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Article

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Strongly Coordinating Ligands to Form Weakly Coordinating yet Functional Organometallic Anions.

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KEYWORDS (Weakly Coordinating Anions, Carborane Anions, Gold Catalysis, Carbocations, Silylium Ions)

ABSTRACT: Weakly coordinating anions (WCAs) are generally tailored to act as spectators with little or no function. Here we describe the implementation of strongly coordinating dianionic carboranyl N-Heterocyclic Carbenes (NHCs) to create organometallic ate complexes of Au(I) that serve both as WCAs and functional catalysts. These organometallic WCAs can be utilized to form both heterobimetallic ($Au(I)^-/Ag(I)^+$; $Au(I)^-/Ir(I)^+$) and organometallic/main group ion pairs ($Au(I)^-/(CPh_3^+$ or $SiEt_3^+$). As the parent unfunctionalized dianionic carboranyl NHC complex **3** is unstable in most solvents when paired with CPh_3^+, novel synthetic methodology was devised to create polyhalogenated carboranyl NHCs, which show superior stability towards electrophilic substitution and cyclometalation chemistry. Additionally, the WCAs containing polyhalogenated carboranyl NHCs are among the most active catalysts reported for the hydroamination of alkynes. This investigation has also produced the first examples of low coordinate Au(III) center with two *cis* accessible coordination sites and the first true dianionic carbene. These studies pave the way for the design of functional ion pairs that have the potential to participate in tandem or cooperative small molecule activation and catalysis.

INTRODUCTION

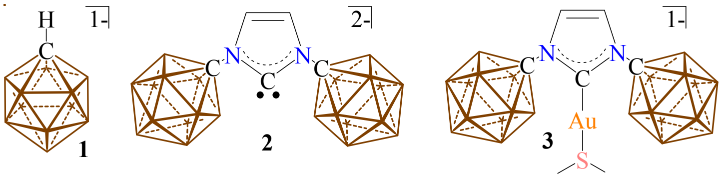


Figure 1. The parent 12-vertex *closo*-carborane anion **1**, its NHC derivative **2**, and its anionic Au(I) complex **3**. Unlabeled vertices = BH.

Weakly coordinating anions (WCAs)[1] are indispensable tools for the study of extremely reactive cationic species, ranging from main group to transition metal compounds. With respect to main group chemistry they have allowed for the isolation of fundamentally important reactive intermediates, such as carbocations and silylium "like" salts,[2-3] and have been utilized to facilitate or catalyze[4] important organic transformations.[5-8] Similarly, in transition metal chemistry WCAs are commonly found as counterions for cationic metal complexes with an unsaturated coordination sphere, which are essential for many homogeneous catalytic processes. In a classical sense, WCAs have little function other than to be spectators for reactive cations, ideally being inert to decomposition. Among the different classes of WCAs, polyhalogenated 12-vertex carborane anions ($[HCB_{11}H_aX_b]^{1-}$; a = 0 or 5 and b = 6 or 11) shine,[9-10] as they are immune to decomposition via electrophilic attack or chemical oxidation even in the presence of the most potent electrophiles and oxidants, as exemplified by the elegant and pioneering work of Reed.[2]

Over the last several years our group has begun to investigate non-classical applications of *closo*-carborane anions **1** (Figure 1).[9, 11] In one embodiment of this approach, we covalently attach the anions to ligand frameworks, such as phosphines[12-15] and N-Heterocyclic Carbenes (NHCs).[16-19] The carborane anions are used as bulky and charged alkyl or aryl surrogates and we have demonstrated the utility of such ligands in catalysis.[13-14, 20-22] The NHC **2** (Figure 1) is technically a dianionic carbenoid[19] as it, and related species,[16, 18] have been isolated as alkali metal complexes. With respect to the NHC **2**, we have only reported a single anionic Au(I) compound **3** and disclosed no reactivity or further synthetic elaboration of this species (Figure 1).[17] One way to view complex **3** is that the entire molecule is in fact a WCA. We envisioned that if **3** behaved as a WCA, perhaps it could also be functional at the Au center. If this were true, then one might be able to use the inherent charge of the strongly coordinating ligand to design complex heterobimetallic, and hybrid organometallic/main group ion pairs that could display interesting chemistry and eventually be utilized as platforms for tandem or cooperative small molecule activation and catalysis. Here we report that in fact **3**, and its polyhalogenated derivatives, *vide infra*, are WCAs that can be used to form heterobimetallic ion pairs, such as Ag^+, Ir^+, and hybrid organometallic/main group ion pairs (e.g. trityl and silylium "like" salts), as well as functional catalysts. Along this journey we also have developed novel synthetic methods to access the first polyhalogenated carboranyl NHCs, isolate the first metal free dianionic NHC and observed an unusual reaction that forms the first low-coordinate Au(III) compound with two *cis* accessible coordination sites.

RESULTS AND DISCUSSION

As salts of Ag^+, CPh_3^+, and SiR_3^+ containing WCAs are the reagents of choice to induce the abstraction of halides (Ag^+ and SiR_3^+) and hydrides/alkides (CPh_3^+) to install WCAs,[1] we decided to see if it were possible to prepare such species with **3** as a counteranion (Figure 2). To synthesize the Ag salt **3[Ag⁺],** we reacted a fluorobenzene (F-C_6H_5) solution of lithium salt **3[Li⁺]** with $AgBF_4$. A precipitate immediately formed which contained solid **3[Ag⁺]** and LiBF4. Washing the precipitate with diethyl ether removes the $LiBF_4$ byproduct as confirmed by the absence of ^{19}F and ^{7}Li resonances in the respective NMR spectra. The structure of the heterobimetallic ion pair **3[Ag⁺]** was unambiguously determined by multinuclear NMR and a single crystal X-ray diffraction study (Figure 2, bottom left). In the solid-state **3[Ag⁺]** forms a dimeric structure where two WCAs **3** are linked primarily via electrostatic interactions between two Ag^+ cations and the carborane cages of the ligands. A single molecule of THF binds each Ag^+ ion, presumably resulting from the liberation of coordinated THF from the Li^+ countercation of **3[Li⁺].**

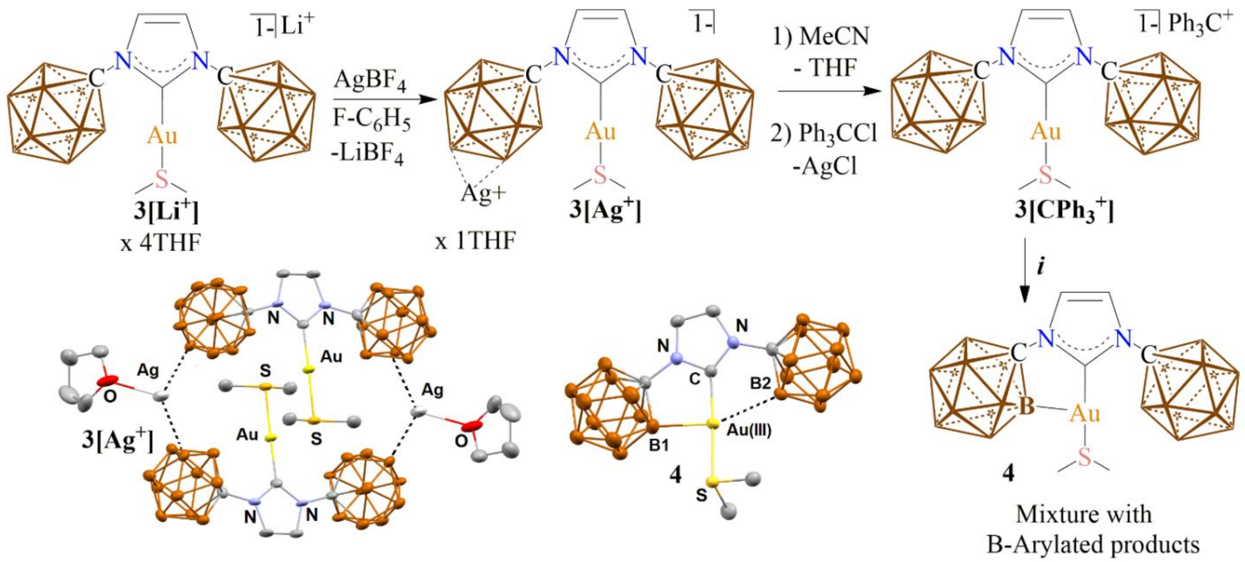


Figure 2. Synthesis of **3[Ag⁺]**, **3[CPh₃⁺],** and the formation of the cyclometalated Au(III) compound **4**. Solid-State structures of **3[Ag⁺]** and **4**. Note: the structure of **3[Ag⁺]** was only of sufficient quality to establish connectivity for an identification. Thermal ellipsoids drawn at the 50% probability level. *i* = CHCl3, CH2Cl2, or F-C_6H_5). Unlabeled grey and brown atoms are carbon and boron, respectively. Unlabeled vertices = BH.

With **3[Ag⁺]** in hand we envisioned utilizing it as a halide scavenger to form the organometallic carbocation ion pair **3[CPh₃⁺]**. When reacting **3[Ag⁺]** with $ClCPh_3$ in acetonitrile rapid salt metathesis was observed, however analysis of the supernatant by ^{1}H NMR revealed the presence of $HCPh_3$ and no resonances for CPh_3^+. We hypothesized that the THF coordinated to **3[Ag⁺]** was acting as a hydride source, quenching the trityl cation. To avoid this decomposition pathway, we first dissolved **3[Ag⁺]** in MeCN to displace the bound THF and concentrated the mixture to dryness, effectively removing the THF as indicated by ^{1}H NMR. Subsequent halide abstraction from ClCPh3 cleanly afforded the trityl salt **3[CPh₃⁺]**, as indicated by multinuclear NMR analysis. Unfortunately**,** we observed that **3[CPh₃⁺]** is only stable in acetonitrile solution, which hampers its broad utilization as a reagent to create silylium "like" salts or truly coordinatively unsaturated metal centers, as acetonitrile is a strongly coordinating solvent. Dissolving **3[CPh₃⁺]** in solvents such as dichloromethane, chloroform, or F-C_6H_5 rapidly leads to a complex mixture of products, which are extremely challenging to separate. However, based on characteristic aryl resonances and high resolution mass spectrometry we are able to tentatively assign some of the decomposition products as species arising from the electrophilic arylation of the carborane cage with the trityl cation, a new reaction that we recently reported.[23] In addition, we were able to inconsistently isolate in pure form an extraordinary cyclometalated Au(III) boryl NHC chelate **4**, which was unambiguously identified by multinuclear NMR and a single crystal X-ray diffraction study (Figure 2, bottom right). *Trans* to the boryl ligand a B-H agostic "like" interaction weakly interacts with a Au orbital. Such interactions are well documented from previous studies in our group[15] and others.[24-25] *Cis* to the boryl ligand and B-H interaction is a potentially labile dimethyl sulfide ligand. Complex **4** is special as it is the only known Au(III) compound with two potentially accessible *cis*-binding sites (the orbital where the B-H interaction is and the orbital coordinated by dimethylsulfide). This is important because if practical synthetic methods to cleanly afford species like **4** can be developed it would lead to prototypical Au(III) systems to explore classical d^8 reaction chemistry. While we are not sure of the mechanism of the formation of **4** we can say that we do observe triphenylmethane and electrophilic arylation where trityl liberates a proton.[23] Thus far, all attempts to induce this reaction via hydride abstraction from **3** with external trityl or protic acids have been unsuccessful.

In an effort to develop more stable organometallic trityl salts similar to **3[CPh$_3^+$]** we envisioned that polyhalogenated carboranyl NHCs might be immune to such electrophilic arylation and cyclometalation reactions. Unfortunately, reaction methodology (amine condensation with glyoxyl followed by ring closure with *p*-formaldehyde) analogous to what we previously reported[19] for the synthesis of NHC precursors was not effective with polyhalogenated carboranyl amines (ESI pgs S96-S106). To solve this problem, we thought that it might be possible to directly and selectively hexahalogenate both carborane cages of the previously reported imidazolium anion **5** (Figure 3). Indeed, the imidazolium anion can be selectively brominated or iodinated utilizing Br_2 or ICl, to form **6Br**$_{\mathbf{12}}$ and **6I**$_{\mathbf{12}}$, respectively. While the iodination stops at hexahalogenation at each cluster, likely for steric reasons, the selective hexabromination requires rigorous spectroscopic monitoring as to not over functionalize the clusters. Chlorination leads to an intractable mixture of over halogenated products, which do not converge to the perchlorinated derivative even under forcing conditions. Both **6Br**$_{\mathbf{12}}$ and **6I**$_{\mathbf{12}}$ can be cleanly converted to the corresponding dianionic NHC **7Br**$_{\mathbf{12}}$ and Li carbenoid **7I**$_{\mathbf{12}}$ via reaction with a strong base. The ^{13}C NMR shifts for the dianionic NHC **7Br**$_{\mathbf{12}}$ and the Li carbenoid **7I**$_{\mathbf{12}}$ are shifted downfield by about 20 ppm (**7Br**$_{\mathbf{12}}$ = 222.2; **7I**$_{\mathbf{12}}$ = 220.6) with respect to the previously reported dianionic Li carbenoid **2** (196.9 ppm). The downfield shift of these species relative to **2**, is likely due to the electron withdrawing effects of the halogens. We know that **7Br**$_{\mathbf{12}}$ is a metal-free dianionic NHC as its structure was unambiguously determined by a single crystal X-ray diffraction study. In contrast, data collection from a poor quality crystal of **7I**$_{\mathbf{12}}$ suggests that the iodinated carbene **7I**$_{\mathbf{12}}$ is coordinated to Li$^+$. The difference in coordination chemistry of these ligands with Li$^+$ is likely due to inductive effects of the more electron withdrawing Br atoms, which temper the nucleophilicity of the NHC to some extent.

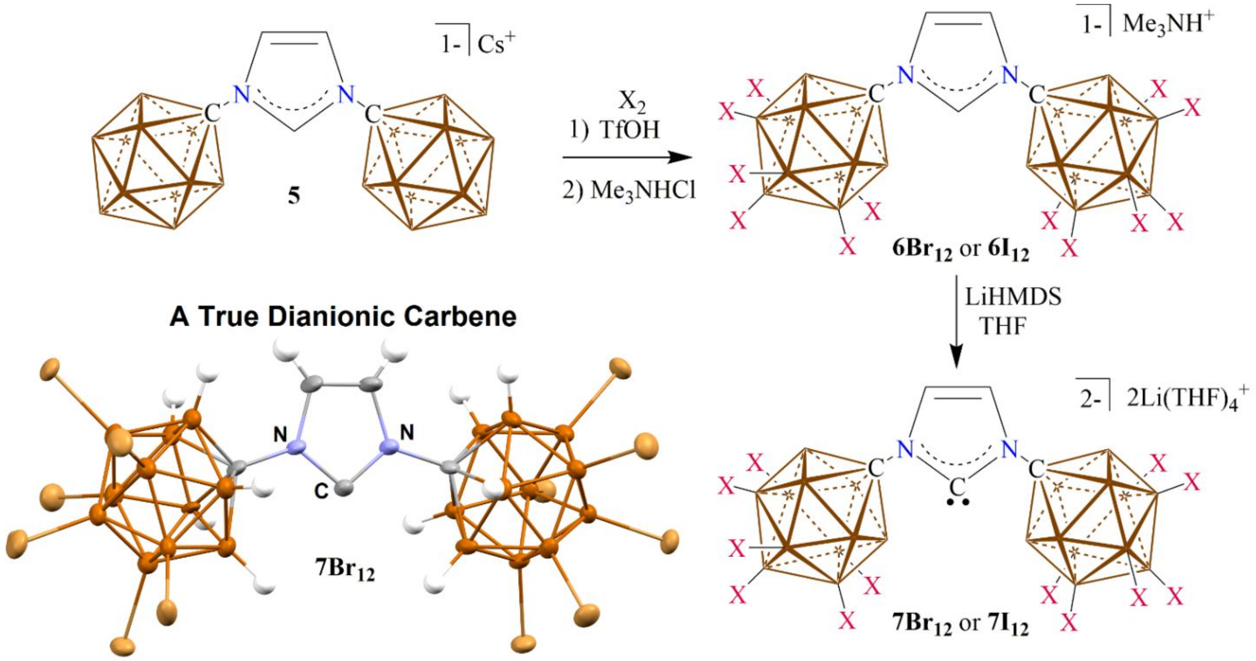


Figure 3. Synthesis of the hexahalogenated imidazoliums **6Br**$_{\mathbf{12}}$ and **6I**$_{\mathbf{12}}$ and the corresponding metal free dianionic NHC **7Br**$_{\mathbf{12}}$ and the analogous carbenoid **7I**$_{\mathbf{12}}$. Solid state structure of **7Br**$_{\mathbf{12}}$ two Li$^+$ countercations coordinated by four THF molecules omitted for clarity, thermal ellipsoids drawn at 50% probability level. Unlabeled grey, brown, light brown and white atoms are carbon, boron, bromine and hydrogen, respectively.

Given the observed coordination chemistry above, we were initially concerned that these NHC ligands might be labile or form unstable complexes when bound to a transition metal element. Gratifyingly, we observed clean metalation with Au(I) to afford the thermally and air stable complexes **$8X_{12}[Li^+]$** (Figure 4). These salts are stable in solution to at least 100 °C, as indicated by NMR analysis.

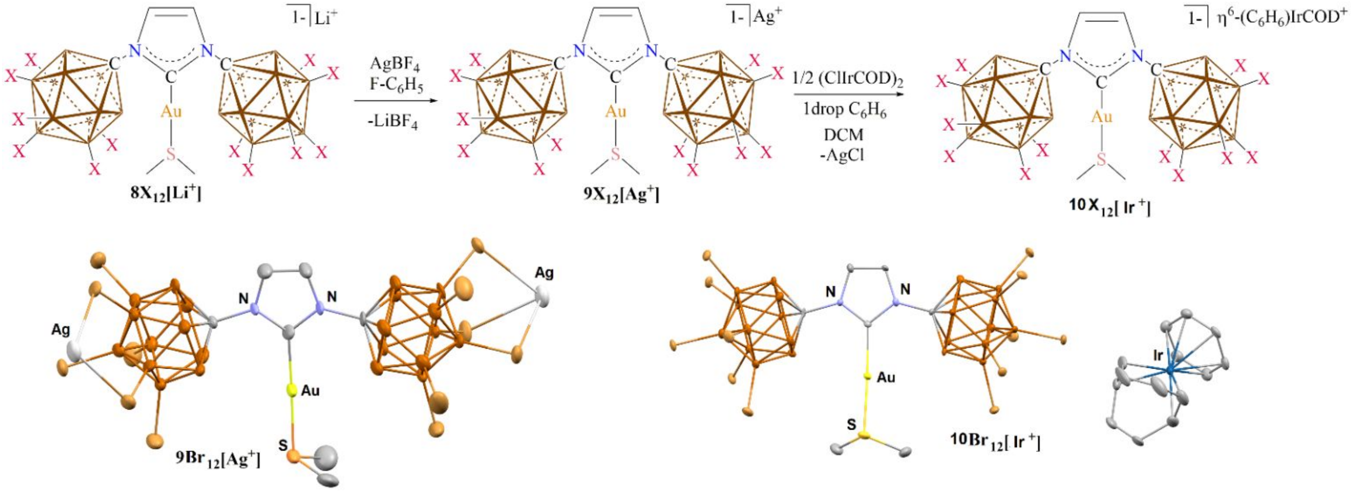


Figure 4. The synthesis of the silver and iridium salts **$9X_{12}[Ag^+]$** an **$10X_{12}[Ir^+]$**, respectively (top) (X = Br or I). Solid-state structures of **$9Br_{12}[Ag^+]$** an **$10Br_{12}[Ir^+]$** (bottom left and right, respectively). Thermal ellipsoids drawn at the 50% probability level. Carbon = unlabeled grey atoms, boron = brown, bromine = light brown, hydrogen atoms omitted for clarity.

To quantify the steric parameters of the new polyhalogenated NHC ligands we calculated their percent buried volumes (%V_{bur}).[26] Compared to the previously reported hydride substituted ligand **2**,[17] which is significantly bulkier (%V_{bur} = 47.2) than Arduengo's diadamantyl substituted NHC (%V_{bur} = 39.8), these ligands are larger (%V_{bur} for **$7Br_{12}$** and **$7I_{12}$** = 48.7 and 49.4, respectively).

Subsequently, we performed salt metathesis with $AgBF_4$ and the salts **$8X_{12}[Li^+]$,** which cleanly afforded the heterobimetallic Ag^+ salts **$9X_{12}[Ag^+]$**. The identity of **$9Br_{12}[Ag^+]$** was unambiguously determined by multinuclear NMR analysis and a single crystal X-ray diffraction study. In the solid state **$9Br_{12}[Ag^+]$** forms a beautiful polymeric structure where the monomeric units of the WCAs are linked together by B-Br---Ag^+---Br-B linkages. The corresponding iodinated species was too insoluble to obtain solution state NMR data or single crystals for X-ray diffraction but its identity can be inferred from subsequent reactions with $ClCPh_3$, *vide infra*.

In order to probe if the silver salts **$9X_{12}[Ag^+]$** could act as halide scavengers towards other transition metals, we investigated the reaction of these species with $(ClIrCOD)_2$. Specifically, we targeted the formation of the classical Ir cation [η^6-$C_6H_6IrCOD^+$].[27-28] We found that while **$9I_{12}[Ag^+]$** does not react, likely for solubility reasons, **$9Br_{12}[Ag^+]$** rapidly reacted with $(ClIrCOD)_2$ with a drop of benzene in dichloromethane solvent (Figure 4). After filtration of the AgCl and concentration of the solution the Au^-/Ir^+ ion pair **$10Br_{12}[Ir^+]$** was isolated in 90% yield. The structure of **$10Br_{12}[Ir^+]$** was unambiguously determined via multi nuclear and 2-D correlation NMR analysis, high resolution mass spectrometry and a X-ray diffraction study (Figure 4).

After demonstrating the potential of these silver salts to act as halide abstracting reagents for transition metal complexes, we next sought to apply these reagents to the formation of main group cations. Reaction of the heterobimetallic Ag^+ salts **$9X_{12}[Ag^+]$** with $ClCPh_3$ in DCM rapidly induced the precipitation of AgCl and formation of the corresponding trityl salts **$11X_{12}[CPh_3^+]$**, the identity of which was unambiguously determined by multinuclear NMR spectroscopy and in the case of **$11Br_{12}[CPh_3^+]$**, a single crystal X-ray diffraction study (Figure 5). In the solid-state the closest interaction between the weakly coordinating organometallic anion and the carbocation of **$11Br_{12}[CPh_3^+]$** is 2.927 Å, which is out of range for any kind of covalent interaction. Importantly, hexahalogenation of the ligand substituents completely prevents any cyclometalation chemistry, as evidenced by the compatibility of **$10X_{12}[CPh_3^+]$** in any solvent that trityl is tolerant of.

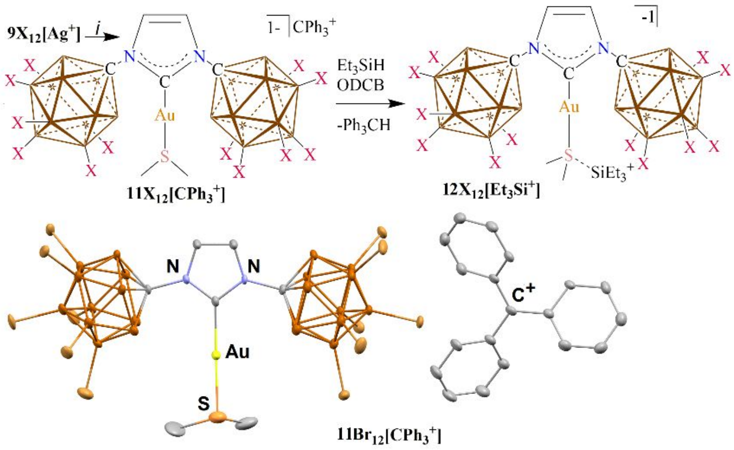
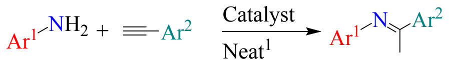


Figure 5. Synthesis of the trityl **$11X_{12}[CPh_3^+]$** and silylium salts **$12X_{12}[SiEt_3^+]$**. *i* = $ClCPh_3$. Thermal ellipsoids drawn at the 50% probability level. Carbon = unlabeled grey atoms, boron = brown, bromine = light brown, hydrogen atoms omitted for clarity.

With the trityl salts **$11X_{12}[CPh_3^+]$** in hand we next turned our attention to the possibility of preparing silylium "like" ions, featuring organometallic counteranions. The term silylium "like", coined by Reed,[2] is utilized to indicate that the silylium orbital is not vacant but contains a weakly interacting ligand of some sort (e.g. halide lone pairs from a carborane anion, π-arene complexation, C-H σ-bonding electrons) that engenders the complex with reactivity one would expect from a free silicon cation. Treatment of the highly colored salts **$11X_{12}[CPh_3^+]$**, dissolved in dichlorobenzene (ODCB), with $HSiEt_3$ (1.1 eq) rapidly quenched the colorful trityl cation (Figure 5). While the purified white powder of **$12Br_{12}[Et_3Si^+]$** is soluble enough to perform complete solution state NMR analysis, **$12I_{12}[Et_3Si^+]$** was insoluble. The ^1H spectrum of **$12Br_{12}[Et_3Si^+]$** showed the absence of the Si-H hydride as well as aromatic resonances for the trityl cation and signals for triphenylmethane, which suggests hydride abstraction had occurred. In addition, signals for the NHC, SMe_2 ligands, as well as Et resonances for a $SiEt_3$ fragment were observed. Close examination of the NHC backbone and SMe_2 resonances shows two sets of peaks, nearly superimposed, suggesting that there are two very similar species in solution. The ^{13}C NMR spectrum show one resonance for the carbene carbon (178.0 ppm), the backbone carbons (124.5 ppm) and the dimethylsulfide methyl carbons (25.6 ppm). However, the ethyl carbons now give rise to two sets of peaks (7.2/6.9 and 7.1/6.1 ppm), indicating two very similar compounds in solution. The single peaks for the resonances further downfield are likely actually two resonances superimposed by coincidence. The ^{11}B NMR spectrum shows three broad resonances in 1:5:5 ratio, indicating that the local C_{5v} symmetry of the clusters is retained. Finally, the ^{29}Si-^1H HSQC displays two peaks at 61.3 and 66.1 ppm, further indicating the existence of two compounds in solution. Reed has observed similar phenomenon for silylium[29] and methyl[30] "like" cations paired with simple hexahalogenated trityl salts, and explained this phenomenon via a population of complexes that differ by coordination mode to the antipodal B-X and pentahalogenated belt of B-X lone pairs, which have similar basicities. However, in our case the magnitude of the ^{29}Si shifts are not consistent with simple carborane B-X adducts (106-112 ppm),[30] but suggest the formation of a complex between the silylium and one of the SMe_2 lone pairs.[31-33] The observation of two species perhaps can be explained by secondary and dynamic interactions with the cage bromides. Due to the very low solubility of **$12Br_{12}[Et_3Si^+]$** we were unable to further investigate this hypothesis by variable temperature NMR experiments. Although **$12I_{12}[Et_3Si^+]$** is completely insoluble we performed cross polarization magic angle spinning (CP-MAS) solid-state ^{29}Si NMR analysis and saw a similar magnitude shift (57 ppm) that does not correspond to $HSiEt_3$, and is of a similar magnitude to that observed for **$12Br_{12}[Et_3Si^+]$.** Additionally, ^{13}C resonances for the NHC, SMe2 and ethyl groups of the Si fragment are observed. Neither compound is compatible with DCM, as upon contact they undergo an exothermic reaction indicated by boiling of the DCM. Although all our attempts to obtain single crystals for an X-ray diffraction study have been unsuccessful, the NMR evidence and this chemical incompatibility with DCM is consistent with the formation of silylium "like" species paired with weakly coordinating organometallic anions.

Given that we had shown that these organometallic anions are weakly coordinating and suitable for the preparation of heterobimetallic and organometallic/main group ion pairs, we next sought to probe if these counteranions were functional in Au catalysis. Previously we have shown that the combination of a perchlorinated carboranyl phosphine with Au(I), created single component zwitterionic systems that display the highest activity reported for the hydroamination of terminal alkynes with arylamines (turnover numbers (TONs) approaching 100,000 in some cases).[14] We decided to test the Li^+ salts of the WCAs (**$3[Li^+]$**, **$8Br_{12}[Li^+]$**, **$8I_{12}[Li^+]$)** as these countercations should have minimal effect on the catalysis, particularly as they are solvated by THF, and likely, amines during the catalysis under neat conditions (80 °C, 24h). Indeed, as outlined in Table

Table 1. Catalytic activity of weakly coordinating anions **8**, **$13Br_{12}$**, and **$13I_{12}$**



Entry	Catalyst	Ar^1	Ar^2	Catalyst Loading (%)	Yield (%)	TON
1	**$8[Li^+]$**	Ph	Ph	0.1	84	840
2	**$13Br_{12}[Li^+]$**	Ph	Ph	0.1	95	950
3	**$13I_{12}[Li^+]$**	Ph	Ph	0.1	95	950
4	**$8[Li^+]$**	Ph	F-C_6H_4	0.1	80	800
5	**$13Br_{12}[Li^+]$**	Ph	F-C_6H_4	0.1	95	950
6	**$13I_{12}[Li^+]$**	Ph	F-C_6H_4	0.1	94	940
7	**$8[Li^+]$**	Ph	MeO-C_6H_4	0.01	90	9000
8	**$13Br_{12}[Li^+]$**	Ph	MeO-C_6H_4	0.01	93	9300
9	**$13I_{12}[Li^+]$**	Ph	MeO-C_6H_4	0.01	94	9400
10	**$8[Li^+]$**	Mes	Ph	0.01	65	6500
11	**$13Br_{12}[Li^+]$**	Mes	Ph	0.01	>95	>9500
12	**$13I_{12}[Li^+]$**	Mes	Ph	0.01	>95 (96)[a]	>9500
13	**$8[Li^+]$**	Mes	F-C_6H_4	0.01	70	7000
14	**$13Br_{12}[Li^+]$**	Mes	F-C_6H_4	0.01	>95	>9500
15	**$13I_{12}[Li^+]$**	Mes	F-C_6H_4	0.01	>95 (85)[a]	>9500
16	**$8[Li^+]$**	Mes	MeO-C_6H_4	0.01	87	8700
17	**$13Br_{12}[Li^+]$**	Mes	MeO-C_6H_4	0.01	66	66000
18	**$13I_{12}[Li^+]$**	Mes	MeO-C_6H_4	0.001	90	90000
19	**$8[Li^+]$**	Dipp	Ph	0.01	80	8000
20	**$13Br_{12}[Li^+]$**	Dipp	Ph	0.01	94	9400
21	**$13I_{12}[Li^+]$**	Dipp	Ph	0.001	75	75000
22	**$8[Li^+]$**	Dipp	F-C_6H_4	0.01	81	8100
23	**$13Br_{12}[Li^+]$**	Dipp	F-C_6H_4	0.001	87(78)[a]	87000
24	**$13I_{12}[Li^+]$**	Dipp	F-C_6H_4	0.01	68	68000
25	**$8[Li^+]$**	Dipp	MeO-C_6H_4	0.01	93	9300
26	**$13Br_{12}[Li^+]$**	Dipp	MeO-C_6H_4	0.01	93(85)[a]	93000
27	**$13I_{12}[Li^+]$**	Dipp	MeO-C_6H_4	0.001	88	88000

Reactions performed neat, 80 °C, 24 h, under N_2 in Teflon capped vials. NMR yields. [a] Isolated yields in brackets. Ph = phenyl, Mes = 2,4,6-trimethyl phenyl, Dipp= 2,6-diisopropylphenyl.

1 these weakly coordinating organometallic anions are excellent catalysts for such reactions. In some cases, (entries 18, 21, 23-24 and 26-27) the catalysts turnover between 68,000-93,000 times, which is very close to the activity observed in our phosphine based system. In all cases the polyhalogenated catalysts **$8Br_{12}$[Li^+]** and **$8I_{12}$[Li^+]** outperform the hydridic version **3[Li^+]**. This is likely due to the enhanced π-acidity at Au^+, that can be expected by attaching 12 halogens to the carboranyl NHC ligand. Likewise, **$8Br_{12}$[Li^+]** outperforms **$8I_{12}$[Li^+]** in all cases, save for entry 17, which can be rationalized by the greater electronegativity of Br compared to I.

CONCLUSIONS

The study above introduces a new paradigm in molecular design, specifically, using electrostatic interactions to create complex functional polyatomic ion pairs. Furthermore, we show that organometallic WCAs can be robust with respect to chemical decomposition, and at the same time be highly active catalysts. This strategy has allowed for the isolation of heterobimetallic ion pairs of Au^-/Ag^+, Au^-/Ir^+ and hybrid organometallic/main group ion pairs Au^-/ (CPh_3^+ or $SiEt_3^+$). These species are intriguing and will likely find applications as reagents for halide/hydride/alkide abstractions to make various other ion pairs and/or as platforms for tandem or cooperative small molecule activation and catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Contents: Synthetic procedures, spectroscopic data (NMR, IR, X-ray crystallographic, etc).

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

WCA, Weakly Coordinating Anion; NHC, N-Heterocyclic Carbene; TON, Turnover number.

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SYNOPSIS TOC:

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