious role for carboranes can be seen. In a recent contribution Teixidor, Viñas and their associates used hexabrominated bis(dicarbollide) anions to control the pirouetting (rotational) motion of positively charged fumaramide rotaxanes.<sup>124</sup> In one such system (Fig. 23), a thread consisting of a 1,3-dioxohexane-*N,N*-diisooctylfumaramide chain connecting two 3,3'- $Co(1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})$  cobaltacarborane end units is encircled by a macrocycle shown in violet.



**Fig 22** A bis(dicarbollide)cobaltate(1-)-based rotaxane.

Owing to their almost noncoordinating nature, rotation in this system is much faster than occurs with more strongly coordinating anions such as trifluoroacetate.

#### Nanovehicles

A current objective in nanotechnology is the creation of molecular-scale vehicles that can move in a controlled way on a two-dimensional surface. Although molecules in general can be manipulated in a hopping motion using scanning tunnelling microscopy (STM), typically the direction of movement is not controllable.<sup>125</sup> Potentially more useful are vehicles or “nanocars” capable of rolling motion in a desired direction, for which suitable

wheels are required. Although several possibilities have been explored, including the use of triptycene and  $C_{60}$  fullerene wheels,<sup>125</sup> the best results to date have been achieved using *p*-carborane cages, which are nearly spherical and rotate on acetylenic axles. This finding by Tour and his colleagues led to the first true nanocars, which were equipped with dye labels that allowed detection of their motion on glass surfaces via single molecule fluorescence imaging.<sup>126-128</sup> The early "motorized" nanocars were chemically driven<sup>129</sup> or equipped with fluorescent organic groups that harvested light, powering an attached paddle-like rotor that propelled the vehicles forward.<sup>130,131</sup> Subsequently, a second-generation light-driven nanocar has been developed (Fig. 23) which features a thioxanthene stator (chassis) shown in blue and a chiral cyclopentanylidene rotor drawn in purple, single-molecule images of which have been obtained on a Cu(111) surface via STM.<sup>132</sup>

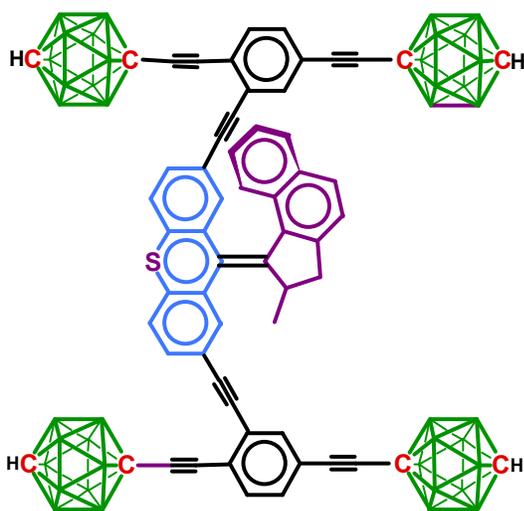


Fig 23 Second-generation light-powered nanocar.

Insight into the nature of nanocar-surface interactions on graphene and graphyne (a planar array of independent  $C_6$  hexagons linked by  $C\equiv C$  chains) is afforded by a recent MP2-level DFT study on a model system (Fig. 24), which found that considerably more energy is required (0.74 vs. 0.19 eV) to move the car on graphene than on graphyne, owing to higher binding energy with the former.<sup>133</sup> From this and other findings it is evident that the behavior of nanocars strongly depends on the surface material chosen, a fact that will certainly shape the direction of future research in this area.

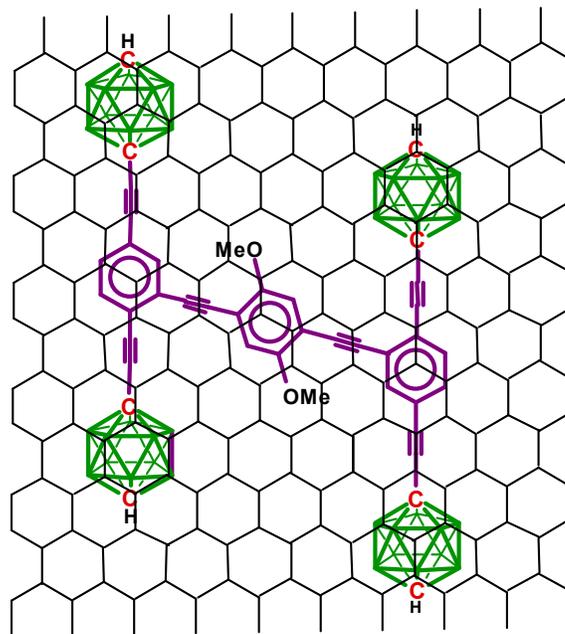


Fig 24 Top-down view of a *p*-carboranyl nanocar on a graphene surface showing one calculated mode of interaction.

### Carboranes in Metal-Organic Frameworks

Coordination polymers with high porosity, which are of considerable interest in several applications including catalysis, gas separation and storage, and ion exchange, have been studied for decades. In recent years, owing to their unique combination of steric and electronic properties and controllable reactivities, carboranes and metallacarboranes have attracted attention as candidates for designed synthesis of metal-organic frameworks (MOFs), and a number of important advances have been reported. Early work produced a *p*-carborane-based compound,  $\{Zn_3(OH)[1,12-(CO_2)_2C_2B_{10}H_{10}]_{2.5}(diethylformamide)_4\}_n$ , analogous to a well-known MOF,  $[Zn_4O(benzene-1,4-dicarboxylate)_3]_n$ , with *p*-carborane units replacing the benzene rings.<sup>134</sup> A similar compound employing dimethylformamide (DMF) in place of DEF, at 300 °C loses its DMF and efficiently separates  $CO_2$  from  $CH_4$ ;<sup>135</sup> this material compares favorably with zeolites, whose regeneration requires higher temperatures.

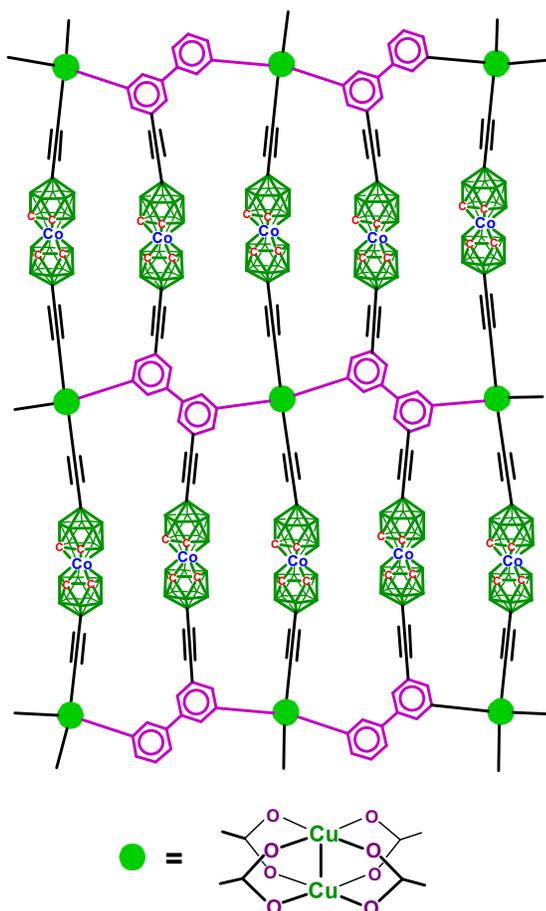
Recently, a highly porous copper-*p*-carborane MOF with a very large surface area (ca. 2600  $m^2/g$ ) has been prepared and demonstrated to have extremely high  $CH_4$  and  $H_2$  storage capacities, which compare favorably with current methane and hydrogen storage technology.<sup>136</sup> For example, under only 65 bar pressure, the  $CH_4$  storage capacity of this MOF is comparable to that of a compressed natural gas tank at 212 bar. A theoretical study restricted to metallacarboranes, which included 7-vertex  $M(C_2B_4H_6)$  and 14-vertex  $M_2(C_4B_8H_{12})$  as well as 12-vertex  $M(C_2B_9H_{11})$  and  $M_2(C_2B_8H_{11})$  systems, found that metallacarborane-based MOFs are excellent candidates for hydrogen storage, with a capacity of up to five  $H_2$  molecules per transition metal atom; scandium and titanium are predicted to have the highest capacity (~8 weight %).<sup>137</sup>

Other theoretical investigations, on titanium sandwiches with planar  $C_3B_2H_5$  rings,<sup>138</sup> Li and Na complexes with planar  $C_4B_2H_6$

rings,<sup>139</sup> and scandium-carborane complexes,<sup>140</sup> have similarly predicted high H<sub>2</sub> binding capacities for such materials. Cobalt-containing p-carboranyl MOFs of the formula [Co<sub>4</sub>(OH)<sub>2</sub>(O<sub>2</sub>C-CB<sub>10</sub>H<sub>10</sub>C-CO<sub>2</sub>)<sub>3</sub>(DMF)<sub>2</sub>]<sub>n</sub> employing a variety of solvents have been prepared, all of which crystallize as 3D networks with large open channels between the carborane cages and efficiently separate CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, and O<sub>2</sub>/N<sub>2</sub> mixtures.<sup>141,142</sup>

Structurally novel MOFs incorporating dabco (diazabicyclooctane) bridging ligands have also been synthesized, one type of which features *closo*-CB<sub>9</sub>, *closo*-CB<sub>11</sub>, or Co(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> units in one-dimensional coordination networks held together by Ag-H-B and Ag-I-B interactions.<sup>143</sup> Another variety, obtained when an excess of dabco was used, has the composition [Ag<sub>2</sub>(dabco)<sub>3</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sub>2</sub>[Co(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] in a 3D network.<sup>144</sup>

Recent work by Mirkin and coworkers on the designed synthesis of metallacarborane-based MOFs has generated novel materials containing 3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> anions bearing phenylethynyl substituents on the antipodal boron vertices. By employing this very long linker in combination with Cu<sub>2</sub>O<sub>8</sub> “paddlewheel” nodes, three architecturally distinct MOFs were obtained, one of which is depicted in Fig. 25.<sup>145</sup>



**Fig 25** Connectivity diagram of a copper-cobaltacarborane MOF

In this work, the remarkable isolation and characterization of materials with three different topologies prepared with the same

components under the same conditions illustrates the fact that even carefully designed syntheses can lead to unexpected results.

A distinctly different type of solid material incorporating the same 3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> anion, a noncrystalline polymeric composite, has been prepared via spontaneous precipitation of the anion with poly(ethylene oxide) (PEO) in aqueous solution. Solid state NMR spectroscopy and wide-angle X-ray scattering (WAXS) data established that the cobaltacarborane anions are dispersed within the PEO matrix, forming a polymeric chain that coexists with another chain of sodium cations.<sup>146</sup>

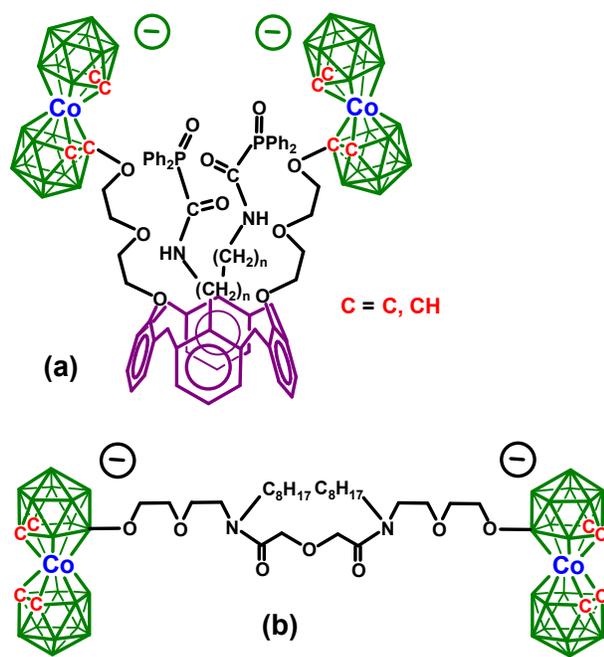
## Carboranes in metal ion extraction

High level waste (HLW) generated by nuclear reactors contains the minor actinides <sup>241</sup>Am, <sup>243</sup>Am, <sup>245</sup>Cm and <sup>237</sup>Np together with long-lived fission products <sup>93</sup>Zr, <sup>99</sup>Tc, <sup>129</sup>I, and <sup>135</sup>Cs, but the principal hazard over a time scale of one to two centuries is posed by the isotopes <sup>137</sup>Cs and <sup>90</sup>Sr, whose half-lives are ca. 30 years and together account for 90% of the radioactivity emanating from HLW.<sup>147</sup> The efficient extraction of <sup>137</sup>Cs<sup>+</sup> and <sup>90</sup>Sr<sup>2+</sup> is a major goal, not only as a way of reducing the radiation hazard to workers involved in handling HLW, but also to make these substances available for productive usage; <sup>137</sup>Cs, for example, is a source of gamma radiation for sterilization of foods and medical accessories.

The search for chemically based alternatives to the burial of HLW in deep repositories is ongoing, and among the most effective methods, originating with Czech workers in the 1970s,<sup>148,149</sup> are those utilizing the ubiquitous 3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> anion or its B-halogenated derivatives. Several attributes of these cobaltacarborane ions are well-suited to this purpose: they are extremely hydrophobic (transferring quantitatively from diethyl ether to water, for example), can serve as nearly noncoordinating counterions, and, in the case of the hexachloro species 3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Cl<sub>3</sub>)<sub>2</sub><sup>-</sup>, are stable in 3 M HNO<sub>3</sub> and therefore usable in the acidic media encountered in handling nuclear waste.

A number of different approaches have been explored, including liquid-liquid extraction of cations of the Group 1 and 2 elements, lanthanides, actinides, and other metals, using Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>n</sub>X<sub>n</sub>)<sub>2</sub><sup>-</sup> derivatives (especially 3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>Cl<sub>3</sub>)<sub>2</sub><sup>-</sup>) or their iron and nickel analogues<sup>150</sup> in conjunction with crown ethers, calix[n]arenes, polyethylene glycol, polyethers, and other complexing agents.<sup>151-156</sup> Synergistic methods employing cobaltacarborane anions together with other complexing agents, such as the U.S.-Russian Universal Extraction (UNEX) process<sup>157</sup> employing carbamoyl methyl phosphane oxide (CMPO), are also of interest.

Bifunctional extraction agents that contain both cobaltacarborane and CMPO or similar groups efficiently remove lanthanides and actinides from highly acidic nuclear waste. Figure 26 illustrates two such species, employing calix[4]arene<sup>153,158</sup> (a) and N,N,N',N'-tetraoctyldiglycolamide (TODGA) (b) assemblies, the first of which, employed with *t*-octylbenzo-18-crown-6, complexes strongly with Cs<sup>+</sup> ions<sup>153</sup> while the latter efficiently separates Am(III) and Eu(III).<sup>154</sup>



**Fig 26** Bis(dicarbollyl)cobaltate-calix[4]arene (a) and  $N,N,N',N'$ -tetraoctyldiglycolamide (b) metal extraction agents.

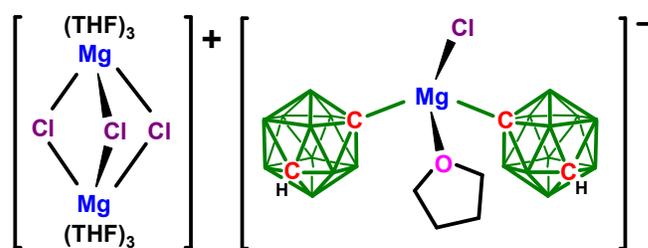
Metal ion separation technology has been advanced by several recent modifications, including the development of membrane-based systems which require less solvent and generate less waste than solvent extraction or ion exchange methods. In an electrolytic process for extracting cesium from nuclear waste,  $\text{Cs}^+$  ions complexed with  $3\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_8\text{Cl}_3)_2^-$  anions are selectively transported with 100% efficiency through cellulose triacetate (CTA) and polyvinyl chloride (PVC) polymer inclusion membranes. With the PVC membrane, the process can be conducted in high acid concentrations (3 M  $\text{HNO}_3$ ).<sup>159</sup> Supported liquid membrane (SLM) techniques are also being applied to the problem, and a recent report describes a flat sheet SLM process for  $^{137}\text{Cs}$  extraction that employing the hexachlorinated cobalt dicarbollide anion in 40% *n*-dodecane/60% 2-nitrophenyloctyl ether.<sup>160</sup>

### Carboranes in battery design

The development of reliable, safe, and economical batteries for electrically powered vehicles and other applications is, of course, a major focus of industrial research. Here again, a role for carborane chemistry is emerging. Lithium ion batteries are widely employed in portable electronic devices because of their light weight and high energy density, and the search for improved anodes, cathodes, and electrolytes is ongoing. In particular, there is interest in replacing the toxic halogens used in most lithium ion electrolytes with halogen-free ions.<sup>161</sup> A study of a number of such systems by Jena and coworkers has identified  $\text{Li}^+\text{CB}_{11}\text{H}_{12}^-$ , a relatively accessible compound, as an attractive candidate based on its low toxicity, its small cation-anion binding energy allowing ease of movement of  $\text{Li}^+$

ions between electrodes, and its low affinity toward  $\text{H}_2\text{O}$  which promotes increased battery life.<sup>161</sup>

Carborane derivatives also show promise as electrolytes for rechargeable magnesium batteries, which offer the advantages of high capacity, low cost of magnesium, and relative safety compared to lithium; in contrast to Li, Mg is not susceptible to dendrite formation.<sup>162,163</sup> A problem that has slowed the development of workable magnesium batteries is the lack of a viable electrolyte/solvent combination that avoids the formation of nonconductive material on the electrodes.<sup>164</sup> Mohtadi and associates have addressed this issue with a *m*-carboranyl-magnesium electrolyte, shown in Figure 27, that exhibits high oxidative stability, is noncorrosive, and is compatible with magnesium electrodes.<sup>165</sup> Batteries charged with this electrolyte display high reversible specific capacity of about  $90 \text{ mAh g}^{-1}$  and high coulombic efficiency (90%), properties which augur well for further studies.



**Fig 27** Structure of  $\text{Mg}_2\text{Cl}_3(\text{THF})_6^+(1,7\text{-C}_2\text{B}_{10}\text{H}_{11})_2\text{MgCl}(\text{THF})^-$

### Conclusion

This article highlights just a few areas in which carborane-based chemistry, physics, and materials science are impacting developing technology. I have barely scratched the surface of the burgeoning field of biomedical applications, on which a formidable literature has accumulated.<sup>63</sup> Among a number of important topics not specifically covered are nonlinear optical materials,<sup>166-172</sup> liquid crystals,<sup>173-179</sup> and ionic liquids,<sup>180</sup> among others. What should be clear from this discussion is the versatility of carboranes and metallocarboranes as tools that can be applied to a broad range of problems in the laboratory and in the realm of applied technology. This is a fast-moving stream, with new developments constantly appearing and workers in many areas discovering useful, often unique roles, for these remarkable compounds. And the toolbox is still growing: the regular intrusion of serendipity,<sup>181</sup> still a hallmark of boron cluster chemistry a century after its inception,<sup>182</sup> serves to continually revitalize this area of science with unexpected discoveries and new insights.

## Acknowledgements

I am indebted to the Department of Chemistry at the University of Virginia for continuing to provide office space and services long after my retirement from the active faculty.

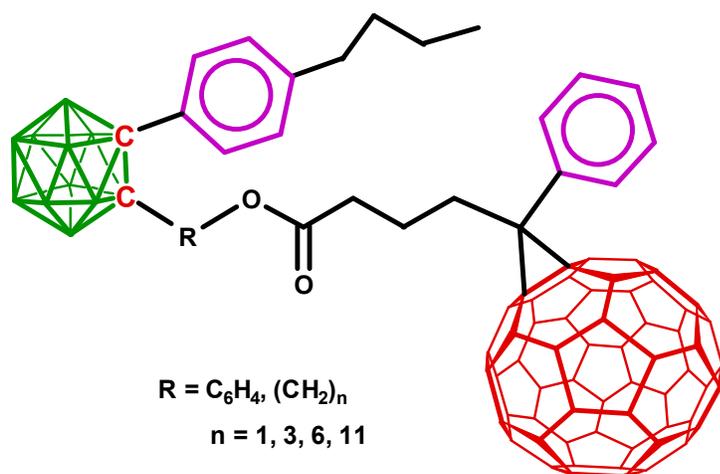
## Notes and references

† The distinction is not always absolute, as there are systems in which exo-metallated complexes and metallacarborane structures coexist in equilibrium.

- C. Douvris and J. Michl, *Chem. Rev.* 2013, **113**, PR179.
- S. H. Strauss, *Chem. Rev.* 1993, **93**, 927.
- C. A. Reed, *Accounts Chem. Res.* 2010, **43**, 121.
- R. N. Grimes, *Carboranes 2<sup>nd</sup> Ed.*, Elsevier, Amsterdam, 2011.
- M. Nava, I. V. Stoyanova, S. Cummings, E. S. Stoyanov, and C. A. Reed, *Angew. Chem. Int. Edit.* 2014, **53**, 1131.
- C. A. Reed, *Accounts Chem. Res.* 2013, **46**, 2567.
- A. S. Jalilov, A. S.; L. Han, S. F. Nelsen, and I. A. Guzei, *J. Org. Chem.* 2013, **78**, 11373
- I. Zharov, I., B. T. King, Z. Havlas, A. Pardi, A., and J. Michl, *J. Am. Chem. Soc.* 2000, **122**, 10253.
- J. L. Garate-Morales, F. S. Tham, and C. A. Reed, *Inorg. Chem.* 2007, **46**, 1514.
- A. S. Larsen, J. D. Holbrey, F. S. Tham, and C. A. Reed, *J. Am. Chem. Soc.* 2000, **122**, 7264.
- J. L. Belletire, S. Schneider, B. A. Wight, S. L. Strauss, and S. A. Shackelford, *Synth. Commun.* 2010, **42**, 155.
- K.-C. Kim, F. Hauke, A. Hirsch, P. D. W. Boyd, E. Carter, E. R. S. Armstrong, P. A. Lay, and C. A. Reed, *J. Am. Chem. Soc.* 2003, **125**, 4024.
- R. H. Xie, G. W. Bryant, G. Y. Sun, M. C. Nicklaus, D. Heringer, T. Frauenheim, M. R. Manaa, V. H. Smith, Y. Araki, and O. Ito, *J. Chem. Physics* 2004, **120**, 5133.
- S. Duttwyler, Y. Zhang, A. Linden, C. A. Reed, K. Baldrige, and J. S. Siegel, *Angew. Chem. Int. Ed.* 2009, **48**, 3787.
- E. S. Stoyanov, I. V. Stoyanova, and C. A. Reed, *J. Am. Chem. Soc.* 2011, **133**, 8452.
- E. S. Stoyanov, I. V. Stoyanova, F. S. Tham, and C. A. Reed, *J. Am. Chem. Soc.* 2010, **132**, 4062.
- E. S. Stoyanov, G. Gunbas, N. Hafezi, M. Mascial, M.; I. V. Stoyanova, F. S. Tham, and C. A. Reed, *J. Am. Chem. Soc.* 2012, **134**, 707.
- J. H. Wright, G. W. Mueck, F. S. Tham, and C. A. Reed, *Organometallics* **2010**, **29**, 4066
- E. S. Stoyanov, S. P. Hoffmann, K.-C. Kim, F. S. Tham, and C. A. Reed, *J. Am. Chem. Soc.* 2005, **127**, 7664.
- E. S. Stoyanov, K.-C. Kim, and C. A. Reed, *J. Am. Chem. Soc.* 2006, **128**, 1948.
- Z. Xie, Z. R. Bau, R. and C. A. Reed, *Inorg. Chem.* 1995, **34**, 5403.
- L. J. Mueller, D. W. Elliot, K.-C. Kim, C. A. Reed, and P. D. W. Boyd, *J. Am. Chem. Soc.* 2002, **124**, 9360
- C. A. Reed, K.-C. Kim, R. D. Bolskar, and L. J. Mueller, *Science* 2000, **289**, 101.
- R. Ramirez-Contreras, N. Bhuvanesh, J. Zhou, and O. V. Ozerov, *Angew. Chem. Int. Edit.* 2013, **52**, 10313.
- R. D. Kennedy, C. L. Stern, and C. A. Mirkin, *Inorg. Chem.* 2013, **52**, 14064.
- S. V. Ivanov, D. V. Peryshkov, S. M. Miller, O. P. Anderson, A. K. Rappé, and S. H. Strauss, *J. Fluorine Chem.* 2012, **143**, 9927.
- A. El-Hellani, and V. Lavallo, *Angew. Chem. Int. Edit.* 2014, **53**, 4489.
- N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost, and A. S. Weller, *Chem. Eur. J.* 2002, **8**, 2088.
- O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldrige, and J. S. Siegel, *Science* 2011, **332**, 574.
- V. Lavallo and J. H. Wright, *Angew. Chem. Int. Edit.* 2013, **52**, 3172.
- S. Y. Lee, S. Neufeind, and C. G. Fu, *J. Am. Chem. Soc.* 2014, **136**, 8899.
- T. Peymann, C. B. Knobler, S. I. Khan, and M. F. Hawthorne, *Inorg. Chem.* 2001, **40**, 1291.
- I. Zharov, T.-C. Weng, A. M. Orendt, D. H. Barich, J. Penner-Hahn, D. M. Grant, Z. Havlas, J. Michl, *J. Am. Chem. Soc.* 2004, **126**, 12033.
- M. J. Ingleson, G. Kociok-Köhn, and A. S. Weller, *Inorg. Chim. Acta* 2005, **358**, 1571.
- B. T. King, B. C. Noll, A. J. McKinley, and J. Michl, *J. Am. Chem. Soc.* 1996, **118**, 10902.
- I. Zharov, Z. Havlas, A. M. Orendt, D. H. Barich, D. M. Grant, M. G. Fete, and J. Michl, *J. Am. Chem. Soc.* 2006, **128**, 6089.
- S. Moss, S., B. T. King, A. de Meijere, S. I. Kozhushkov, P. E. Eaton, and J. Michl, *J. Org. Lett.* 2001, **3**, 2375.
- Valásek, M.; Štursa, J.; Pohl, R.; Michl, J., *Inorg. Chem.* **2010**, **49**, 10255
- K. Vyakaranam, S. Körbe, and J. Michl, *J. Am. Chem. Soc.* 2006, **128**, 5680.
- K. Vyakaranam, J. B. Barbour, and J. Michl, *J. Am. Chem. Soc.* 2006, **128**, 5610.
- V. Volkis, C. Douvris, and J. Michl, *J. Am. Chem. Soc.* 2011, **133**, 7801.
- V. Volkis, R. K. Shoemaker, and J. Michl, *Macromolecules* 2012, **45**, 9250.
- Ref. 4, Chapter 15 and references cited therein.
- H. Wang, H.-S. Chan, J. Okuda, and Z. Xie, *Organometallics* 2005, **24**, 3118.
- G. Zi, H.-W. Li, and Z. Xie, *Organometallics* 2002, **21**, 3850.
- H. Shen and Z. Xie, *Chem. Commun.* 2009, 2431.
- Wang, H.; Li, H.-W.; Xie, Z., *Organometallics* 2003, **22**, 4522.
- Hong, E.; Kim, Y.; Do, Y., *Organometallics* 1998, **17**, 2933.
- H. Tsurugi, Z. Qiu, K. Yamamoto, R. Arteaga-Müller, and K. Mashima, *Organometallics* **2011**, **30**, 5960.
- S. E. Lyubimov, I. V. Kuchurov, A. A. Tyutyunov, P. V. Petrovskii, V. N. Kalinin, S. G.; Zlotin, V. A. Davankov, E. Hey-Hawkins, *Catal. Commun.* **2010**, **11**, 419.
- S. E. Lyubimov, V. A. Ol'shevskaya, P. V. Petrovskii, E. A. Rastorguev, T. A. Verbitskaya, V. N. Kalinin, and V. A. Davankov, *Russ. Chem. Bull.* 2010, **59**, 1836
- S. E. Lyubimov, P. V. Petrovskii, E. A. Rastorguev, T. A. Verbitskaya, V. N. Kalinin, and V. A. Davankov, *Russ. Chem. Bull.* 2011, **60**, 2074.
- S. E. Lyubimov, I. V. Kuchurov, A. A. Vasil'ev, A. A. Tyutyunov, V. N. Kalinin, V. A. Davankov, S. G. Zlotin, *J. Organomet. Chem.*, 2009, **694**, 3047.
- S. E. Lyubimov, T. A. Verbitskaya, E. G. Rys, P. V. Petrovskii, M. M. Il'in, V. A. Davankov, V. N. Kalinin, *Izv. Akad. Nauk, Ser. Khim.*, 2010, 1620 [*Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 1665].
- G. Liu, J. Zhang, B. Wu, and J. Wang, *Org. Lett.* 2007, **9**, 4263.
- Z. Yinghui, K. Carpenter, C. C. Bun, S. Bahnmüller, C. P. Ke, V. S. Srid, L. W. Kee, and M. F. Hawthorne, *Angew. Chem. Int. Ed.* 2003, **42**, 3792.
- M. Yoshida, D. J. Crowther, and R. F. Jordan, *Organometallics* 1997, **16**, 1349.
- M. Yoshida and R. F. Jordan, *Organometallics* 1997, **16**, 4508.
- M. A. Curtis, M. G. Finn, and R. N. Grimes, *J. Organomet. Chem.* 1998, **550**, 469.
- P. C. Wailes, H. Weigold, and A. P. J. Bell, *J. Organomet. Chem.* 1971, **27**, 373.

- 61 K. L. Houseknecht, K. E. Stockman, M. Sabat, M. G. Finn, and R. N. Grimes, R. N. *J. Am. Chem. Soc.* 1995, **117**, 1163.
- 62 E. A. Boring, M. Sabat, M. G. Finn, and R. N. Grimes, *Organometallics* 1998, **17**, 3865.
- 63 Ref. 4, Chapter 16, and references cited therein.
- 64 M. F. Hawthorne and A. Pushechnikov, *Pure Appl. Chem.* 2012, **84**, 2279.
- 65 V. I. Bregadze and S. A. Glazun, *Russ. Chem. Bull.* 2007, **56**, 643.
- 66 I. B. Sivaev and V. I. Bregadze, *Eur. J. Inorg. Chem.* 2009, 1433.
- 67 3-V. A. Ol'shevskaya, A. V. Zaitsev, E. G. Kononova, P. V. Petrovskii,, E. Hey-Hawkins, A. A. Shtil, and V. N. Kalinin, *Dokl. Chem.* 2007, **414**, 120.
- 68 C-H. Wu, L-X. Shi, Q-N. Li, J-A. Zhao, M. Selke, H. Yan, and X-M. Wang, *J. Neurosci. Nanotechnology* 2011, **11**, 3091.
- 69 C. Wu, L. Shi, Q. Li, H. Jiang, M. Selke, H. Yan, and X. Wang, *Nanomedicine, Nanotechnology, Biology, and Medicine* 2012, **8**, 860
- 70 N. Li, P. Zhao L. Salmon, J. Ruiz, M. Zabawa, N. S. Hosmane, and D. Astruc, D., *Inorg. Chem.* 2013, **52**, 11146.
- 71 A. Gonzales-Campo, A. Ferrer-Ugalde, C. Vinas, F. Teixidor, R. Sillanpaa, J. Rodriguez-Romero R. Santillan, N. Farfan, and R. Nunez, *Chem. Eur. J.* 2013, **19**, 6299.
- 72 Dash, B. P.; R. Satapathy, B. P. Bode, C. T. Reidl, J. W. Sawicki, A. J. Mason, J. A. Maguire, and N. S. Hosmane, *Organometallics* 2012, **31**, 2931
- 73 S. Sumitani, S.; M. Oishi, T. Yaguchi, H. Murotani, Y. Horiguchi, M. Suzuki, K. Ono, H. Yanagie, and Y. Nagasaki, *Biomaterials* 2012, **33**, 3568.
- 74 P. Bauduin, S. Prevost, P. Farras, F. Teixidor, O. Diat, and T. Zemb, *Angew. Chem. Int. Edit.* 2011, **50**, 5298.
- 75 C. Chen, J. Yang, G. Lu, P. C. Liu, Q. Chen, Z. Xie, and C. Wu, *Molec. Pharmaceutics* 2014, **11**, 3291.
- 76 S-H. Li, C. Y. Wu, X. Tang, S-P. Gao, X-Q. Zhao, H. Yan, and X-M. Wang, *Sci. China Chem.* 2013, **56**, 595
- 77 M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, and D. Neuhauser, *Science* 2004, **303**, 1849.
- 78 A. M. Spokoyny, T. C. Li, O. K. Farha, C. W. Machan, C. She, C. L. Stern, T. J. Marks, J. T. Hupp, and C. A. Mirkin, *Angew. Chem. Int. Edit.* 2010, **49**, 5339.
- 79 T. C. Li, F. Fabregat-Santiago, O. K. Farha, A. M. Spokoyny, S. R. Raga, J. Bisquert, C. A. Mirkin, T. J. Marks, and J. T. Hupp, *J. Phys. Chem.* 2011, **115**, 11257.
- 80 V. I. Bregadze, I. B. Sivaev, I. A. Lobanova, O. N. Kazheva, G. G. Alexandrov, A., V. Kravchenko, V. A. Starodub, L. I. Buravov, L. V. Titov, and O. A. Dyachenko, *J. Chem. Sci. (India)* 2010, **122**, 37.
- 81 E. Crespo, S. Gentil, C. Vinas, and F. Teixidor, *J. Phys. Chem. C*, 2007, **111**, 18381.
- 82 S. Gentil, E. Crespo, I. Rojo, A. Friang, C. Vinas, F. Teixidor, B. Gruener, and D. Gabel, *Polymer*, 2005, **46**, 12218.
- 83 D. Caballero, L. Fumagalli, F. Teixidor, J. Samitier, and A. Errachid, *Sensors and Actuators B – Chemical*, 2013, **177**, 1003.
- 84 C. Masalles, S. Borros, C. Vinas, and F. Teixidor, *Adv. Mater.*, 2002, **14**, 449.
- 85 N. Zine, J. Bausells, F. Teixidor, C. Vinas, C. Masalles, J. Samatier, and A. Errachid, *Mater. Sci. Eng. C Biomim. Supramol. Syst.*, 2006, **26**, 399.
- 86 D. O. Kirsanov, O. V. Mednova, E. N. Pol'shin, A. V. Legin, M. Yu. Alyapyshev, I. I. Eliseev, V. A. Babain, and Yu. G. Vlasov, *Russ. J. Appl. Chem.* 2009, **82**, 247.
- 87 D. O. Kirsanov, A. V. Legin, V. A. Babain, and Yu. G. Vlasov, *Russ. J. Appl. Chem.* 2005, **78**, 568.
- 88 V. David, C. Vinas, and F. Teixidor, *Polymer* 2006, **47**, 4694.
- 89 F. Barrière, B. Fabre, E. Hao, C. M. LeJeune, E. Hwang, J. C. Garno, E. E. Nesterov, and M. G. H. Vicente, *Macromolecules* 2009, **42**, 2981.
- 90 D. Anthopoulos, S. E. Watkins, P. Beavis, and M. Heaney, *J. Mater. Chem. C* 2014, **2**, 232.
- 91 J. Marshall, Z. P. Fei, C. P. Yau, N. Yaacobi-Gross, S. Rossbauer, T. J. Marshall, B. C. Schroeder, H. Bronstein, H. I. Meager, S. Rossbauer, N. Yaacobi-Gross, E. Buchaca-Domingo, T. D. Anthopoulos, N. Stingelin, P. Beavis, and M. Heaney, *Macromolecules* 2014, **47**, 89.
- 92 J. J. Peterson, M. M. Werre, Y. C. Simon, E. B. Coughlin, K. R. Carter, *Macromolecules* 2009, **42**, 8594.
- 93 J. J. Peterson, A. R. Davis, M. Werre, E. B. Coughlin, and K. R. Carter, *Applied Mater. Interfaces* 2011, **3**, 1796.
- 94 A. R. Davis, J. J. Peterson, and K. R. Carter, *ACS Macro Letters* 2012, **1**, 469.
- 95 K-R. Wee, Y-J. Cho, S. Jeong, S. Kwon, J-D. Lee, I-H Suh, and S. O. Kang, S. O., *J. Am. Chem. Soc.* 2012, **134**, 17982.
- 96 S. Kwon, K-R. Wee, Y-J. Cho, and S. O. Kang, *Chem. Eur. J.* 2014, **20**, 5953.
- 97 K. Kokado and Y. Chujo, *Dalton Trans.* 2011, **40**, 1919.
- 98 J-F. Nicoud, F. Bolze, X-H. Sun, A. Hayek, and P. Baldeck, *Inorg. Chem.* 2011, **50**, 4272.
- 99 A. Harriman, M. A. H. Alamiry, J. P. Hagon, D. Hablot, and R. Ziessel, *Angew. Chem. Int. Edit.* 2013, **52**, 6611.
- 100 K. Vidya and E. D. Jemmis, *RSC Adv.* 2014, **4**, 30013.
- 101 Y. I. Lyakhovetsky, E. A. Shilova, A. I. Belokon, L. I. Panz, and B. L. Tumanskiy, *J. Am. Mass Spectrom.* 2013, **24**, 579.
- 102 M. Eo, H. J. Bae, M. Hong, Y. Do, S. Cho, and M. H. Lee, *Dalton Trans.* 2013, **42**, 8104.
- 103 C. I. Li, T. M. Shen, P. Kuo, R. Liu, M. Chan, C. L. Yang, J. Y. Wu, B. Colombeau, B. N. Guo, T. Thanigaivelan, T. Toh, H. L. Sun, T. Wu, and S. Lu, *IEEE Electric Device Lett.* 2011, **32**, 548.
- 104 T. Baše, Z. Bastl, V. Havránek, J. Macháček, J. Langecker, and V. Malina, *Langmuir* 2012, **28**, 12518.
- 105 J. F. Lübben, T. Baše, P. Rupper, T. Künniger, J. Macháček, and S. Guimond, *J. Colloid Interface Sci.* 2011, **354**, 168.
- 106 T. Baše, Z. Bastl, V. Havránek, K. Lang, J. Bould, M. G. S. Londesborough, J. Macháček, and J. Plešek, *Surface Coatings Technol.* **2010**, **204**, 2639.
- 107 F. Von Wrochem, F. Scholz, D. Gao, H-G. Nothofer, A. Yasuda, J. M. Wessels, S. Roy, X. Chen, and J. Michl, *J. Phys. Chem. Lett.* 2010, **1**, 3471.
- 108 K. Z. Kabytaev, T. A. Everett, A. V. Safronov, Y. Sevryugina, S. S. Jalisatgi, and M. F. Hawthorne, *Eur. J. Inorg. Chem.* **2013**, 2488.
- 109 J. Kim, Y. S. Rim, Y. Liu, A. C. Serino, J. C. Thomas, H. Chen, Y. Yang, and P. S. Weiss, *Nano Lett.* 2014, **14**, 2946.
- 110 A. M. Cioran, A. D. Musteti, F. Teixidor, Z. Krpetić, I. A. Prior, Q. He, C. J. Kiely, M. Brust, and C. Viñas, *J. Am. Chem. Soc.* 2012, **134**, 212.
- 111 J. U. Kahlert, A. Rawal, J. M. Hook, L. M. Rendina, and M. Choucair, *Chem. Commun.* 2014, **50**, 11332
- 112 V. Stengl, S. Bakardjieva, M. Bakardjiev, B. Stibr, and M. Kormunda, *Carbon* 2014, **67**, 336.
- 113 E. J. Juarez-Perez, M. Granier, C. Vinas, P. H. Mutin, and R. Nunez, *Chem. Asian J.* 2012, **7**, 277.
- 114 P. A. Jelliss, S. S. Graham, A. Josipovic, S. Boyko, S. D. Minter, and V. Svoboda, *Polyhedron* 2013, **50**, 36.
- 115 K. Kirakci, V. Šicha, J. Holub, P. Kubát, and K. Lang, *Inorg. Chem.* 2014, **53**, 13012
- 116 F. L. Pasquale and J. A. Kelber, *Appl. Surface Sci.* 2012, **258**, 2639.
- 117 J. Brus, A. Zhigunov, J. Czernek, L. Kobera, M. Uchman, and P. Matějček, P., *Macromolecules* 2014, **47**, 6343 and references cited therein.
- 118 Ref. 4, Section 17.4.
- 119 L. Kobr, K. Zhao, Y. Shen, A. Comotti, S. Bracco, R. K. Shoemaker, P. Sozzani, N. A. Clark, J. C. Price, C. T. Rogers, and J. Michl, *J. Am. Chem. Soc.* 2012, **134**, 10122.

120. L. Kobr, K. Zhao, Y. Shen, K. Polívková, R. K. Shoemaker, N. A. Clark, J. C. Price, C. T. Rogers, and J. Michl, *J. Org. Chem.* 2012, **78**, 1768
121. A. Prokop, J. Vacek, and J. Michl, *ACS Nano* 2012, **6**, 1901.
122. F. Teixidor and C. Vinas, *Pure Appl. Chem.* 2012, **84**, 2457
123. J-P Sauvage, and C. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots: A Journey through the World of Molecular Topology*, John Wiley & Sons: New York, NY, 2008.
124. P. Farràs, E. C. Escudero-Adán, C. Viñas, and F. Teixidor, *Inorg. Chem.* 2014, **53**, 8654.
125. C. J. Villagómez, T. Sasaki, J. M. Tour, and L. Grill, *J. Am. Chem. Soc.* 2010, **132**, 16848.
126. S. Khatua, J. M. Guerrero, K. Claytor, G. Vives, A. B Kolomeisky, J. M. Tour, and S. Link, *ACS Nano* 2009, **3**, 351.
127. J. Godoy, G. Vives, and J. M. Tour, *Org. Lett.* 2010, **12**, 1464.
128. S. Khatua, J. Godoy, J. M. Tour, and S. Link, *J. Phys. Chem. Lett.* 2010, **1**, 3288
129. J. Godoy, G. Vives, and J. M. Tour, *ACS Nano* 2011, **5**, 85.
130. J-F. Morin, Y. Shirai, and J. M. Tour, *Org. Lett.* 2006, **8**, 1713.
131. T. Sasaki and J. T. Tour, *Org. Lett.* 2008, **10**, 897.
132. P-T. Chiang, J. Mielke, J. Godoy, J. M. Guerrero, I. Alemany, C. J. Villagomez, A. Saywell, L. Grill, and J. M. Tour, *ACS Nano* 2012, **6**, 592
133. M. D. Ganji, M. G. Ahangari, and S. M. Emami, *Mater. Chem. Phys.* 2014, **148**, 435.
134. O. K. Farha, A. M. Spokoyny, K. L. Mulfort, M. F. Hawthorne, C. A. Mirkin, and J. T. Hupp, *J. Am. Chem. Soc.* 2007, **129**, 12680.
135. Y-S. Bae, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, J. T. Hupp, and R. Q. Snurr, *Chem. Commun.* 2008, 4135.
136. R. D. Kennedy, V. Krungleviciute, D. J. Clingerman, J. E. Mondloch, Y. Peng, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, J. T. Hupp, T. Yildirim, O. K. Farha, and C. A. Mirkin, *Chem. Mater.* 2013, **25**, 3539.
137. A. K. Singh, A. Sadrzadeh, and B. I. Yakobson, *J. Am. Chem. Soc.* 2010, **132**, 14126.
138. A. K. Kandalam, B. Kiran, and P. Jena, *J. Phys. Chem. C.* 2008, **112**, 6181.
139. K. Srinivasu, and S. K. Ghosh, *J. Phys. Chem. C.* 2011, **115**, 16984.
140. P. L. Bora and A. K. Singh, *J. Chem. Phys.* 2013, **139**, 164319.
141. Y-S. Bae, A. M. Spokoyny, O. K. Farha, R. Q. Snurr, J. T. Hupp, and C. A. Mirkin, *Chem. Commun.* 2010, 3478.
142. O. K. Farha, A. M. Spokoyny, K. L. Mulfort, S. Galli, J. T. Hupp, and C. A. Mirkin, *Small* 2009, **5**, 172.
143. L. Cunha-Silva, M. J. Carr, J. D. Kennedy, and M. J. Hardie, *Cryst. Growth. Design* 2013, **13**, 3162.
144. F. L. Thorp-Greenwood, A. N. Kulak, and M. J. Hardie, *Cryst. Growth. Design* 2014, **14**, 5361.
145. R. D. Kennedy, D. J. Clingerman, W. Morris, C. E. Wilmer, A. A. Sarjeant, C. L. Stern, M. O'Keefe, R. Q. Snurr, J. T. Hupp, O. K. Farha, and C. A. Mirkin, *Cryst. Growth Design* 2014, **14**, 1324.
146. P. Matějčiček, J. Brus, A. Jigounov, J. Pleštil, M. Uchman, K. Procházka and M. Gradzielski, *Macromolecules* 2011, **44**, 3847.
147. P. Kandwal and P. K. Mohapatra, *J. Membrane Sci.* 2014, **469**, 59.
148. J. Plešek, *J. Chem. Rev.* 1992, **92**, 269.
149. J. Rais, P. Selucky, and M. J. Kyrš, *J. Inorg. Nucl. Chem.* 1976, **38**, 1376.
150. C. Viñas, S. Gomez, J. Bertran, J. Barron, F. Teixidor, J-F. Dozol, H. Rouquette, R. Kivekäs, and R. Sillanpää, *R. J. Organomet. Chem.* 1999, **581**, 188.
151. Ref. 4, Section 17.2 and references cited therein.
152. E. Makrlík, P. Selucky, and P. Vaňura, P., *J. Radioanal. Nucl. Chem.* 2012, **293**, 103.
153. J. Kriz, J. Dybal, E. Makrlík, P. Vanura, and B. A. Moyer, *J. Phys. Chem. B* 2011, **115**, 7578.
154. M. Bubenikova, P. Selucky, J. Rais, B. Grüner, and P. Svec, P., *J. Radioanal. Nucl. Chem.* 2012, **293**, 403.
155. R. S. Herbst, D. R. Peterman, P. R. Zalupski, K. L. Nash, R. D. Tillotson, and L. H. Delma, *Solvent Extr. Ion Exchange* 2010, **28**, 563.
156. T. J. Tranter, R. D. Tillotson, N. R. Mann, and G. R. Longhurst, *Nuclear Technology* 2011, **176**, 290.
157. T. A. Luther, R. S. Herbst, D. R. Peterman, R. D. Tillotson, T. G. Garn, V. A. Babain, I. V. Smirnov, E. S. Stoyanov, and N. G. Antonov, *J. Radioanal. Nucl. Chem.* 2006, **267**, 603.
158. L. Mikulášek, B. Grüner, C. Dordea, V. Rudzevich, V. Böhmer, J. Haddaoui, V. Hubscher-Bruder, F. Arnaud-Neu, J. Časlavský, and P. Selecký, *Eur. J. Org. Chem.* 2007, 4772.
159. S. Chaudhury, A. Bhattacharyya, and A. Goswami, *Env. Sci. Technol.* 2014, **48**, 12994.
160. P. Kandwal and P.K. Mohapatra, *J. Membrane Sci.* 2014, **469**, 59.
161. S. Giri, S. Behera, and P. Jena, *Angew. Chem. Int. Edit.* 2014, **126**, 14136, and references therein.
162. H. D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, and D. Aurbach, *Energy Environ. Sci.* 2013, **6**, 2265.
163. J. Muldoon, C. B. Bucur, A. G. Oliver, T. Sugimoto, M. Matsui, H. S. Kim, G. D. Allred, J. Zajicek, and Y. Kotani, *Energy Environ. Sci.* 2012, **5**, 5941.
164. M. Matsui, *J. Power Sources* 2011, **196**, 7048.
165. T. J. Carter, R. Mohtadi, T. S. Arthur, F. Mizuno, R. Zhang, S. Shirai, and J. W. Kampf, *Angew. Chem. Int. Edit.* 2014, **53**, 3173.
166. J. Taylor, W. Vargas, A. Torvisco, K. Ruhlandt-Senge, and J. T. Spencer, *Dalton Trans.* 2011, **40**, 10585.
167. C. D. Entwistle and T. B. Marder, *Angew. Chem. Int. Edit.* 2002, **41**, 2927.
168. X-Q. Li, C-H. Wang, M-Y. Zhang, H-Y. Zou, N-N. Ma, and Y-Q. Qiu, *J. Organomet. Chem.* 2014, **749**, 327.
169. Y. Li, H-L. Xu, H-Q. Wu, R-L. Zhong, S-L. Sun, and Z-L. Su, *Dalton Trans.* 2014, **43**, 2656.
170. F. Di Salvo, M. Y. Tsang, F. Teixidor, C. Viñas, J. G. Planas, J. Crassous, N. Vanthuyne, N. Aliaga-Alcalde, E. Ruiz, G. Coquerel, S. Clevers, V. Dupray, D. Choquesillo-Lazarte, M. E. Light, and M. B. Hursthouse, *Chem. Eur. J.* 2014, **20**, 1081.
171. Y. Liu, G. C. Yang, S. L. Sun, F. Yu, Z. M. Su, and L. Z. Hao, *J. Theoret. Comput. Chem.* 2012, **11**, 1121.
172. Y. Liu, G. Yang, S. Sun, and Z. Su, *Comput. Theor. Chem.* 2012, **992**, 142.
173. P. Kaszynski, "Closo-Boranes as Structural Elements for Liquid Crystals", in *Boron Science: New Technologies and Applications*, N. S. Hosmane, Ed., CRC Press, London and New York, 2011, Chapter 14.
174. B. Ringstrand and P. Kaszynski, *Accounts Chem. Res.* 2013, **46**, 214.
175. A. Jankowiak and P. Kaszynski, *Inorg. Chem.* 2014, **53**, 8762.
176. J. Pecyna, B. Ringstrand, R. P. Denicola, P. Kaszynski, and H. M. Gray, *Liq. Cryst.* 2014, **41**, 1188.
177. J. Pecyna, D. Pocięcha, and P. Kaszynski, *J. Mater. Chem. C* 2014, **2**, 1585.
178. A. Jankowiak, A. Sivaramamoorthy, D. Pochiecha, and P. Kaszynski, P., *RSC Adv.* 2014, **4**, 53907.
179. P. Kaszynski, A. Januszko, and K. L. Glab, *J. Phys. Chem. B* 2014, **118**, 2238.
180. Y. Q. Li, U. Kusari, P. J. Carroll, M. G. Bradley, and L. G. Sneddon, *Pure Appl. Chem.* 2006, **78**, 1349.
181. R. N. Grimes, *J. Organomet. Chem.* 2013, **747**, 4.
182. A. Stock and E. Kuss, *Ber* 1923, **56**, 789.



A carborane-fullerene dyad for organic field-effect transistors