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Anionic and zwitterionic carboranyl N-heterocyclic carbene Au(I) complexes†

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The syntheses of the first carboranyl N-heterocyclic carbene complexes with transition metals are reported. Both unsymmetrical mono-anionic and symmetrical dianionic NHCs readily react with ClAuSMe_2 to afford unusual zwitterionic and anionic Au(I) dimethyl sulfide adducts. The compounds are characterized by NMR, mass spectrometry, and single crystal X-ray diffraction studies. Percent buried volume ($\%V_{\text{bur}}$) calculations indicate that replacement of an adamantyl group by a hydride substituted icosahedral carborane anion results in a 3.7% increase in $\%V_{\text{bur}}$.

Ligands are usually designed with pendant alkyl and aryl substituents that can be utilized to manipulate the behavior of transition metal complexes. An alternative to hydrocarbon ligand R-groups are 3-dimensionally aromatic icosahedral carboranes.¹ The typical carboranes used in ligand design are derivatives of the icosahedral dicarbaboranes ($\text{H}_2\text{C}_2\text{B}_{10}\text{H}_{10}$).^{1b} Due to its facile synthesis from decaborane,² the *ortho*-carborane isomer is the most common cluster fragment implemented for these purposes. While this cluster has many intriguing properties, such as a large spherical steric profile, as well as the ability to form H–H hydrogen bonds,^{1b} it displays chemical reactivity that might be problematic for catalysis, such as facile B–H cyclometalation³ and cluster opening reactions. The latter reactions have been implemented by Teixidor and Viñas to design anionic ligands, featuring *nido*-cluster substituents.^{1b,4}

Compared to neutral C_2B_{10} clusters, the isoelectronic anionic carba-*closo*-dodecaborate cluster [1] ($\text{HCB}_{11}\text{H}_{11}^-$)^{1c} (Fig. 1) and its derivatives do not undergo cluster opening reactions and are more resistant to B–H cyclometalation.⁵ In addition, when polyhalogenated these clusters are among the

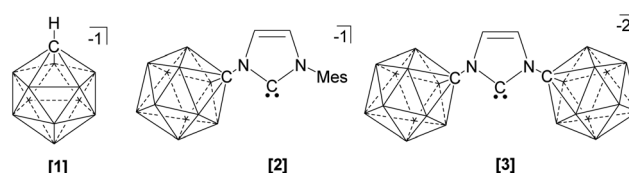


Fig. 1 The carba-*closo*-dodecaborate anion [1] ($\text{HCB}_{11}\text{H}_{11}^-$) (left). Monoanionic unsymmetrical carboranyl NHC [2] (center) and symmetrical dianionic NHC [3] (right). Unlabeled cluster vertices = B–H.

weakest coordinating and robust counter anions known. These properties have been utilized to prepare isolable versions of highly reactive cations⁶ and superior systems for silylium catalysis.⁷ Furthermore, in contrast to C functionalized *o*-carborane, [1] acts as a strong electron donor, similar to an alkyl group.^{8a}

We recently reported the first utilization of cluster [1] and its derivatives as ligand substituents for transition metal-based catalysts.⁸ Notably, it was shown that when complexed to Au(I) a phosphine bearing a perchlorinated carborane anion substituent forms an exceptionally active catalyst for the hydroamination of alkynes.^{8b} In addition, this system is a single component zwitterionic species that does not require the addition of an acid or Ag initiator. As an extension of this work we have reported the synthesis of symmetrical and unsymmetrical anionic carboranyl N-heterocyclic carbenes⁹ (NHCs) [2]^{10a} and [3]^{10b} (Fig. 1). Depending on the base employed to generate the NHC, such ligands can be prepared as either Li^+ , Na^+ , or K^+ salts.

Having a van der Waals volume^{1h} of approximately $141\text{--}148 \text{ \AA}^3 \text{ cm}^{-3}$, [1] is an exceptionally large ligand substituent. Coupling these anions to the wing-tips of NHCs should direct the steric bulk of the substituent into the coordination sphere of the ensuing metal center. Considering the size of the anion and the geometry imposed by the rigid NHC 5-membered ring framework, one might ask are these ligands too large to effectively bind transition metals? Herein we show that both carboranyl NHCs [2] and [3] will readily bind

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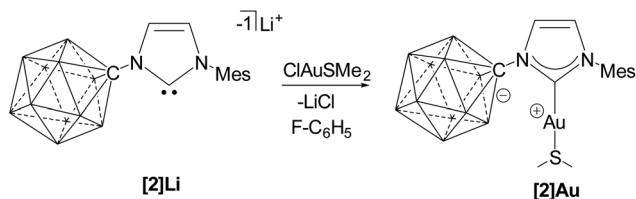


Fig. 2 The unsymmetrical carboranyl NHC Li salt **[2]Li** reacts with ClAuSMe_2 to form the corresponding zwitterionic gold complex **[2]Au**. Unlabelled vertices = B–H.

transition metals, through the preparation of unusual zwitterionic and anionic Au(i) carbene complexes. These compounds are thoroughly characterized and their structural parameters elucidated by single crystal X-ray diffraction studies as well as percent buried volume ($\%V_{\text{bur}}$)¹¹ calculations.

To begin this investigation we chose to target Au(i) complexes, since they nearly always adopt dicoordinate, linear geometries that are accommodating to large ligands. Moreover, Au(i) complexes are usually thermally stable and easy to handle. This approach was borne out *via* reacting ClAuSMe_2 with the lithium carbene **[2]Li** in a 1:1 ratio with $\text{F-C}_6\text{H}_5$ solvent (Fig. 2). Within minutes a white precipitate of LiCl formed and the solution was analysed by ^{11}B , ^1H , and ^{13}C NMR spectroscopy. The ^{11}B spectrum shows the expected three resonances (1:5:5 ratio) for the C_{5v} symmetric cluster, indicating that the cluster is intact. Analysis of the ^1H spectrum shows the expected downfield shift for the NHC backbone resonances (^1H NMR: **[2]Li** 7.40 and 6.79 ppm; d , $^3J_{\text{H-H}} = 1.5$ Hz; **[2]Au** = 7.71 and 6.83 ppm; d , $^3J_{\text{H-H}} = 2.1$ Hz), suggesting an NHC Au adduct had formed. In addition, the presence of a bound dimethyl sulfide resonance (free $\text{S}(\text{Me})_2$ 2.09 ppm; bound $\text{S}(\text{Me})_2$ 2.60 ppm) is consistent with the formation of the zwitterionic gold complex **[2]Au** (Fig. 2). Furthermore, the ^{13}C spectrum clearly shows a downfield resonance at 175.2 ppm for the bound NHC ligand.

Gold zwitterions that retain a dative thioether ligand are rare but have been observed by us,^{8b} as well as Tamm^{12a} and Bourissou,^{12b} when weakly coordinating anions are built into ligand scaffolds. The composition of **2[Au]** was confirmed by high resolution mass spectrometry and a single crystal X-ray diffraction study (Fig. 3). In the solid-state the complex displays a distorted linear geometry (C1-Au-S angle = 171.7°), which is likely due to the asymmetry of the carboranyl NHC ligand. Interestingly, the carborane anion is canted away from the cationic gold center, which highlights its weakly coordinating nature. The closest B–H approach to the gold center is 2.81 Å, which is in range for a van der Waals contact but outside the range for cluster B–H agostic bonding.^{5a,13} In turn, the mesityl ring is tilted toward the gold center, suggesting a cation π interaction (Au-C3 distance = 3.168 Å). The NHC Au bond length (2.007(2) Å) falls in the typical range for NHC Au(i) complexes.⁹ The N-heterocyclic core bond lengths are also in the expected range for standard imidazolylidene Au complexes (bond lengths in Å; $\text{C1-N1} = 1.349(3)$, $\text{C1-N2} =$

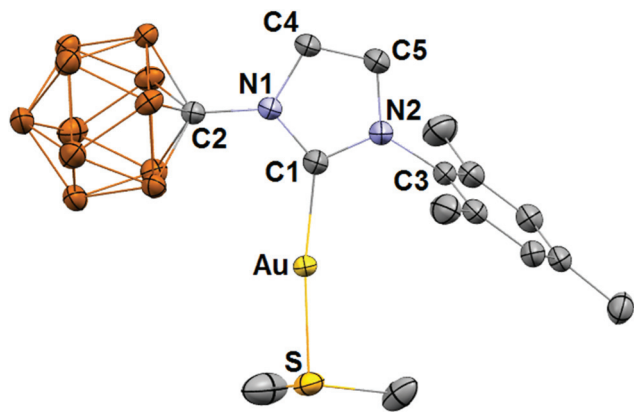


Fig. 3 Solid state structure of **[2]Au**. Hydrogens and a THF solvent molecule of crystallization are omitted for clarity. Color code: C = grey, B = brown, N = blue, Au = yellow, S = Orange.

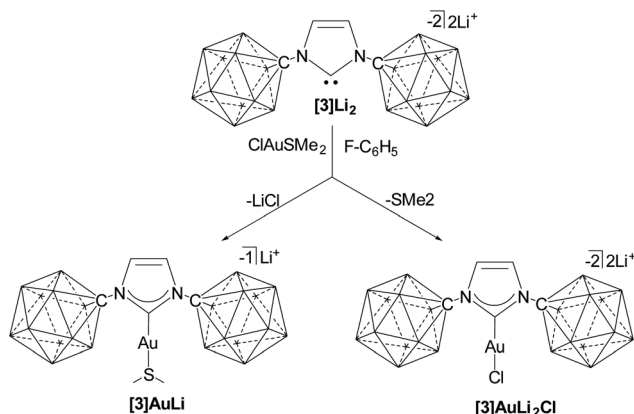


Fig. 4 Reaction of dianionic NHC **[3]Li₂** with ClAuSMe_2 yields two distinct species **[3]AuLi** and **[3]AuLi₂Cl**, which can be easily separated by their differences in solubility. Unlabelled vertices = B–H.

1.353(3), $\text{N1-C4} = 1.399(3)$, $\text{N2-C5} = 1.382(3)$, $\text{C4-C5} = 1.342(3)$).⁹ In addition, the dative SMe_2 bond length to Au(i) (2.2971(12)) is similar to that reported for other zwitterionic gold thio ether complexes (2.3026–2.456 Å).^{8b,12}

We next turned our attention to the synthesis of an analogous monoanionic complex **[3]AuLi**, featuring the symmetrical dianionic carboranyl NHC ligand **3**. Thus, ClAuSMe_2 was reacted with the lithium carbene **[3]Li₂** in a 1:1 ratio with $\text{F-C}_6\text{H}_5$ solvent (Fig. 4). Copious amounts of oily precipitate rapidly formed in the reaction. Filtration and subsequent concentration of the solution under high vacuum yields the monoanionic Au(i) complex **[3]AuLi** in 22% yield and high purity. The identity of **[3]AuLi** was corroborated by multinuclear NMR spectroscopy. The ^{11}B spectrum shows the expected three resonances (1:5:5 ratio) for the cluster. The ^1H NMR spectrum displays a single downfield shifted resonance for the NHC backbone (^1H NMR: **[3]Li₂** = 6.91; **[3]AuLi** = 7.34 ppm) as well as a methyl group corresponding to bound dimethyl sulfide and four THF molecules coordinated to the lithium counter

cation. The ^{13}C spectrum shows a downfield resonance at 174.3 ppm for the bound NHC ligand.

Puzzled by the low yield of this reaction we postulated that perhaps a distinct species, which is not soluble in $\text{F-C}_6\text{H}_5$, precipitated from the reaction and lowered the isolated yield of $[3]\text{AuLi}$. Indeed, analysis of the residue by multinuclear NMR reveals the formation of a distinct carbene complex that lacks a dimethyl sulfide ligand. The low solubility of this compound in $\text{F-C}_6\text{H}_5$ suggests the formation of a more ionic species that we tentatively assign as the dianionic Au(I) complex $[3]\text{AuLi}_2\text{Cl}$ (Fig. 4, bottom right). This assignment is also corroborated by high resolution mass spectrometry that shows a molecular ion peak corresponding to $[3]\text{AuCl}^{-2}$. Furthermore, $[3]\text{AuLi}_2\text{Cl}$ can be independently synthesized in quantitative yield by performing the analogous reaction in THF solvent instead of $\text{F-C}_6\text{H}_5$. In THF, LiCl is completely soluble and therefore salt metathesis does not occur; instead dimethyl sulfide is liberated. In addition, $[3]\text{AuLi}_2\text{Cl}$ can be synthesised by reacting $[3]\text{AuLi}$ with a solution of LiCl in THF, which shows the substitutional lability of dimethyl sulfide in the presence of dissolved Cl^- ions. The lability of the dimethyl sulfide ligand of $[3]\text{AuLi}$ compared to $[2]\text{Au}$ is perhaps due to the enhanced steric bulk of the symmetrical dicarboranyl NHC ligand $[3]$.

Seeking data for a comparison with $[2]\text{Au}$ we performed a single crystal X-ray diffraction study of monoanionic complex $[3]\text{AuLi}$ (Fig. 5). In contrast to $[2]\text{Au}$, $[3]\text{AuLi}$ is perfectly linear in the solid-state (C1-Au-S angle = 179.7°), which is likely due to the symmetric orientation of the two carborane anions about the gold center. The closest B-H contacts with the gold center are 2.61 and 2.57 Å, which are in range for B-H agostic bonding;^{5a} however, we see no evidence for this kind of interaction by solution NMR studies. Therefore, the close proximity of the carborane anions is likely due to steric effects. The NHC Au bond length (2.030(3) Å) of $[3]\text{AuLi}$ is only slightly elongated compared to $[2]\text{Au}$. The N-heterocyclic core bond lengths as well as the Au-SMe₂ (bond lengths in Å; C1-N1 =

1.349(3), C1-N2 = 1.353(3), N1-C4 = 1.399(3), N2-C5 = 1.382(3), C4-C5 = 1.342(3); Au-S = 2.2907(10)) are also similar to $[2]\text{Au}$.

To gain further insight into the steric parameters that define carboranyl NHC ligands $[2]$ and $[3]$ percent buried volume ($\%V_{\text{bur}}$) calculations were performed.¹¹ We found that ligands $[2]$ and $[3]$ have $\%V_{\text{bur}}$ volumes of 44.6 and 47.2, respectively. These values are close to the bulkiest known NHCs (51.2 and 47.7).^{11b} While $\%V_{\text{bur}}$ is an effective way to calculate the amount of the ligand periphery occupying the coordination sphere it is a function of substituent conformation. Most of the bulkiest NHCs have somewhat flexible R-groups or contain substituted aromatics that change conformations in solution, giving a range of different $\%V_{\text{bur}}$ values depending on the atomic coordinates utilized. Therefore, the most informative comparison to make is perhaps between Arduengo's diadamantyl substituted NHC⁹ ($\%V_{\text{bur}}$ = 39.8),^{11b} which due to the substituents spherical shape maintains similar $\%V_{\text{bur}}$ regardless of the *N*-adamantyl bond orientation.

Conclusions

This communication shows that carboranyl NHCs $[2]$ and $[3]$ are suitable ligands for transition metals. If we consider $[3]$ as an analogue of Arduengo's carbene we can conclude that replacement of an adamantyl group by a hydrido substituted icosahedral carborane anion results in a $\%V_{\text{bur}}$ increase of 3.7% ($(47.2\%_{[3]} - 39.8\%_{\text{Arduengo's}})/2$). We are currently investigating the use of $[2]\text{Au}$ and $[3]\text{AuLi}$ as single component Au catalysts as well as the possibility of preparing polyhalogenated carboranyl NHCs with even larger steric profiles.

Acknowledgements

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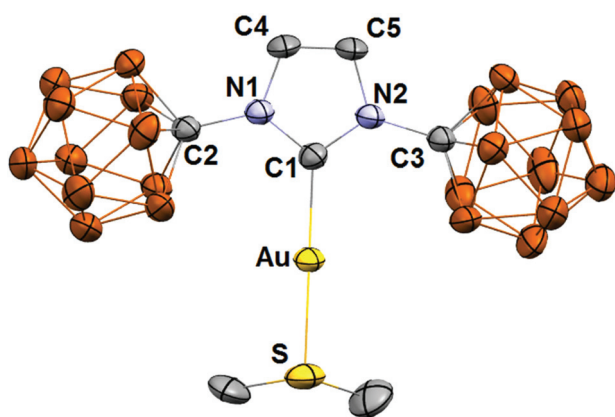


Fig. 5 Solid state structure of $[3]\text{AuLi}$. Hydrogens and Li^+ counter cation tetrahedrally coordinated by four THF molecules omitted for clarity. Color code: C = grey, B = brown, N = blue, Au = yellow, S = orange.

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