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Zwitterionic Weak-Link Approach Complexes Based on Anionic Icosahedral Monocarbaboranes

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Supporting Information

ABSTRACT: The anionic hemilabile phosphinothioether ligand, [1-($Ph_2PCH_2CH_2S$)-*closo*-1-$CB_{11}H_{11}$]$^-$, which is functionalized with an anionic icosahedral monocarbaborane anion, was synthesized in three steps from [$HNMe_3$][*closo*-$CB_{11}H_{12}$]. The ligand was used to synthesize a family of zwitterionic Weak-Link Approach (WLA) complexes that contain platinum(II), palladium(II), and rhodium(I). These complexes were characterized using multinuclear NMR spectroscopy, high-resolution mass spectrometry, and single-crystal X-ray diffraction analyses. Although the *C*-bound [*closo*-$CB_{11}H_{11}$]$^-$ anion behaves as an electron-withdrawing moiety, hemilabile phosphinothioether ligands that are based on this unit are strongly chelating, as determined via the measurement of the chloride association constant. The chelating strength is comparable to that of hemilabile ligands that are functionalized with the very electron-rich *B*-bound *closo*-1,7-$C_2B_{10}H_{11}$ moiety, thus demonstrating the use of *charge* to influence ligand coordination strength. The anionic Rh(I) WLA complex that is synthesized using this ligand can act as the noncoordinating anion of a regular cationic Rh(I) WLA complex. Thus, an unprecedented type of salt, in which the anion and cation are mutually isostructural and isoelectronic WLA complexes, has been synthesized and characterized crystallographically.

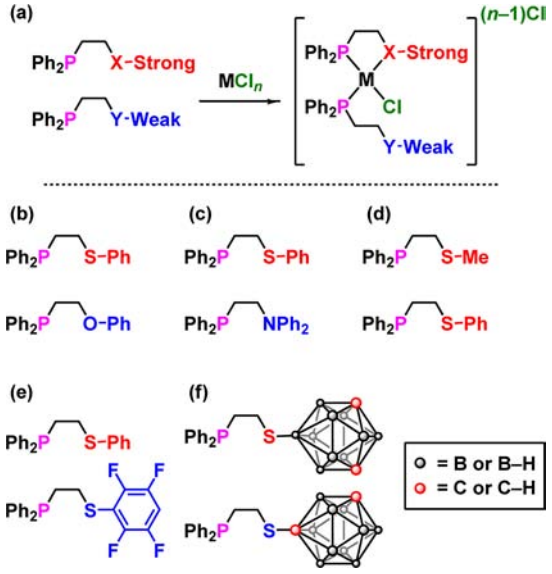
INTRODUCTION

The use of synthetic chemistry to produce systems that mimic biological structures is an important and active area of scientific research.[1] Supramolecular coordination chemistry is at the forefront of these efforts as it provides a means to construct large, complicated assemblies rapidly and cleanly.[2] The Weak-Link Approach (WLA)[3] and the Directional Bonding Approach (DBA)[4] have emerged as particularly powerful tools with which to construct such assemblies. The WLA is unique in that it can be used to synthesize stimuli-responsive supramolecular constructs that undergo structural changes upon treatment with elemental ions or small-molecule effectors. When catalytic moieties are introduced into WLA complexes, these structural changes may be linked to changes in the properties of the system,[5] or in catalytic activity.[6−8]

WLA complexes are formed via the reaction between phosphine-based hemilabile ligands and d^8 metal centers [e.g., rhodium(I),[9] iridium(I),[10] palladium(II),[11] or platinum(II)[12−14]] paired with noncoordinating anions. An important development in the WLA is the Halide-Induced Ligand Rearrangement (HILR) reaction (Scheme 1), which allows for the synthesis of *heteroligated* complexes.[3,15,16] In order for heteroligated complexes to form cleanly, there must be a sufficiently great difference in the coordinating strengths of the weakly binding atoms.

Several methods have been developed to differentiate the two hemilabile ligands. For example, hard (e.g., O, N) and soft (e.g., S, Se) heteroatoms have been utilized with rhodium(I)[15,17] and platinum(II) systems[13] (Scheme 1b−c). The difference in coordination strength between alkyl- and aryl-substituted chalcoethers has also been exploited[18] (Scheme 1d). Electron-poor aryl substituents have been paired with regular aryl groups while keeping the identity of the chalcoether the same (Scheme 1e).[14] A recent development has been the use of icosahedral dicarbaborane-based hemilabile ligands, in which the position of attachment of the thioether to the

Scheme 1[a]



[a](a) The synthesis of heteroligated WLA complexes via the HILR reaction. (b)−(f) Pairs of hemilabile phosphine ligands that lead to heteroligated complexes. [M = d^8 metal, e.g., Rh(I) or Pt(II)]. Strongly coordinating 'weak links' are shown in red; weakly coordinating 'weak links' are shown in blue.

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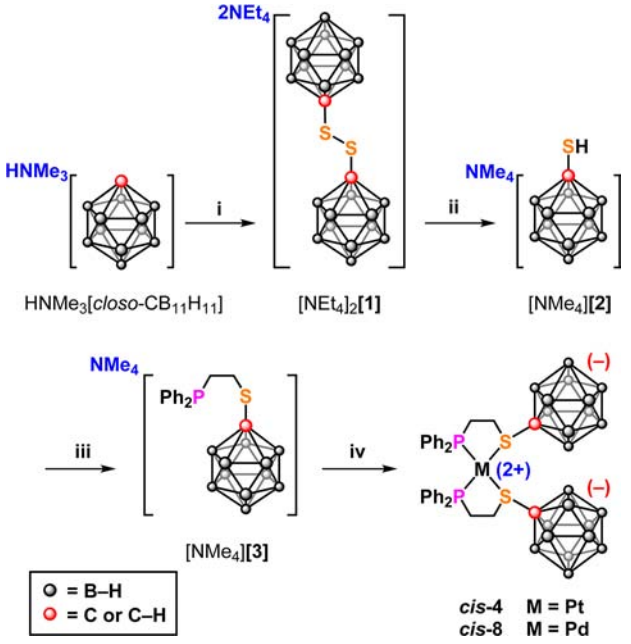
dicarbaborane cage dictates the strength of coordination (Scheme 1f).[19] We are interested in developing new methods to modulate the coordinating strength of hemilabile ligands in order to expand the capabilities of the WLA. Herein we present the utilization of *charge* as a means to influence the strength of coordination, specifically via the incorporation of the non-coordinating anionic monocarbaborane residue[20] {*closo*-$CB_{11}H_{11}$}$^-$ into a hemilabile phospinothioether ligand. The use of these anionic hemilabile ligands leads to an interesting and previously unknown class of zwitterionic WLA complexes. We report on the syntheses and properties of these novel species, and describe the solid-state structure of a rare type of salt in which both the cation and anion are large, rigid, and mutually isostructural and isoelectronic. Salts such as these are unprecedented, as the ions must be mutually unreactive and redox-inactive. *closo*-Carbaboranes are uniquely suited for the preparation of these salts, as they are generally chemically inert and redox-stable, yet their charge may be tailored by changing the number of carbon atoms within the cage.

RESULTS AND DISCUSSION

Hemilabile ligand [NMe_4][**3**] was synthesized in a straightforward and high yield fashion from the anionic monocarbaborane thiol, [NMe_4][1-SH-*closo*-1-$CB_{11}H_{11}$] [NMe_4][**2**] (Scheme 2).[21] Specifically, the lithiated monocarbaborane Li[$LiCB_{11}H_{11}$] was treated with elemental sulfur to produce a mixture of thiol [**2**]$^-$, a small quantity of disulfide [**1**]$^{2-}$, and unreacted monocarbaborane, which was isolated as a mixture of tetraethylammonium salts. It was not possible to isolate [**2**]$^-$ from this mixture in good yield or high purity. Therefore, the mixture was treated with elemental iodine in wet acetonitrile, which resulted in the quantitative conversion of thiol [**2**]$^-$ to the disulfide [**1**]$^{2-}$, as determined via ^{11}B NMR spectroscopy. Column chromatography was then used to separate the disulfide from the unreacted monocarbaborane. Subsequent quantitative reduction of the disulfide using zinc metal in acetic acid produced the thiol [**2**]$^-$, which was isolated as the tetramethylammonium salt. The yield was 71% over two steps. The phosphinoethyl group was installed using chloroethylphosphine in acetonitrile to give ligand [NMe_4][**3**] in ca. 86% yield.

Scheme 2. Synthesis of *cis*-4 and *cis*-8[a]



[a]Reaction conditions: (i) *n*-BuLi, S_8, THF; I_2, MeCN/H_2O; [NEt_4]Cl, H_2O. (ii) HCl/H_2O/Et_2O; Zn, AcOH; [NMe_4]Cl, H_2O. (iii) $Ph_2PCH_2CH_2Cl$, Cs_2CO_3, MeCN. (iv) MCl_2(cod) [M = Pt, Pd], CH_2Cl_2; MeOH; DMF. (cod) = 1,5-cyclooctadiene.

The reaction between 2 equiv of compound [NMe_4][**3**] with a single equiv of $PtCl_2$(cod) [(cod) = 1,5-cyclooctadiene] in dichloromethane at room temperature (Scheme 2 and Figure 1) produced a mixture of several complexes, as determined via in situ $^{31}P\{^1H\}$ NMR spectroscopy (see Supporting Information). The mixture contained semichelated *cis* and *trans* bisligand species ([***cis*-5**] and [***trans*-5**], respectively), in which one ligand is chelating and the other is bound through the phosphorus atom, and fully chelated *cis* and *trans* bisligand species (***cis*-4** and ***trans*-4**, respectively). The signals that correspond to the various species are sharp and well-defined, suggesting that ligand exchange is slow, and that there are no fast fluxional processes occurring that involve a change in coordination at the platinum center. When the mixture was dissolved in methanol, a white microcrystalline solid precipitated from the solution over the course of a few hours. Subsequent $^{31}P\{^1H\}$ NMR spectroscopic analysis in *N*,*N*-dimethylformamide (DMF) revealed this solid to be a clean mixture of fully chelated *cis* and *trans* complexes (***cis*-4** and ***trans*-4**, respectively). Compound ***cis*-4** could then be obtained cleanly via thermal isomerization in DMF at 50 °C and isolated in a 76−80% yield. Single-crystal X-ray crystallographic analysis (Figure 2) confirmed the structure of compound ***cis*-4**, in which both ligands are chelated to the square planar Pt(II) center, and the phosphines have a mutual *cis* orientation. Remarkably, the zwitterionic, charge-neutral complex ***cis*-4** is isoelectronic and essentially isostructural with previously described dicationic complexes, [*cis*-Pt($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$}-κ^2)$_2$]$^{2+}$ ([**6**]$^{2+}$) and [*cis*-Pt($Ph_2PCH_2CH_2S$-{1-*closo*-1,7-

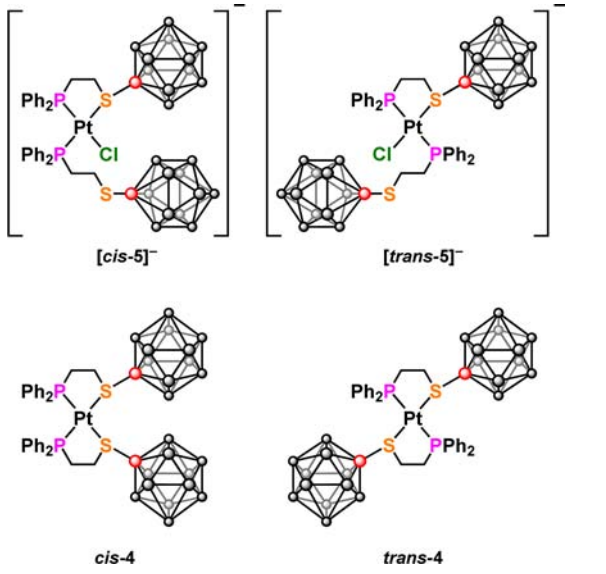


Figure 1. Mixture of semichelated and fully chelated *cis* and *trans* complexes obtained via the reaction between [NMe_4][**3**] and 0.5 equiv of $PtCl_2$(cod). Gray and red circles represent B−H and C vertices, respectively.

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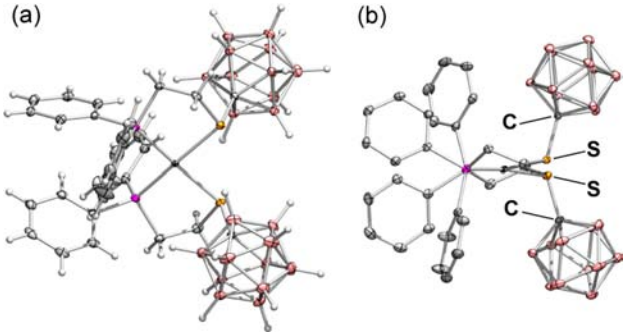

Figure 2. Crystallographically determined molecular structure of compound ***cis*-4**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are represented as spheres with an arbitrary radius of 0.14 Å in (a). Hydrogens are omitted for clarity in (b). Atom color code: Pt = black; C = gray; H = white; B = pink; P = magenta; S = orange.

$C_2B_{10}H_{11}\}$-$\kappa^2)_2]^{2+}$ ($[\mathbf{7}]^{2+}$), that contain the $\{1,7\text{-}C_2B_{10}H_{11}\}$ residue.[19] Closer inspection reveals that the dihedral angle C−S−S−C in compound ***cis*-4** [149.24(8)°] is significantly larger than those of compounds $[\mathbf{6}]^{2+}$ [120.1(4)°] and $[\mathbf{7}]^{2+}$ [115.8(3)°] (Figure 2b). The distance between the centroids of the icosahedra in compound ***cis*-4** [7.6864(3) Å] is greater than the corresponding distances in compounds $[\mathbf{6}]^{2+}$ [7.1856(3) Å] and $[\mathbf{7}]^{2+}$ [6.8625(2) Å]. This may be due to the electrostatic repulsion between the anionic cages, although crystal-packing forces may also influence the molecular structures. The analogous palladium(II) complex, ***cis*-8**, was obtained following an identical reaction procedure starting from $PdCl_2$(cod).

Mulliken population analysis is frequently used as a way of estimating atomic charge. A recent study showed that the Mulliken charge of the sulfur atom within a hemilabile phosphinothioether ligand correlated well with the strength of the Pt−S bond in a series of WLA complexes.[19] As a starting point for the determination of the coordinating strength of anionic ligand $[\mathbf{3}]^-$, the Mulliken charge was calculated for the sulfur atom of the model thiol anion, $[1\text{-SH-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ ($[\mathbf{2}]^-$). Details of the calculations are included in the Supporting Information (SI). This value was compared with the Mulliken charges associated with other model thiols: dicarbaboranethiol 9-SH-*closo*-1,7-$C_2B_{10}H_{11}$ (**9**), methanethiol (**10**), and benzenethiol (**11**) (Figure 3). The calculations show

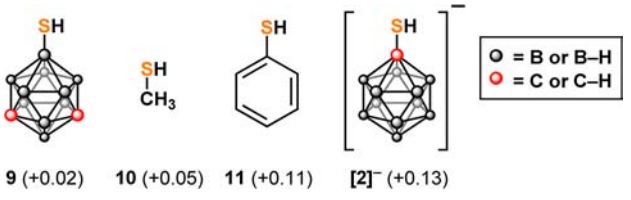

Figure 3. Model thiols and calculated Mulliken charges for the sulfur atoms (see Supporting Information for details of calculations).

that the partial atomic charge of the sulfur atom of $[1\text{-SH-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ (+ 0.13) is slightly more positive than that of the sulfur atom of benzene thiol (+ 0.11), and considerably more positive than that of the sulfur atom of the electron-rich dicarbaborane thiol, (**9**), which has a partial atomic charge of +0.02. This is reasonable, as the carbon atom of the icosahedral monocarbaborane anion, $[closo\text{-}CB_{11}H_{12}]^-$, is 'electron poor' and may be compared to the carbon atoms of the icosahedral dicarbaboranes. For example, it is known that the chemistry at the carbon atom of $[closo\text{-}CB_{11}H_{12}]^-$ closely resembles that of the carbon atoms of icosahedral dicarbaboranes.[20−22] The pK_a values, measured in DMSO, of the C−H hydrogens of the $[closo\text{-}CB_{11}H_{12}]^-$ anion (pK_a = 21.7) and *closo*-1,2-$C_2B_{10}H_{12}$ (pK_a = 22.0) are very similar. Furthermore, the pK_a of the ammonium-containing zwitterion 1-NMe_2H-*closo*-$CB_{11}H_{11}$ (pK_a = 5.7 in DMSO) is similar in magnitude to *aryl*ammonium species such as $[PhNMe_2H]^+$ (pK_a = 5.2), rather than *alkyl*ammoniums, for example, $[Et_3NH]^+$ (pK_a = 10.5). Thus, from this simple analysis and literature precedent, one would expect ligand $[\mathbf{3}]^-$ to have a similar binding strength to the phenylthioether ligand, $Ph_2PCH_2CH_2SPh$, rather than a more strongly coordinating thioether.

Several experimental methods are available with which to probe the strength of the Pt−S bond between the hemilabile ligand and the platinum(II) center. For example, one can measure the manifestations of the *trans* influence via NMR spectroscopy or via the analysis of the solid-state structure. For complex ***cis*-4**, a $^{31}P-^{19S}Pt$ coupling constant of 3137 Hz is observed in the $^{31}P\{^1H\}$ NMR spectrum. This value may be compared conveniently to the coupling constants exhibited by the isostructural complexes $[cis\text{-}Pt(Ph_2PCH_2CH_2S\text{-}\{9\text{-}closo\text{-}1,7\text{-}C_2B_{10}H_{11}\}\text{-}\kappa^2)_2]^{2+}$ ($[\mathbf{6}]^{2+}$; $^1J_{P-Pt}$ = 3135 Hz), which contains a strongly coordinating ligand, and $[cis\text{-}Pt(Ph_2PCH_2CH_2S\text{-}\{1\text{-}closo\text{-}1,7\text{-}C_2B_{10}H_{11}\}\text{-}\kappa^2)_2]^{2+}$ ($[\mathbf{7}]^{2+}$; $^1J_{P-Pt}$ = 3207 Hz), which contains a weakly coordinating ligand. Thus, from the perspective of the *trans* influence as determined using NMR spectroscopy, the thioether in compound ***cis*-4** behaves as a relatively strongly binding ligand. Further comparison with other complexes, for example, those based on the phenyl and methyl phosphinothioether ligands, $Ph_2PCH_2CH_2SPh$ and $Ph_2PCH_2CH_2SMe$, respectively, is complicated by steric effects. In certain circumstances, small variations in the length of the P−Pt bond *trans* to a ligand, measured crystallographically, may also be used to estimate the *trans* influence. In the present case, however, there appears to be no trend across the series of model complexes. This may be in part due to crystal packing forces, which influence the orientation of the ligands and thus their orbital overlap with the platinum(II) center.

In order to probe the strength of the Pt−S bond between the hemilabile ligand and the platinum(II) center in ***cis*-4**, and thus the coordinating strength of the thioether, ^{31}P NMR spectroscopy was utilized to measure the chloride association constant (K_c) as defined in Scheme 3. For comparison, the isostructural complex $[cis\text{-}Pt(Ph_2PCH_2CH_2S\text{-}\{9\text{-}closo\text{-}1,7\text{-}C_2B_{10}H_{11}\}\text{-}\kappa^2)_2]\text{-}[BF_4]_2$ ($[\mathbf{6}][BF_4]_2$), which possesses two strongly chelating ligands, was also investigated.[19] In order to bring the association constants into a range that could be measured conveniently via NMR spectroscopy[23] while maintaining solubility, the measurements were conducted on ca. 3−5 mg of complex in a 1:1 mixture of methanol and dimethylformamide. Aliquots of $[NEt_4]Cl$ were added as the chloride source (experimental details are provided in the Supporting Information). The association constant for complex ***cis*-4** is ca. 84 M^{-1}, which is essentially identical to that of $[\mathbf{6}][BF_4]_2$ (K_c = ca. 84 M^{-1}). This suggests that, although the *C*-bound monocarbaborane anion has electron-withdrawing properties, as evidenced by reactivity and Mulliken population analysis, phosphinothioether ligands that are based upon the *C*-bound monocarbaborane anion act as very strong chelating ligands. We suggest that significant contributions to this may arise from

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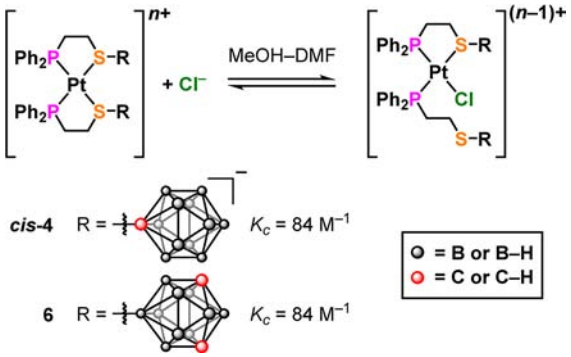
Scheme 3. Chloride Association Constants for Fully Chelated Platinum(II) WLA Complexes *cis*-4 (n = 0) and $[6][BF_4]_2$ (n = 2)

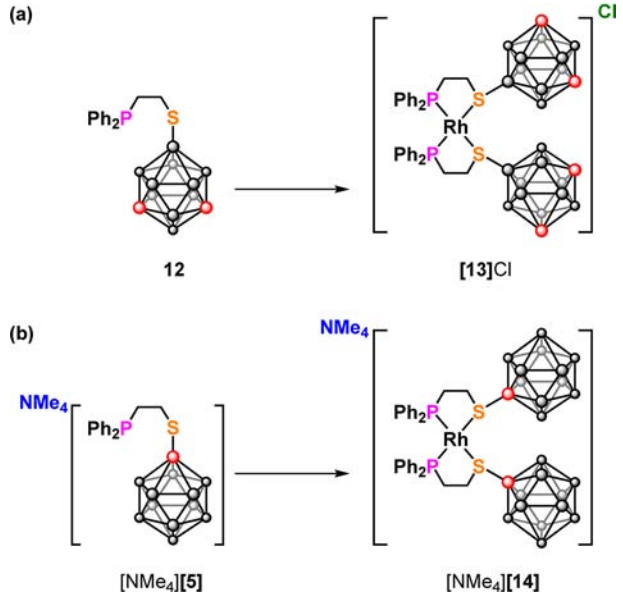


the electrostatic interaction between the noncoordinating carbaborane cage and the dicationic platinum(II) center.

In general, WLA complexes studied thus far are cationic when they are in their fully chelated forms, and usually exist as salts of noncoordinating anions. The new platinum and palladium complexes, ***cis*-4** and ***cis*-8**, respectively, are neutral zwitterionic species and thus represent a novel class of WLA complex in which, effectively, the noncoordinating anion is incorporated intimately into the hemilabile ligand. The generation of *anionic* WLA complexes using anionic ligands is an interesting concept, particularly because such complexes are isoelectronic and isostructural with regular WLA complexes, yet possess the opposite charge. This would raise the possibility of synthesizing a salt in which both the cation and the anion are isostructural WLA complexes. Such salts, in which the anion and cation are large, rigid, and isostructural, are interesting from the perspective of crystal packing. Furthermore, the exteriors of fully chelated WLA complexes are rather greasy, have no localization of charge on their surfaces, and present no coordinating functional groups. In this case, would packing be dictated by charge or by molecular shape?

Thus, the rhodium(I) complexes [*cis*-Rh($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$}-κ^2)$_2$]Cl ([**13**]Cl) and NMe_4[*cis*-Rh-($Ph_2PCH_2CH_2S$-{1-*closo*-$CB_{11}H_{11}$}-κ^2)$_2$] ([NMe_4][**14**]) were synthesized via modifications of published procedures (Scheme 4).[17] [**13**]**Cl** was synthesized via the reaction between $[Rh(coe)Cl]_2$ and {9-($Ph_2PCH_2CH_2S$)-*closo*-1,7-$C_2B_{10}H_{11}$} (**12**) in dichloromethane at room temperature [(coe) = cyclooctene]. A single doublet at δ +66.2 ppm ($^1J_{P-Rh}$ = 167 Hz) is observed in the $^{31}P\{^1H\}$ NMR spectrum, indicating that, in solution, [**13**]Cl exists as a fully chelated species with an outer-sphere chloride ion. In the case of [NMe_4][**14**], the reaction between $[Rh(coe)Cl]_2$ and [NMe_4][**3**] in dichloromethane resulted in the precipitation of [NMe_4]Cl, leaving compound [NMe_4][**14**] in solution. In a similar fashion to the cationic complex $[\mathbf{13}]^+$, anion $[\mathbf{14}]^-$ gives rise to a single doublet at $\delta(^{31}P)$ +62.3 ppm ($^1J_{P-Rh}$ = 166 Hz). This suggests that the two species have similar solution-phase structures. In both cases, no other phosphorus-containing species were observed during the course of the reactions. In the solid state, cation $[\mathbf{13}]^+$ and anion $[\mathbf{14}]^-$ are essentially isostructural, as illustrated in Figure 4. The extended crystal structures of $[\mathbf{13}]^+$, which crystallizes in the $P\bar{1}$ space group, and $[\mathbf{14}]^-$, which crystallizes in the $C2/c$ space group, are dissimilar. This is expected, and is due to the differences in shape and size of the counterion (i.e., chloride and tetramethylammonium for

Scheme 4. Synthesis of Rhodium(I) Complexes [13]Cl and [NMe_4][14][a]



[a]Reaction conditions for (a) and (b): $[Rh(coe)Cl]_2$, CH_2Cl_2, rt. [(coe) = cyclooctene]. Gray circles represent B or B–H vertices. Red circles represent C or C–H vertices.

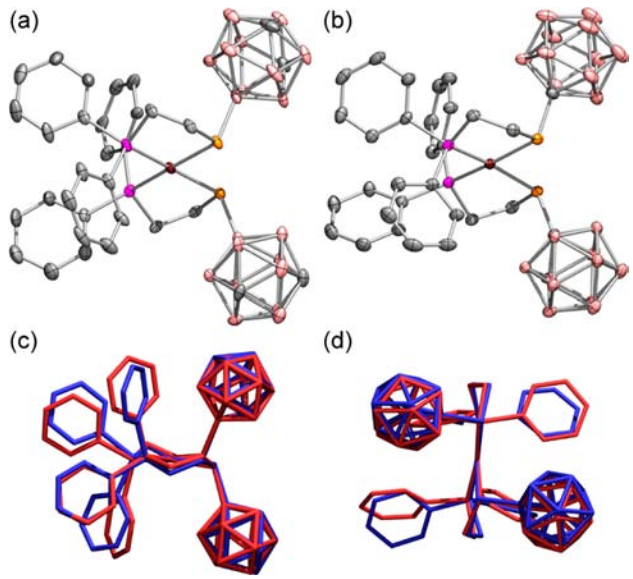


Figure 4. (a) ORTEP-type representation of the crystallographically determined molecular structure of complex cation $[\mathbf{13}]^+$ in its chloride salt. Thermal ellipsoids are shown at 30% probability. (b) ORTEP-type representation of the crystallographically determined molecular structure of complex anion $[\mathbf{14}]^-$ in its $[NEt_4]^+$ salt. Thermal ellipsoids are shown at 50% probability. (c) and (d) Approximately perpendicular views of the superposition of the molecular structures of $[\mathbf{13}]^+$ (blue) and $[\mathbf{14}]^-$ (red). In all cases, hydrogen atoms and counterions are omitted for clarity. Atom color code: Rh = brown; C = gray; B = pink; P = magenta; S = orange.

$[\mathbf{13}]^+$ and anion $[\mathbf{14}]^-$, respectively) and the occlusion of different solvents of crystallization.

Despite their size and complexity, $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$ are essentially isoelectronic. Furthermore, $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$ are almost isoprotonic in that they contain 448 and 446 protons,

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respectively. Conceptually, $[\mathbf{14}]^-$ may be generated simply from $[\mathbf{13}]^+$ via the removal of two protons and the redistribution of two protons: a proton is removed from the nucleus of a carbon atom in each of the two carbaborane cages, thus creating two boron atoms. In each cage, a proton is then 'transferred' from the remaining carbon atom to the boron atom connected to the sulfur, thus swapping the identities of these atoms. Ions $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$ can be regarded as WLA analogues of the potassium cation and the chloride anion, respectively. These species are also isoelectronic and differ only by the number of protons in their nuclei. However, whereas the ionic radii of K^+ is ca. 27% smaller than Cl^-, the molecular shapes and volumes of $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$ are essentially identical.

When methanolic solutions of [13]Cl and $[NMe_4][\mathbf{14}]$ are combined, immediate precipitation of a yellow solid occurs. The $^{31}P\{^1H\}$ NMR spectrum of a solution of the solid in CD_2Cl_2 is essentially a superposition of the spectra of $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$, and exhibits two doublets of approximately equal intensity at δ +66.2 ppm ($^1J_{P-Rh}$ = 166 Hz) and δ +61.9 ppm ($^1J_{P-Rh}$ = 166 Hz). Similarly, the $^1H\{^{11}B\}$ spectrum is a superposition of the spectra of the constituent WLA ions in a 1:1 ratio. Importantly, there is no signal corresponding to the tetramethylammonium ion, and no evidence of ligand exchange between the two species. These analyses suggest that the yellow solid is the complex salt $[\mathbf{13}][\mathbf{14}]$. Diffusion of ether into a solution of $[\mathbf{13}][\mathbf{14}]$ in dichloromethane resulted in the growth of single crystals. Single-crystal X-ray diffraction analysis subsequently revealed the structure of $[\mathbf{13}][\mathbf{14}]$ (Figure 5), which is described in detail below. High-resolution mass-spectrometry experiments on the single crystal that was used for diffraction revealed that both $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$ were present. The salt $[\mathbf{13}][\mathbf{14}]$ crystallizes in the space group $C2/c$ with *three* complexes in the asymmetric unit, and Z = 8. In terms of bond lengths, angles, and molecular conformation, the three complexes are essentially identical. One of the most salient features of the crystal structure is that the carbaborane cages are disordered. In each of the six unique carbaborane cages, atoms 1, 7, and 9 were refined with equal B/C occupancy. The presence of three complexes in the asymmetric unit is interesting because, on first inspection, this seems incompatible with a system that contains only a cation and an anion. However, considering the great similarity in structure between $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$, and assuming the molecular shape defines the crystal packing and symmetry, it is reasonable that $[\mathbf{13}]^+$ and $[\mathbf{14}]^-$ can occupy each of the three independent sites within the crystal lattice with equal probability. The absence of observable cation−anion ordering may be explained in a number of ways: (a) The ions may be ordered over short length scales, but the crystal may be partitioned into larger domains where the lattice spaces are occupied with the opposite ions. (b) Order may be present along certain axes, for example, in chain-like or sheet-like motifs throughout the crystal, yet the relationship between ions in adjacent chains or sheets may be random. (c) Because of the large size of the ions, and the delocalization and shielding of charge, there may be no local cation−anion ordering.

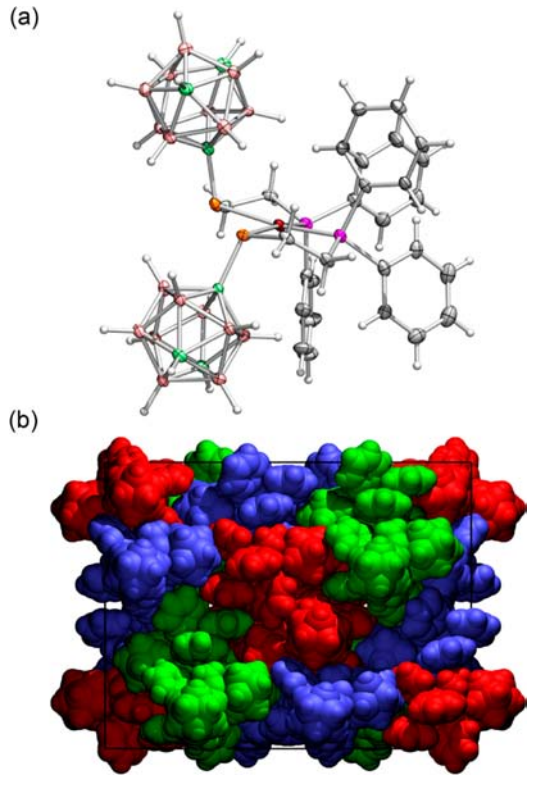

Figure 5. Representations of the crystal structure of $[\mathbf{13}][\mathbf{14}]$. (a) ORTEP-type representation of the molecular structure of a single complex in the asymmetric unit. Thermal ellipsoids drawn at 50% probability. Atom color code: Rh = brown; C = gray; B = pink; B/C = green; P = magenta; S = orange. (b) Space-filling representation of the unit cell viewed along the *c* axis. Blue, green, and red represent the three independent complexes in the asymmetric unit.

CONCLUSION

In previous work, we have found that within the framework of the Weak-Link Approach, the chelating strength of the hemilabile ligand is of critical importance in the formation of architecturally sophisticated supramolecular structures. As mentioned in the Introduction, a recent development has been the utilization of icosahedral dicarbaboranes in the synthesis of either very weakly or strongly chelating hemilabile ligands. We have taken advantage of properties unique to polyhedral boron-containing clusters, and used a conceptual vertex exchange to produce an *anionic* monocarbaborane-based hemilabile ligand with essentially identical structure and reactivity to dicarbaborane-based ligands. Using simple reactivity-based arguments and Mulliken population analyses, one would expect these anionic ligands, which are functionalized at the carbon vertex, to behave as weak chelators similar to, for example, phenyl thioether-based ligands. However, the anionic ligand has a similar chelating strength to very strongly binding ligands based on dicarbaboranes that are functionalized at a boron vertex, as determined via the measurement of chloride association constants. Thus, it has been shown that, in addition to the use of simple electron-withdrawing and electron-donating substituents, *charge* can be used to greatly influence the binding strength of a ligand. More generally, the charge-based modification of ligand coordination strength has great potential in the fine-tuning of the reactivity of catalytic systems.[24]

Another intriguing aspect of this work is formation of the novel anionic WLA complex $[\mathbf{14}]^-$ via the reaction between two anionic hemilabile ligands and rhodium(I). Thus, it is possible to synthesize and crystallographically characterize an unusual salt in which the anionic WLA complex acts as the noncoordinating anion of an isostructural, cationic WLA complex. Because of the great similarity in shape and size

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between the anion and cation, they occupy the same sites within the crystal lattice, thus making it impossible to distinguish them crystallographically. Examples of salts with isostructural, isoelectronic molecular ions are very rare,[25] as these species are often chemically incompatible with one another. The incorporation of anionic, noncoordinating moieties into functional ligands may also be of great importance in chemistry that utilizes cationic metal complexes, as it will eliminate the need for separate, noncoordinating counteranions, for example, in the area of alkene polymerization catalysis.[26] Along these lines, we are currently investigating the use of anionic boron-functionalized monocarbaboranes as exceedingly electron-rich ligands, and pursuing the incorporation of anionic monocarbaboranes into other ligand frameworks to produce zwitterionic 'charge-compensated' metal complexes.

EXPERIMENTAL SECTION

General Methods/Instrument Details. The syntheses of platinum(II) complexes and all subsequent manipulations were done under ambient conditions. Rhodium(I) complexes were prepared and manipulated under an atmosphere of dry nitrogen in a Vacuum Atmospheres glovebox. All solvents were anhydrous grade, purchased from Sigma-Aldrich, and either used as received or dried using a Grubbs-type solvent system (J. C. Meyer). Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Compounds **6**$[BF_4]_2$ and **12** were prepared according to literature procedures or adaptations thereof.[19] All other chemicals were purchased from Aldrich Chemical Co. and were used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^{1}H and ^{1}H{^{11}B} NMR spectra were referenced internally to residual protons in the deuterated solvents (acetone-d_6 = δ 2.05; acetonitrile-d_3 = δ 1.94; dichloromethane-d_2 = δ 5.32; *N*,*N*-dimethylformamide-d_7 = δ 2.92). ^{13}C{^{1}H} NMR spectra were referenced internally to the solvent signal (acetone-d_6 = δ 29.92; acetonitrile-d_3 = δ 1.32; dichloromethane-d_2 = δ 54.00). ^{31}P and ^{31}P{^{1}H} NMR spectra were referenced to an external 85% H_3PO_4 standard (δ 0), ^{19}F{^{1}H} NMR spectra were referenced an external $CFCl_3$/$CDCl_3$ standard (δ 0), and ^{11}B and ^{11}B{^{1}H} NMR spectra were referenced to an external BF_3·OEt_2 standard (δ 0). The ^{13}C{^{1}H} NMR spectra of the Pt(II), Pd(II), and Rh(I) complexes were uninformative. Presumably the signals are multiply split and broadened by the restricted fluxionality of the molecule; this is often observed in complexes of this type. Elemental analyses were performed by Intertek Pharmaceutical Services, Whitehouse, NJ. Electrospray ionization (ESI) mass spectra were recorded on an Agilent 6120 LC−TOF instrument.

[NEt$_4$]$_2$[(1-S-*closo*-1-CB$_{11}$H$_{11}$)$_2$] ([NEt$_4$]$_2$[1]. A solution of *n*-BuLi in hexanes (1.6 M, 29.5 mL, 47.2 mmol) was added to a solution of [Me_3NH][*closo*-1-$CB_{11}H_{12}$] (4.00 g, 19.7 mmol) over 45 min, and the resulting solution was stirred at room temperature for 1 h. With vigorous stirring, solid sulfur (884 mg, 27.6 mmol) was added in one portion and the mixture was stirred for 16 h at 55 °C. Aqueous 5% HCl (100 mL) was added cautiously, resulting in a slight exotherm, followed by diethyl ether (120 mL). The layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 100 mL). The ethereal layers were combined and concentrated to ca. 30 mL under reduced pressure. H_2O (100 mL) was added to the ether, and the mixture was concentrated under reduced pressure (55 °C, 40 mbar) to give a brown solution with a small amount of suspended black solid. The solution was filtered, and the filtrate was treated with a solution of [NEt_4]Cl (4.0 g) in H_2O (50 mL). A dense, pale brown solid precipitated. The mixture was filtered through a glass frit, and the retentate was washed with copious H_2O. The retentate was washed through the frit with acetone (ca. 100 mL), and H_2O (5 mL) was added to the resulting brown solution. The acetone was removed from the solution under reduced pressure to give a brown crystalline solid in a small volume of H_2O. The solid was isolated via filtration and dried briefly on the frit (6.8 g). A portion of the crystalline solid (3.4 g) was dissolved in a mixture of acetonitrile (100 mL) and H_2O (20 mL). With stirring, iodine (600 mg) was added in small portions until all the thiol had been oxidized (ca. 4 h), as determined using ^{11}B{^{1}H} NMR spectroscopy. H_2O (100 mL) was added to the solution, resulting in the precipitation of a solid. A solution of potassium hydroxide (0.5 g) in H_2O (10 mL) was then added, decolorizing the solution. The mixture was filtered through a glass frit, and the retentate was washed with H_2O (2 × 100 mL). The solid was subject to column chromatography on silica (ca. 700 mL) using a 4:1 mixture of dichloromethane and acetonitrile. [NEt_4][*closo*-1-$CB_{11}H_{12}$] eluted first, followed by the disulfide. Fractions that contained the disulfide were combined and concentrated to a volume of ca. 5 mL. H_2O (2 mL) was added, and the remainder of the acetonitrile was removed under reduced pressure to give the disulfide as a white crystalline solid (2.2 g, 3.61 mmol, 73%). The remaining 3.4 g portion of crude product was treated in an identical fashion. ^{1}H{^{11}B} NMR (400 MHz, acetone-d_6) δ 1.41 (tt, $^3J_{H-H}$ = 7.2 Hz, $^2J_{H-N}$ = 1.4 Hz, 12H, NCH_2CH_3) (1H, B−*H*), 1.59 (6H, B−*H*), 2.01 (5H, B−*H*), 3.49 (q, $^3J_{H-H}$ = 7.2 Hz, 8H, NCH_2); ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ 7.84 (NCH_2CH_3), 53.24 (t, $^2J_{C-N}$ = 3.0 Hz, NCH_2), cage C not observed; ^{11}B NMR (128 MHz, acetone-d_6) δ −12.3 (d, $^1J_{B-H}$ = 144 Hz, 10B), −8.1 (d, $^1J_{B-H}$ = 136 Hz, 1B). Anal. Calcd for $C_5H_{24}B_4NS$: C 24.09, H 9.71, N 5.62. Found: C 24.74, H 9.31, N 5.40; HRMS (ESI−) *m*/*z* Calcd for [($C_2H_{22}B_{22}S_2$)($C_8H_{20}N$)]$^-$: 478.4965. Found: 478.4981.

[NMe$_4$][1-SH-*closo*-1-CB$_{11}$H$_{11}$] ([NMe$_4$][2]). Compound [NEt_4]$_2$[**1**] (1.04 g, 1.71 mmol) was stirred vigorously in a mixture of diethyl ether (70 mL) and aqueous 10% HCl (70 mL) for 1 h. The mixture was transferred to a separating funnel, and the ethereal layer and a yellow oily layer were separated from the aqueous layer. The aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined ethereal extracts and the yellow oily layer were concentrated under reduced pressure to give a yellow oil. To the oil was added acetic acid (40 mL), followed by granular zinc (30−100 mesh, 1.60 g, 24.5 mmol). The mixture was stirred at 70 °C for 16 h. The mixture was cooled to room temperature and filtered through a glass frit. The retentate was washed with acetic acid (10 mL). To the filtrate was added [NMe_4]Cl (560 mg, 5.11 mmol) in H_2O (40 mL), resulting in the precipitation of a white solid. The mixture was filtered through a glass frit, and the retentate was washed with H_2O. The retentate was dissolved in acetone (50 mL) and the resulting solution was concentrated in vacuo to give thiol [NMe_4][**2**] as a white microcrystalline solid (825 mg, 3.31 mmol, 97%). ^{1}H{^{11}B} NMR (400 MHz, CD_3CN) δ 1.42 (1H, B−*H*), 1.51 (5H, B−*H*), 1.92 (5H, B−*H*), 3.08 (12H, NCH_3) 3.36 (ca. 1H, *SH*); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 56.30 (t, $^2J_{C-N}$ = 4.0 Hz, NCH_3), cage C not observed; ^{11}B NMR (128 MHz, CD_3CN) δ −12.2 (d, $^1J_{B-H}$ = 146 Hz, 5B), −11.3 (d, $^1J_{B-H}$ = 158 Hz, 5B), −10.0 (d, $^1J_{B-H}$ = 158 Hz, 1B); Anal. Calcd for $C_{18}H_{62}B_{22}N_2S_2$: C 35.52, H 10.27, N 4.60. Found: C 35.69, H 10.27, N 4.45; HRMS (ESI−) *m*/*z* Calcd for $CH_{12}B_{11}S]^-$: 175.1762. Found: 175.1767.

[PPN][1-SH-*closo*-1-CB$_{11}$H$_{11}$] ([PPN][2]). The [$PPN]^+$ salt of the [1-SH-*closo*-1-$CB_{11}H_{11}]^-$ anion was isolated as follows: [NMe_4][1-SH-*closo*-1-$CB_{11}H_{11}$] (23 mg, 92 μmol) was shaken in a mixture of aqueous 10% HCl (5 mL) and ether (5 mL) in a sealed 20 mL vial. The layers were separated, and the aqueous layer was extracted with ether (3 × 5 mL). The combined ethereal extracts were concentrated under reduced pressure to a volume of ca. 5 mL, and H_2O (10 mL) was added. The remainder of the ether was removed under reduced pressure (40 °C, 50 mbar). To the resulting aqueous solution was added a solution of [PPN]Cl (82 mg, 140 μmol) in H_2O (15 mL). The solid that precipitated was isolated via filtration through a glass frit. The solid was washed with H_2O (100 mL) and dried in vacuo (36 mg, 72 μmol). Yield 80%. HRMS (ESI−) *m*/*z* Calcd for [$CH_{12}B_{11}S]^-$: 175.1762. Found: 175.1772. Crystals suitable for single-crystal X-ray diffraction were grown by layering diethyl ether on top of a solution of [PPN][**2**] (ca. 5 mg) in dichloromethane (ca. 100 μL) in a 5 mm NMR tube.

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[NMe_4][1-($Ph_2PCH_2CH_2S$)-*closo*-1-$CB_{11}H_{11}$] ([NMe_4][3]). [NMe_4][1-SH-*closo*-1-$CB_{11}H_{11}$] (500.0 mg, 2.01 mmol) and (chloroethyl)diphenylphosphine (628 mg, 2.52 mmol) and cesium carbonate (1.31 g, 4.02 mmol) were dissolved in degassed acetonitrile (20 mL), and the mixture was stirred at reflux under nitrogen for 2 h. The mixture was cooled to room temperature and filtered through a glass frit. The retentate was washed with acetonitrile (10 mL). The filtrate was concentrated under reduced pressure to a volume of ca. 2 mL. Diethyl ether (50 mL) was added, resulting in the precipitation of a white solid. The mixture was briefly sonicated and then filtered through a glass frit. The retentate was washed on the frit with diethyl ether (10 mL). The retentate was then suspended in dichloromethane (20 mL), and sonicated for ca. 1 min. The suspension was then filtered through a 0.2 μm PTFE membrane, and the filtrate was concentrated under reduced pressure to give a white solid (927 mg, 86%, containing <4% phosphine oxide by ^{31}P NMR spectroscopy). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.54 (br s, ca. 6H, B−*H*), 1.92 (br s, ca. 5H, B−*H*), 2.26 (m, 4H, CH_2), 2.75 (m, 4H, CH_2), 3.20 (s, 12H, NCH_3), 7.3−7.5 (m, 10H, Ar−*H*); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 28.24 (d, J_{P-H} = 14 Hz, CH_2), 32.87 (d, J_{P-H} = 23 Hz, CH_2), 57.20 (t, J_{C-N} = 4 Hz, NCH_3), 129.09 (d, $^3J_{P-C}$ = 6 Hz), 129.34, 133.22 (d, $^2J_{P-C}$ = 19 Hz); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ −15.95; ^{11}B NMR (CD_2Cl_2, 128 MHz) δ −13.5 (d, $^1J_{B-H}$ = 137 Hz, 10B), −9.7 (d, $^1J_{B-H}$ = 135 Hz, 1B); Anal. Calcd for $C_{19}H_{37}B_{11}NPS$: C 49.45, H 8.08, N 3.04. Found: C 48.69, H 7.26, N 2.65; HRMS (ESI−) *m*/*z* Calcd for [$C_{15}H_{25}B_{11}PS$]$^-$: 387.2525, found: 387.2546.

[*cis*-Pt($Ph_2PCH_2CH_2S$-{1-*closo*-$CB_{11}H_{11}$}-κ^2)$_2$] (*cis*-4). With vigorous stirring, a solution of $PtCl_2$(cod) (121.6 mg, 325.1 μmol) in dichloromethane (6 mL), was added to a solution of compound [NMe_4][**3**] (316 mg, 685 μmol) in dichloromethane (10 mL). A white solid precipitated immediately. The suspension was stirred for 2 h. The volume of the dichloromethane was reduced to ca. 1 mL under reduced pressure, and diethyl ether (15 mL) was added. After stirring for 15 min, the mixture was filtered. The retentate was washed with diethyl ether, and suspended in methanol (15 mL). The suspension was sonicated and then stirred for 4 h at room temperature. The mixture was filtered, and the white retentate was washed on the frit with methanol (10 mL). The mass of retentate (^{31}P{^{1}H} NMR spectroscopy in DMF-d_7 revealed a ca. 4:1 mixture of *cis* and *trans* species) was 300 mg, indicating a 95% yield, based on $PtCl_2$(cod). The retentate was dissolved in DMF (3 mL) and heated at 50 °C for 48 h. *In situ* ^{31}P{^{1}H} NMR spectroscopy revealed complete conversion to the *cis* product. Methanol (20 mL) was added, and the mixture was stirred. Upon standing at room temperature for 24 h, crystalline material precipitated. The mixture was filtered through a glass frit, and the retentate was washed on the frit with methanol (5 mL) and dried in vacuo (240 mg, 247 μmol, 76%). ^{1}H{^{11}B} NMR (400 MHz, DMF-d_7) δ 1.83 (ca. 5H, B−*H*), 1.98 (ca. 1H, B−*H*), 2.25 (ca. 5H, B−*H*), 2.85 (br m, ca. 2H, CH_2), 3.47 (br m, ca. 4H, CH_2), 3.84 (br m, ca. 2H, CH_2), 7.04 (dd, *J* = 8.0, 12.2 Hz, 4H, Ar−*H*), 7.40 (t, *J* = ca. 7.3 Hz, 4H, Ar−*H*), 7.60 (m, 6H, Ar−*H*), 7.79 (t, *J* = 8.0 Hz, 2H, Ar−*H*), 7.95 (dd, *J* = 7.9, 12.1 Hz, 4H, Ar−*H*); ^{31}P{^{1}H} NMR (162 MHz, DMF-d_7) δ 45.43 (s [d, $^1J_{Pt-P}$ = 3138 Hz]); ^{11}B NMR (128 MHz, DMF-d_7) δ −12.04, −4.89; Anal. Calcd for $C_{30}H_{50}B_{22}P_2PtS_2$: C 37.16, H 5.20. Found: C 36.59, H 5.10; HRMS (ESI−) *m*/*z* Calcd for [$C_{30}H_{50}B_{22}ClP_2S_2Pt$]$^-$: 1005.4358. Found: 1005.4364. Crystals suitable for single-crystal X-ray diffraction were grown by layering diethyl ether on top of a solution of ***cis*-4** (ca. 5 mg) in dimethylformamide (ca. 100 μL) in a 5 mm NMR tube.

[*cis*-Pd($Ph_2PCH_2CH_2S$-{1-*closo*-$CB_{11}H_{11}$}-κ^2)$_2$] (*cis*-8). A solution of $PdCl_2$(cod) (15.6 mg, 54.6 μmol) in dichloromethane (1 mL) was added to a solution of compound [NMe_4][**3**] (52.6 mg) in dichloromethane (4 mL) in a 20 mL vial. The vial was sealed and stirred at room temperature for 1 h. Diethyl ether (10 mL) was added, and the resulting suspension was stirred for 15 min. The mixture was filtered through a glass frit, and the retentate was washed with diethyl ether (10 mL). The retentate was suspended in methanol (10 mL) and the suspension was stirred at room temperature for 4 h. The mixture was filtered, and the yellow retentate was washed with methanol (5 mL) and dried in vacuo (33.4 mg, 37.9 μmol, 70%). Crystals suitable for single-crystal X-ray diffraction were grown by layering diethyl ether on top of a solution of ***cis*-8** (ca. 5 mg) in dimethylformamide (ca. 100 μL) in a 5 mm NMR tube. ^{1}H{^{11}B} NMR (400 MHz, DMF-d_7) δ 1.80 (br s, ca. 5H, B−*H*), 1.95 (br s, ca. 1H, B−*H*), 2.23 (br s, ca. 5H, B−*H*), 3.48 (br, ca. 4H, CH_2), 3.73 (br, ca. 4H, CH_2), 7.0−8.2 (br m, ca. 20H, Ar−*H*); ^{31}P{^{1}H} NMR (162 MHz, DMF-d_7) δ 63.60; ^{11}B NMR (128 MHz, DMF-d_7) δ −12.08 (br, ca. 10B), −5.29 (br, ca. 1B); Anal. Calcd for $C_{30}H_{50}B_{22}P_2PdS_2$: C 40.90, H 5.72. Found: C 40.30, H 5.42; HRMS (ESI−) *m*/*z* Calcd for [$C_{30}H_{50}B_{22}ClP_2PdS_2$]$^-$: 916.3762. Found: 916.3759.

[*cis*-Rh($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$}-κ^2)$_2$]Cl ([13]Cl). The following procedure was conducted in a nitrogen-filled glovebox using degassed solvents. In a 3/4 oz. vial at room temperature, a solution of compound [NMe_4][**3**] (49.9 mg, 128.4 μmol) in dichloromethane (3 mL) was added dropwise to a stirring solution of [Rh(coe)Cl]$_2$ (23.1 mg, 32.2 μmol) in dichloromethane (3 mL). The mixture was stirred for 20 min. Hexanes (17 mL) were added resulting in the precipitation of a yellow solid. The mixture was filtered through a glass frit, and the yellow retentate was washed with hexanes (ca. 5 mL) and dried on the frit (83%, 48.9 mg, 53.4 μmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.4−3.6 (vbr m, 30 H (B−*H*/C−*H*/CH_2) δ 2.46 (br s, ca. 4H), 2.53 (br s, ca. 4H), 3.37 (br s, ca. 10H, B−*H*), 7.18 (t, 8H, Ar−*H*), 7.31 (br m, 12H, Ar−*H*); ^{31}P{^{1}H} (162 MHz, CD_2Cl_2) δ 66.21 (d, $^1J_{Rh-P}$ = 167 Hz]); ^{11}B NMR (128 MHz, CD_2Cl_2) δ −2.2 (s, 1B, *B*−S), −7.2 (d $^1J_{B-H}$ = 149 Hz, 2B), −10.5 (d $^1J_{B-H}$ = 153 Hz, 1B), −13.9 (d $^1J_{B-H}$ = 158 Hz, 4B), −17.6 (d $^1J_{B-H}$ = ca. 206 Hz, 2B); Anal. Calcd for $C_{32}H_{50}B_{20}ClP_2RhS_2{\cdot}0.75(CH_2Cl_2)$: C 40.17, H 5.30. Found: C 40.12, H 3.91; HRMS (ESI+) *m*/*z* Calcd for [$C_{32}H_{50}B_{20}P_2RhS_2$]$^+$: 879.3891. Found: 879.3899. Crystals suitable for single-crystal X-ray diffraction were grown by layering diethyl ether on top of a solution of [**13**]Cl (ca. 5 mg) in dimethylformamide (ca. 100 μL) in a 5 mm NMR tube.

NMe_4[*cis*-Rh($Ph_2PCH_2CH_2S$-{1-*closo*-$CB_{11}H_{11}$}-κ^2)$_2$] ([NMe_4][14]). The following procedure was conducted in a nitrogen-filled glovebox using degassed solvents. In a 3/4 oz. vial, a solution of compound [NMe_4][**3**] (50.0 mg, 108.4 μmol) in dichloromethane (3 mL) was added dropwise to a stirring solution of [Rh(coe)Cl]$_2$ (19.4 mg, 27.0 μmol) in dichloromethane (3 mL). A small quantity of colorless solid precipitated. The mixture was stirred for 15 min, and filtered through a 0.2 μm PTFE membrane. To the filtrate was added hexanes (12 mL), and the milky yellow mixture was allowed to stand overnight at room temperature. Yellow-orange crystalline material precipitated. The mixture was filtered through a glass frit, and the retentate was washed with hexanes (ca. 5 mL) and allowed to dry on the frit (46%, 24.0 mg). ^{1}H{^{11}B} NMR (400 MHz, DMF-d_7) δ 1.75 (br s, ca. 10H, B−*H*), 1.84 (br s, ca. 2H, B−*H*), 2.31 (br s, ca. 10H, B−*H*), 2.7−2.9 (br, ca. 4H, CH_2), 3.2−3.6 (br, ca. 4H, CH_2), 3.39 (s, ca. 12 H, NCH_3), 6.87 (br s, 4H), 7.11 (br s, 4H), 7.38 (br t, *J* = 44 Hz, 8H), 8.07 (br s, 4H); ^{31}P{^{1}H} NMR (162 MHz, DMF-d_7) δ 62.30 (d, $^1J_{Rh-P}$ = 167 Hz]); ^{11}B NMR (128 MHz, DMF-d_7) δ −13.06 (d, $^1J_{B-H}$ = 110 Hz, 10B), −6.93 (1B); Anal. Calcd for $C_{34}H_{62}B_{22}NP_2RhS_2$: C 42.91, H 6.57, N 1.47; found: C 42.28, H 6.39, N 1.40; HRMS (ESI−) Calcd for [$C_{30}H_{50}B_{22}P_2RhS_2$]$^-$: 877.4077. Found: 877.4097. Crystals suitable for single-crystal X-ray diffraction were grown by layering diethyl ether on top of a solution of [NMe_4][**14**] (ca. 5 mg) in dimethylformamide (ca. 100 μL) in a 5 mm NMR tube.

[*cis*-Rh($Ph_2PCH_2CH_2S$-{9-*closo*-1,7-$C_2B_{10}H_{11}$}-κ^2)$_2$][*cis*-Rh($Ph_2PCH_2CH_2S$-{1-*closo*-$CB_{11}H_{11}$}-κ^2)$_2$] ([13][14]). The following procedure was conducted in a nitrogen-filled glovebox using degassed solvents. A solution of [**13**]Cl (5.2 mg, 5.5 μmol) in methanol (1 mL) was added to a stirring solution of [NMe_4][**14**] (5.0 mg, 5.5 μmol) in methanol. A yellow solid precipitated immediately. The mixture was filtered through a glass frit and the retentate was washed with methanol (ca. 0.5 mL) and dried on the frit (6.0 mg, 3.5 μmol, 64%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ ca. 1−3.5 (v br, ca. 42H, B−*H*), 1.80 (br m, ca. 4H, CH_2), 2.41 (br m, ca. 4H, CH_2), 2.54 (br s, ca. 4H, CH_2), 2.87 (br m, ca. 4H, CH_2), 3.23 (br, m 4H, cage-C*H*), 6.85 (br m, 4H, Ar−*H*), 6.98 (br m, 4H, Ar−*H*), 7.16−7.35 (br m, 28H, Ar−*H*), 7.97 (br m, 4H, Ar−*H*); ^{31}P{^{1}H} (162 MHz, CD_2Cl_2) δ 66.23 (d, $^1J_{Rh-P}$ = 166 Hz]), δ 61.86 (d, $^1J_{Rh-P}$ = 166 Hz]). HRMS (ESI+) *m*/*z*

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Calcd for $[C_{32}H_{50}B_{20}P_2RhS_2]^+$: 879.3891, found: 879.3899; HRMS (ESI−) m/z Calcd for $[C_{30}H_{50}B_{22}P_2RhS_2]^-$: 877.4077. Found: 877.4097. Crystals suitable for single-crystal X-ray diffraction were grown by layering hexanes on top of a solution of [**13**][**14**] (ca. 2 mg) in dichloromethane (ca. 100 μL) in a 5 mm NMR tube.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for all compounds. Crystallographic data for compound [PPN][**2**], and complexes ***cis*-4**, ***cis*-8**, [**13**]Cl, [NMe_4][**14**], and [**13**][**14**], tabulated and in cif format. Computational details, measurement of K_c. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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