A coordination chemistry dichotomy for icosahedral carborane-based ligands

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Although the majority of ligands in modern chemistry take advantage of carbon-based substituent effects to tune the sterics and electronics of coordinating moieties, we describe here how icosahedral carboranes—boron-rich clusters—can influence metal-ligand interactions. Using a series of phosphine–thioether chelating ligands featuring meta- or ortho-carboranes grafted on the sulfur atom, we were able to tune the lability of the platinum–sulfur interaction of platinum(II)–thioether complexes. Experimental observations, supported by computational work, show that icosahedral carboranes can act either as strong electron-withdrawing ligands or electron-donating moieties (similar to aryl- or alkyl-based groups, respectively), depending on which atom of the carborane cage is attached to the thioether moiety. These and similar results with carborane-selenol derivatives suggest that, in contrast to carbon-based ligands, icosahedral carboranes exhibit a significant dichotomy in their coordination chemistry, and can be used as a versatile class of electronically tunable building blocks for various ligand platforms.

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sequence of cage functionalization (because it provides a direct ortho groups such as substituents on the sulfur atom. Indeed, strongly electron-donating strengths. To test this hypothesis, we designed and synthesized a containing icosahedral carboranes to probe their relative binding analogues of these complexes in the context of hemilabile ligands 

This dichotomous behaviour in coordination chemistry is extremely unusual and may become a versatile tool for regulating the electronic properties of ligands without altering steric.

**Results and discussion**

Phosphine–thioether (P,S) hemilabile ligands can be used to synthesize a wide variety of monoligated and bisligated Pt(II) complexes in high yield (Fig. 1a)\(^\text{38}\). These structures are ideal for studying the coordination strength of the thioether moieties as a function of substituents on the sulfur atom. Indeed, strongly electron-donating groups such as \(-\mathrm{CH}_3\) result in thioethers capable of displacing a \(\mathrm{Cl}^-\) ligand from the inner coordination sphere, while strongly electron-withdrawing groups such as \(-\mathrm{F}\) result in thioethers capable of displacing a \(\mathrm{Cl}^-\) ligand from the inner coordination sphere, while strongly electron-withdrawing groups such as \(-\mathrm{F}\).

**Figure 1 | Coordination chemistry and electronic characteristics of phosphine-thioether (P,S) ligands.** a, Coordination-based motifs derived from various possible interactions of hemilabile (P,S) ligands with Pt(II). b, Comparison of carbon-based and carborane-based ligands and corresponding Mulliken charge densities on sulfur atoms associated with the thioether moieties of the ligands.

shows that this is probably a general characteristic of carboranes as heteroatom substituents. This dichotomous behaviour in coordination chemistry is extremely unusual and may become a versatile tool for regulating the electronic properties of ligands without altering steric.

When one equivalent of ligand 1a is added to one equivalent of Pt(II) precursor (in all cases Pt(cod)Cl\(_2\); cod = 1,5-cyclooctadiene) in dichloromethane (CH\(_2\)Cl\(_2\)), the monochelate species 2a forms instantaneously and quantitatively as determined by \(^{31}\)P[\(^1\)H] NMR spectroscopy (Figs 3 and 4a). The spectrum of complex 2a exhibits a singlet at \(\delta \approx 41\), which is diagnostic of ligand 1a chelating to the Pt(II) centre (I\(_{\text{P-Pt}}\) = 3625 Hz)\(^\text{38}\). Coordinatively similar structures 2e–h are observed when 1-phosphinoethyl-2-thioalkyl (1e, 1f; see Supplementary Information, pp. 7–8) and -aryl (1g, 1h; see Supplementary Information, pp. 10–11) ligands are used instead of 1a. \(^{11}\)B[\(^1\)H] NMR spectroscopy is a very useful technique with which to characterize carborane-based complexes such as 2a in solution, because upon metal coordination of the thioether moiety to the Pt(II) centre, the resonance corresponding to the B9 atom shifts approximately 4 ppm upfield (Fig. 4c).

When one equivalent of ligand 1b was added to the same Pt(II) precursor under conditions identical to those used for ligand 1a, the bis-phosphine adduct 2b was formed instead of a structure analogous to 2a with one equivalent of a chelating hemilabile ligand (Fig. 3). The \(^{31}\)P[\(^1\)H] NMR spectrum of 2b shows a single resonance at \(\delta \approx 7\) (I\(_{\text{P-Pt}}\) = 3638 Hz), which is highly diagnostic of a complex with two monodentate phosphine ligands bound in a cis comparison with 1c). These (P,S) chelate ligands 1a–d were synthesized from carborane thiolos (I, II, III and V; Fig. 2 and Supplementary Information pp. 3–8) in good yields.

Plesek et al. made the original observation that ortho- and meta-carboranes (compounds I and III, respectively, Fig. 2) functionalized with thioles at the B9 position have an acidity that is \(\sim 1 \times 10^6\) to \(1 \times 10^5\) times lower than the corresponding carboranes functionalized on the C1 atom (compound II, Fig. 2)\(^\text{39}\). Such differences in pK\(_a\) are also observed in the case of alkyl- and aryl-based thioles, with the latter being more acidic\(^\text{40}\). This observation raises the question of whether or not one can construct ligands from icosaedral carboranes that exhibit vastly different coordination chemistry simply based upon the position of the heteroatom (S in this case) on the carborane cage.

Others have studied the adsorption properties of I and II (Fig. 2) in the context of self-assembled monolayers (SAMs) on gold, but these studies did not address ligating strength as a function of heteroatom attachment to the carborane\(^\text{40,41}\). Additionally, Lyubimov et al. studied the catalytic properties of Rh(i) complexes of 2,2′-bis-(diphenylphosphino)-1,1′-bi-2-naphthol (BINOL)-based thiophosphate ligands, which are derivatives of I–III\(^\text{42}\). Although the heteroatoms attached to the carborane moieties are not involved in metal–ligand coordination in this work (the thiophosphites coordinate via phosphorus atoms), an enantioselectivity difference of hydrogenated products was observed and proposed by the authors to be the result of different electronic environments imposed by the different carborane ligands. Finally, in contrast with some of these early observations about the electronic consequences of functionalization of the carborane cage, there have been several reports in the recent literature that generalize icosaedral carboranes as electron-withdrawing species\(^\text{43,44}\).

When one equivalent of ligand 1a is added to one equivalent of Pt(II) precursor (in all cases Pt(cod)Cl\(_2\); cod = 1,5-cyclooctadiene) in dichloromethane (CH\(_2\)Cl\(_2\)), the monochelate species 2a forms instantaneously and quantitatively as determined by \(^{31}\)P[\(^1\)H] NMR spectroscopy (Figs 3 and 4a). The spectrum of complex 2a exhibits a singlet at \(\delta \approx 41\), which is diagnostic of ligand 1a chelating to the Pt(II) centre (I\(_{\text{P-Pt}}\) = 3625 Hz)\(^\text{38}\). Coordinatively similar structures 2e–h are observed when 1-phosphinoethyl-2-thioalkyl (1e, 1f; see Supplementary Information, pp. 7–8) and -aryl (1g, 1h; see Supplementary Information, pp. 10–11) ligands are used instead of 1a. \(^{11}\)B[\(^1\)H] NMR spectroscopy is a very useful technique with which to characterize carborane-based complexes such as 2a in solution, because upon metal coordination of the thioether moiety to the Pt(II) centre, the resonance corresponding to the B9 atom shifts approximately 4 ppm upfield (Fig. 4c).

When one equivalent of ligand 1b was added to the same Pt(II) precursor under conditions identical to those used for ligand 1a, the bis-phosphine adduct 2b was formed instead of a structure analogous to 2a with one equivalent of a chelating hemilabile ligand (Fig. 3). The \(^{31}\)P[\(^1\)H] NMR spectrum of 2b shows a single resonance at \(\delta \approx 7\) (I\(_{\text{P-Pt}}\) = 3638 Hz), which is highly diagnostic of a complex with two monodentate phosphine ligands bound in a cis

**Figure 2 | Structures of the carborane thiolos (I, II, III and V) used to synthesize the (P,S) chelate ligands investigated in this study.** The point of attachment of the carborane to the sulfur atom is systematically altered.
configuration\(^{38,45}\). Consistent with this assignment, only half of the Pt(cod)Cl\(_2\) precursor was consumed, which was confirmed by \(^{195}\)Pt NMR spectroscopy (see Supplementary Information, p. 22). For 2b, a triplet at \(\delta = -4,389\) \((^1J_{Pt-P} = 3,638\) Hz) is observed in the \(^{195}\)Pt NMR spectrum \(^{46}\). A similar reactivity is observed when the fluorinated ligand 1i (Fig. 1b) is used with the Pt(II) precursor under nearly identical reaction conditions \(^{38}\), which suggests that the S-functionalized carboranyl moiety in 1b acts as a strongly electron-withdrawing substituent. This conclusion is reinforced by studying the product of the reactions between 2a and 2b with an additional equivalent of hemilabile ligand (1a and 1b), respectively.

In particular, the addition of a second equivalent of ligand 1a to complex 2a (obtained in situ from Pt(cod)Cl\(_2\) and one equivalent of 1a) results in the formation of 3a (Fig. 3). Complex 3a has one hemilabile ligand chelating to the Pt(ii) centre and another bound in monodentate fashion through the phosphine moiety. A Cl\(^-\) ligand that was originally bound to the Pt(ii) centre in 2a has been displaced to the outer coordination sphere to accommodate the additional phosphine ligand. \(^{31}\)P\{\(^1\)H\} NMR spectroscopy shows that the hemilabile ligands in 3a are undergoing rapid exchange in a ‘windshield wiper’ motion involving the thioethers replacing one another at room temperature in CD\(_2\)Cl\(_2\) solution (Fig. 3 and Supplementary Information, p. 22) \(^{38}\). Consistent with this conclusion, when the sample is cooled below -25 °C (Supplementary Information, p. 22), two sharp \(^{31}\)P\{\(^1\)H\} NMR resonances at \(\delta = -5\) \((^1J_{Pt-P} = 3,525\) Hz) and \(\delta = 10\) \((^1J_{Pt-P} = 3,255\) Hz) are observed for 3a, indicative of the semi-open complex. The downfield resonance is assigned to the fully chelating \((\kappa^2)\) (P,S) ligand and the upfield resonance is assigned to the \(\kappa^1\)-phosphine bound ligand and agrees well with literature analogues of isostructural complexes \(^{38,45}\).

At temperatures below coalescence, one can also clearly observe resolved \(^2J_{P-P}\) coupling: 13 Hz for the phosphine moiety of the (P,S) ligand and the upfield resonance is assigned to the \(\kappa^2\)-phosphine bound ligand and agrees well with literature analogues of isostructural complexes \(^{38,45}\). Bulky alkyl-based ligands (1e and 1f) react with the Pt(II) precursor under nearly identical reaction conditions to yield complexes with coordination environments and fluxional behaviour similar to compound 3a (Supplementary Information, pp. 11–13).

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\begin{align*}
\text{Figure 3} & \mid \text{Synthetic scheme outlining the synthesis of Pt(II) complexes.} \\
a, b, Reactions involving ligands 1a (a) and 1b (b). All transformations are quantitative as observed by \textit{in situ} \(^{31}\)P and \(^{31}\)P\{\(^1\)H\} NMR spectroscopy. Full details on synthesis and characterization can be found in the Supplementary Information.
\end{align*}
\]
In contrast, when two equivalents of 1b are added to Pt(cod)Cl$_2$, one observes the exclusive formation of the fully open non-chelated complex 2b, with concomitant consumption of the Pt(II) precursor (no Pt(cod)Cl$_2$ was observed in the $^{195}$Pt NMR spectrum). This observation is consistent with the conclusion that ligand 1a is a weaker chelating ligand than 1b.

Additional evidence in support of the proposed dichotomy in coordination-based chemistry for this novel class of carborane-based hemilabile ligands comes from studying the fluxional behaviour of 3b (Fig. 3), the product formed from abstracting a single Cl$^-$ ligand from 2b with one equivalent of NaBArF (BArF = tetra-kis[(3,5-trifluoromethyl)phenyl]borate) and comparing it to the BArF$^-$ salt of 3a, 3a', formed by metathesis with NaBArF (Fig. 3). Although 3a' still exhibits the fluxionality of 3a, as observed by $^{31}$P($^1$H) NMR spectroscopy (Fig. 4a and Supplementary Information, p. 14), semi-open complex 3b (measured from

Figure 4 | Characterization of the ligands. a c. Representative $^{31}$P/$^{31}$P($^1$H) NMR spectra of complexes with ligand 1a (a), ligand 1b (b) and $^{11}$B/$^{11}$B($^1$H) NMR data highlighting changes associated with the transformations involving ligand 1a (c). As B9 is the only substituted boron atom in the carborane cluster, it does not exhibit B–H coupling and can therefore be easily distinguished from other resonances assigned to other boron atoms of the carborane cage.

Figure 5 | Crystallographically derived X-ray structure representations of closed carborane-based Pt(II) complexes 4a–4d. Solvent molecules and anions are omitted for clarity. Atom colour code: pale red, B; grey, C; blue, P; black, Pt; white, H. Full details on crystallographic refinement can be found in Supplementary Section 3. (CCDC no. 824088–824091.)
resolved $^{31}$P/$^1$H NMR spectrum with a singlet at $\delta$ 48 ($J_{P,Pt}$ = 3,135 Hz) and $\delta$ 43 ($J_{P,Pt}$ = 3,207 Hz) for 4a and 4b, respectively. Similarly to the above-mentioned correlation between the $trans$ effect of the thioether and the $J_{P,Pt}$ value, we observed a 70 Hz difference, indicating that the thioether moiety in 4a exhibits a smaller $trans$ effect than in 4b. Single-crystal X-ray diffraction studies of 4a and 4b further corroborate the effect of the thioether $trans$ influence (Fig. 5), where the S–Pt bond length in 4a is 0.04 Å shorter than in 4b.

Density functional theory (DFT) calculations on the geometry-optimized structures of ligands 1a–i provide a clear account of the observed coordination behaviour. Mulliken charge density distributions at the sulfur atoms of these ligands (Fig. 1 and Supplementary Section 4) show that the sulfur atoms in B9-functionalized carboranes are significantly more electron-rich than those of the C1-functionalized analogue 1b. Moreover, these values suggest that the thioether in 1b is more electron-poor than in the fluorinated analogue 1i, whereas the same moieties in 1a, 1c, and 1d are more electron-rich than in the bulky alkyl-based ligands 1e and 1f. For all of the ligands 1a–i, calculated Mulliken charges on the phosphorus atoms remain nearly identical, signifying that the ethyl spacer between the thioether and phosphine moieties screens any potential electronic influence. According to these calculations, ligands 1c and 1d should exhibit a qualitatively similar coordination strength at their thioether moieties to ligand 1a. This was confirmed through a series of experiments under identical conditions to that of 1a shown in Fig. 3 (Supplementary Sections 1–2).

The introduction of two methyl groups on the o-carborane (ligand 1d, Fig. 1) had minimal effect on the coordination chemistry observed, suggesting that functionalization via this route can retain both the steric and electronic parameters of this system and provide a strategy for orthogonal ligand functionalization. Furthermore, our studies indicate that 1a acts as an electron-donating ligand in the halide-induced ligand rearrangement reaction (HILR) when paired with an electron- withdrawing ligand 1i (Supplementary Information, pp. 19–20).

Driven by the temptation to suggest that the observed phenomena are general with respect to other heteroatoms, we synthesized two carborane selenol derivatives (5a and 5b), which allowed us to probe directly the electronic environment of the heteroatom nuclei (selenium) via $^{77}$Se NMR spectroscopy (Supplementary Information, pp. 20–21). Strikingly, the $^{77}$Se/$^1$H NMR spectrum of the C-functionalized m-carborane selenol 5b (Fig. 6) exhibits a resonance very far downfield at $\delta$ 347 in CD$_2$Cl$_2$. As a point of reference, the $^{77}$Se NMR spectrum of CF$_3$SeH, perhaps the most electron-withdrawing carbon-based selenol derivative, exhibits a resonance at $\delta$ 287 (ref. 48). In contrast, the B9-functionalized m-carborane selenol 5a exhibits an extremely upfield resonance at $\delta$ = 280, which appears as a quartet due to coupling to the adjacent $^{11}$B nuclei ($S = 3/2$). This resonance indicates that the electron-donating B9-functionalized m-carborane cage is far more shielding than any known alkyl-based substituent. Indeed, theoretical calculations of Mulliken charges (0.038 for Se in 5a and 0.270 in 5b) and $^{77}$Se NMR shielding constants support these experimental observations (Supplementary Section 4). Although a shift difference of $\sim$625 ppm is virtually unattainable with the same carbon-based substituent, one single carborane-based moiety (m-carborane) can successfully serve as an extremely electron-withdrawing or extremely electron-donating moiety.

**Conclusions**

Our work suggests that a thioether moiety attached to different vertices oficosahedral carboranes can experience either a strongly electron-withdrawing (similar to fluorinated aryls) or strongly electron-donating (similar to electron-donating bulky alkyils) influence. This
dichotomy is an intrinsic property of the carborane moiety, and thus one can envision that many heteroatoms attached in a fashion similar to sulfur can be tuned in such a manner. This conclusion is supported by the unprecedented difference in the 77Se NMR chemical shifts obtained for B9 and C1-functionalized meta-carborane selenols. This also suggests that referring to a carborane (or carboranoyl) moiety solely as electron-withdrawing, without specifying its point of attachment, is not rigorously correct. Nevertheless, applications of this concept may not be limited only to the tuning of hemiﬀability detailed here. For example, C-functionalized derivatives have been predicted to have promising route for accessing B-functionalized carborane applications of this concept may not be limited only to the tuning of hemiﬀability detailed here. For example, C-functionalized derivatives have been predicted to have promising route for accessing B-functionalized carborane anions. This also suggests that referring to a carborane (or carborane-termed “metallacarborane”19). Carborane-based thiols have been characterized by B–Hg–B bonds: synthesis and structure of cyclo-[(Bu3Si)(C6H4)2(B2H6)]. J. Am. Chem. Soc. 117, 12383–12393 (1995).


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Author contributions
A.M.S. originated and developed the concept with C.A.M., who supervised and guided the research. All experiments were designed and performed by A.M.S., C.W.M., D.J.C., M.S.R., M.J.W. and R.D.K. A.M.S. and C.W.M. performed all computational studies. C.L.S., A.A.S. and R.D.K. performed all crystallographic studies. A.M.S. and C.A.M. co-wrote the manuscript. All authors discussed the results and commented on the manuscript during its preparation.

Additional information
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