Carborane Ligands

DOI: 10.1002/ange.201209107

Perhalogenated Carba-*closo*-dodecaborate Anions as Ligand Substituents: Applications in Gold Catalysis**

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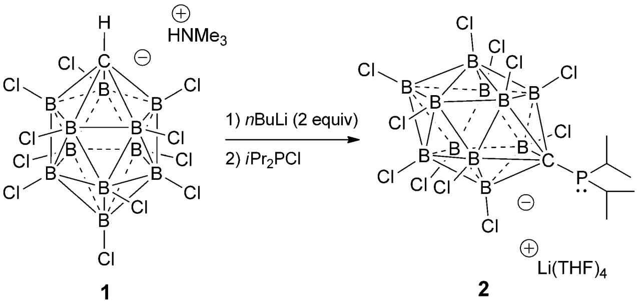
The success of modern transition-metal catalysis is largely due to the availability of a diverse range of ligand frameworks. One of the most universal aspects of ligand design is the strategic attachment of bulky substituents to influence the activity of catalysts. Sterically demanding substituents kinetically protect the active metal center and, at the same time, promote substrate exchange and low coordination, two processes necessary for turnover. Bulky ligand substituents also influence the selectivity of the metal center for product formation and substrate consumption. For these purposes, the most common groups appended to ancillary ligands are alkyl and aryl groups, such as adamantyl or 2,6-diisopropylphenyl. Far less common is the use of dicarba-*closo*-dodecaborane (C_2B_{10}) clusters[1] as surrogates for alkyl or aryl groups.[2] The three-dimensional aromatic nature of these species and their icosahedral shape lend them properties akin to those of both alkyl and aryl groups. However, owing to the hydridic nature of the B–H vertices, ligands bearing these substituents tend to undergo undesirable B–H activation reactions, such as cyclometalation.[3] It is this tendency for such intramolecular reactions to occur that has limited the synthetic utility of dicarba-*closo*-dodecaborane-bearing ligands in the area of catalysis.

Interestingly, complexes that contain ligands functionalized with related carba-*closo*-dodecaborate anions (CB_{11}^-)[4] directly bound to the coordinating atom through the carborane cage carbon atom have not been reported.[5] Although similar in size to their neutral "dicarba" cousins (C_2B_{10}), isoelectronic (CB_{11}^-) clusters have significantly different properties. The negative charge is delocalized over all of the 12 cage atoms, and as a result, the anion is very weakly coordinating. This weak coordination ability can be enhanced by the substitution of some or all of the B–H vertices for alkyl or halo groups. In the case of alkyl substitution, the cluster becomes more reactive towards substitution and oxidation. On the other hand, exhaustive halogenation of the boron vertices of the cluster introduces a blanket of electron-withdrawing substituents that enhances the inherent weak coordination ability of the anion and also confers upon these molecules exceptional inertness. It has been demonstrated that perhalogenated carborane counteranions are sufficiently unreactive that they can form isolable salts with potent oxidants, such as C_{60}^{+}[6] and CH_3^{+}.[7] Thus, these clusters can be far more inert than even simple hydrocarbons: CH_3^+ abstracts hydrides from *n*-alkanes with loss of methane at room temperature. It is these properties that have generated increasing interest[8] in the use of perhalogenated carborane anions in silylium catalysis[8i,l] and related processes.[8f] The anion of choice for most applications is the $HCB_{11}Cl_{11}^-$ anion (**1**), since it is readily accessible[8g] and arguably the most inert carborane anion (Scheme 1).



Scheme 1. Synthesis of phosphine **2**.

We are interested in using the $HCB_{11}Cl_{11}^-$ cluster (**1**) and related systems not only as weakly coordinating anions, but also as super-bulky, inert, charged ligand substituents. The van der Waals volume (V_{vdW}) of **1** is approximately 350 Å^3,[9] which is more than twice as large as that of an adamantyl group ($V_{\mathrm{vdW}} = 136$ Å^3);[1] thus, **1** is an exceptionally large substituent. Appending ligands with such molecular architectures may lead to catalytic systems that display superior activity and stability, particularly when positively charged intermediates are involved. Herein, we report the synthesis of a ligand containing the $CB_{11}Cl_{11}^-$ cluster as a substituent and demonstrate its utility by the preparation of unique single-component Au$^{\mathrm{I}}$ catalysts with unprecedented activity for the hydroamination of alkynes with primary amines.

To begin our investigation into the properties of ligands containing the $CB_{11}Cl_{11}^-$ moiety, we chose to prepare a phosphine. Specifically, we targeted $i\mathrm{Pr}_2\mathrm{P}(CB_{11}Cl_{11})^-\mathrm{Li}^+$ (**2**), since the isopropyl groups of this phosphine should give distinct resonances in the ^{1}H NMR spectrum that are straightforward to interpret (Scheme 1). Additionally, because the $CB_{11}C_{11}^-$ fragment is very large, the intermediate steric bulk of the isopropyl groups should make the phosphorus lone pair accessible for coordination.

Thus, treatment of the trimethylammonium salt of anion **1** with 2 equivalents of *n*BuLi and subsequent quenching of the dianionic intermediate with $i\mathrm{Pr}_2\mathrm{PCl}$ afforded **2** in 98%

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[**] We are grateful to UCR for financial support of this research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201209107.

yield (Scheme 1). The anionic phosphine **2** is very soluble in common polar solvents (CH_2Cl_2, $CHCl_3$, THF) and is not sensitive to oxygen in solution or the solid state. A single-crystal X-ray diffraction study unambiguously confirmed the structure of **2** and showed a sterically congested environment around the pyramidalized phosphorus center (sum of CPC angles: 325.1°; Figure 1). The bond between the phosphorus atom and the carborane cage carbon atom (P−C1 1.9376(16) Å) is significantly longer than those between the phosphorus atom and the isopropyl groups (P−C2 1.8679(19), P−C3 1.8636(18) Å). The lithium countercation of **2** is coordinated by four THF molecules and does not associate with the halogen substituents on the negatively charged carborane (closest Cl···Li distance: 4.283 Å).

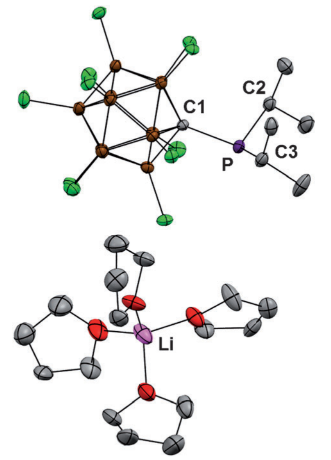


Figure 1. Solid-state structure of phosphine **2** (C gray, P purple, Cl green, B brown, Li pink, O red). Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.

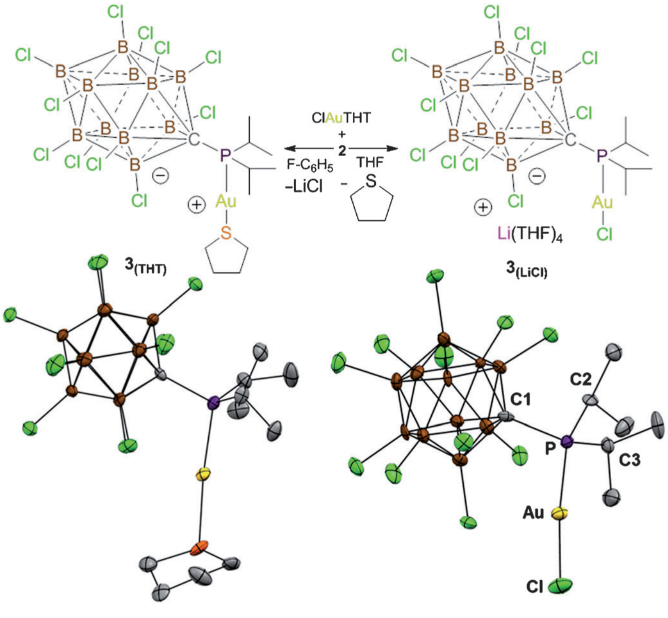


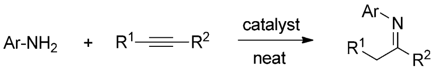
Figure 2. Top: Synthesis of complexes **3**$_{(THT)}$ (left) and **3**$_{(LiCl)}$ (right). Bottom: Solid-state structures of **3**$_{(THT)}$ (left) and **3**$_{(LiCl)}$ (right; C gray, P purple, Au gold, Cl green, B brown, S orange). Selected bond lengths [Å] for **3**$_{(LiCl)}$: P−Au 2.2477(12), P−C1 1.943(5), P−C2 1.858(6), P−C3 1.864(5), Au−Cl 2.2883(12). Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms in both **3**$_{(THT)}$ and **3**$_{(LiCl)}$ are omitted for clarity.

There is growing interest in single-component[10] gold catalysts,[11] which can offer a number of advantages over traditional two-component systems that utilize Ag^+ or strong Brønsted acid additives. These additives not only increase the cost of the systems, but can also promote side reactions or different reactivity.[10] Given that our phosphine **2** contains a pendant weakly coordinating anion, we were intrigued by the idea of combining **2** with a Au^I cation. The typical linear geometry of Au^I is also important, since the $CB_{11}Cl_{11}$ group of **2** will be fixed in a position close to the metal but removed from the *trans* coordination site (with respect to the phosphine), where substrates usually bind during catalysis.

When the anionic phosphine **2** was treated with chloro(tetrahydrothiophene)gold(I) (ClAu(tht)) in monofluorobenzene (FC_6H_5) at room temperature, a large amount of a white precipitate formed within 5 min (Figure 2). Analysis of the precipitate by ^{31}P NMR spectroscopy showed a phosphorus resonance at $\delta = +90$ ppm, which is significantly shifted downfield from that of the starting material **2** (+77 ppm) and in line with the formation of a gold–phosphine complex. The ^{1}H NMR spectrum clearly showed resonances corresponding to the phosphine ligand as well as coordinated tetrahydrothiophene and thus suggested the formation of the zwitterionic Au complex **3**$_{(THT)}$ by ligand coordination and anion metathesis. The driving force for the anion metathesis is the insolubility of LiCl in FC_6H_5. A single-crystal X-ray diffraction study unambiguously confirmed the structure of **3**$_{(THT)}$; however, disorder in the P−*i*Pr groups precludes an accurate discussion of the structural parameters of **3**$_{(THT)}$. This complex is reminiscent of the single-component zwitterionic Au–tht catalyst supported by an anionic N-heterocyclic carbene[12] that was recently reported by Tamm and co-workers.[13] However, in our case, the charged group is bound directly to the coordinating atom and is therefore much closer to the Au center. Interestingly, when the reaction was performed in THF, a solvent in which LiCl is soluble, THT was liberated, and an unusual anionic complex **3**$_{(LiCl)}$ was isolated (**3**$_{(LiCl)}$ can also be prepared by the treatment of isolated **3**$_{(THT)}$ with LiCl in THF). In contrast to **3**$_{(THT)}$, we were able to grow single crystals of **3**$_{(LiCl)}$ without significant disorder and thus examined the solid-state structural aspects of this molecule. The Tolman cone angle[14] for the phosphine ligand is 204°, which indicates that this ligand is much more bulky than a standard sterically demanding phosphine ligand, such as P*t*Bu$_3$ (cone angle: 182°). The P−Au bond length is 2.2477(12) Å, which is close to that reported for a neutral *ortho*-dicarba-*closo*-decaborane-substituted phosphine–AuCl complex (2.232(3) Å).[15] The anionic $CB_{11}Cl_{11}$ substituent displays one chloride interaction with the Au ion (closest Au···Cl−B distance: 3.118 Å). This distance is greater than the sum of the covalent Au/Cl radii but in the range of a van der Waals contact (sum of Au/Cl vdW radii: 3.41 Å). For comparison, the chloride ligand (*trans* to the phosphine) is at a distance of 2.2883(12) Å from the metal center. Hence, the carborane substituent retains a significant amount of weakly coordinating character, even though it is forced into a position close to the metal center.

We next turned our attention to the catalytic properties of complexes **3**, which are air- and light-stable, in the hydroamination[16] of primary amines with alkynes.[17] As a model reaction, we chose the addition of aniline to phenylacetylene. Thus, a 1:1 neat mixture of the amine and the alkyne was added to complex $\mathbf{3}_{\mathbf{(THT)}}$ (0.1 mol %), whereupon an exothermic reaction occurred. We monitored the reaction by ^{1}H NMR spectroscopy and found that the hydroamination was more than 95 % complete after 1 h (Table 1, entry 1). Identical results were obtained with $\mathbf{3}_{\mathbf{(LiCl)}}$ (Table 1, entry 2). Further catalytic tests were carried out only with $\mathbf{3}_{\mathbf{(THT)}}$. When the catalyst loading was decreased to 0.01 % and the mixture was heated at 50 °C for 16 h, the yield of the imine was just as high (Table 1, entry 3). Even at a catalyst loading of 0.004 %, the imine was formed in 88 % yield, which corresponds to a catalyst turnover number (TON) of 22 000 (Table 1, entry 4). The highest reported TON for the gold-catalyzed hydroamination of an alkyne with a primary amine is around 9000, for a multicomponent acid-activated Au system.[17h] Control experiments with ClAu(tht) or $HCB_{11}Cl_{11}^-Cs^+$/ClAu(tht) at a low catalyst loading (0.1 mol %) afforded the imine in only trace amounts (< 5 %). These results demonstrate the benefit of the ligand and show that colloidal gold is unlikely to be responsible for the high activity. A metal-free Brønsted acid catalyzed pathway can also be ruled out, since iPr$_2$P-$(CB_{11}Cl_{11})^-$ H_3NPh^+ does not catalyze the reaction.

Table 1: Hydroamination of alkynes with primary amines in the presence of catalysts **3**.



Entry	Cat.	Ar	R^1	R^2	Catalyst loading [%]	t [h]	T [°C]	Yield [%][a]	TON
1	$\mathbf{3}_{(THT)}$	Ph	H	Ph	0.1	1	25	> 95	> 950
2	$\mathbf{3}_{(LiCl)}$	Ph	H	Ph	0.1	1	25	> 95	> 950
3	$\mathbf{3}_{(THT)}$	Ph	H	Ph	0.01	16	50	> 95	> 9500
4	$\mathbf{3}_{(THT)}$	Ph	H	Ph	0.004	16	50	88	22 000
5	$\mathbf{3}_{(THT)}$	Mes	H	Ph	0.001	24	50	67	67 000
6	$\mathbf{3}_{(THT)}$	Dipp	H	Ph	0.001	24	50	85	85 000
7	$\mathbf{3}_{(THT)}$	Ph	H	4-FC$_6$H$_4$	0.001	24	50	54	54 000
8	$\mathbf{3}_{(THT)}$	Mes	H	4-FC$_6$H$_4$	0.001	24	50	75 (60)[b]	75 000
9	$\mathbf{3}_{(THT)}$	Dipp	H	4-FC$_6$H$_4$	0.001	24	50	92	92 000
10	$\mathbf{3}_{(THT)}$	Ph	H	4-MeOC$_6$H$_4$	0.001	24	50	90	90 000
11	$\mathbf{3}_{(THT)}$	Mes	H	4-MeOC$_6$H$_4$	0.001	24	50	94 (93)[b]	94 000
12	$\mathbf{3}_{(THT)}$	Dipp	H	4-MeOC$_6$H$_4$	0.001	24	50	> 95 (88)[b]	> 95 000
13	$\mathbf{3}_{(THT)}$	Ph	Ph	Ph	0.1	24	80	89.5	895
14	$\mathbf{3}_{(THT)}$	Mes	Ph	Ph	0.1	24	80	67	670
15	$\mathbf{3}_{(THT)}$	Dipp	Ph	Ph	0.1	24	80	78.5	785
16	$\mathbf{3}_{(THT)}$	Ph	H	n-C$_4$H$_9$	0.2	24	80	86.5	435
17	$\mathbf{3}_{(THT)}$	Mes	H	n-C$_4$H$_9$	0.2	24	80	86	430
18	$\mathbf{3}_{(THT)}$	Dipp	H	n-C$_4$H$_9$	0.2	24	80	> 95	> 475

[a] The yield was determined by NMR spectroscopy by the direct integration of the peak for the alkyne starting material with respect to the peak for the imine product and is given as the average for two catalytic reactions. No side reactions were observed. [b] The yield of the isolated product is given in brackets. Dipp = 2,6-diisopropylphenyl, Mes = mesityl (2,4,6-trimethylphenyl).

Because such high catalytic activity is extremely unusual for gold-catalyzed reactions, we examined the hydroamination of phenylacetylene with several different aryl amines at an ultralow loading (0.001 %, 10 ppm). Mesitylamine reacted effectively with phenylacetylene to afford the corresponding imine in 67 % yield after 24 h (TON = 67 000; Table 1, entry 5). With bulkier 2,6-diisopropylphenylamine, the reaction was even more efficient and afforded the analogous imine in 85 % yield (TON = 85 000; Table 1, entry 6). For the latter reaction, the catalyst was also extremely fast, with an initial turnover frequency of 29 000 in the first hour. Even higher turnover numbers were observed for the analogous reactions with 4-fluorophenylacetylene: a maximum turnover number of 92 000 was reached with 2,6-diisopropylphenylamine (Table 1, entries 7–9). The best results were obtained with 4-methoxyphenylacetylene. With this alkyne, the catalyst converted all three amines into the corresponding imines with turnover numbers of 90 000 or greater (Table 1, entries 10–12).

We postulate that the trend of increased reactivity with increased steric bulk of the amine is related to the decreased binding ability of bulkier amines and the resulting imines, which allows for more facile ligand exchange at the Au center. Catalyst $\mathbf{3}_{\mathbf{(THT)}}$ is also effective for the hydroamination of aryl amines with diaryl-substituted alkynes (Table 1, entries 13–15) and terminal alkyl alkynes (Table 1, entries 15–18). Although the activity is lower in these cases, the performance of $\mathbf{3}_{\mathbf{(THT)}}$ compares favorably with that of typical Au catalysts, which often require catalyst loadings of 1–10 mol %. A low catalyst loading (0.2 mol %) with an internal dialkyl alkyne (3-hexyne) or an alkyl amine (tBuNH$_2$) as the substrate produced the expected imines only in trace amounts (< 5 %).

The two mechanisms generally proposed for gold-catalyzed hydroamination either involve the direct addition of the amine to a coordinated alkyne or a coordination–insertion mechanism. In both pathways, charged intermediates undergo proton-transfer steps that lead to the formation of the functionalized amine. Although we cannot speculate at this time on the exact nature of the mechanism operative in the observed catalysis, it is clear that the anionic $CB_{11}Cl_{11}$ group of phosphine **2** is beneficial for the reaction sequence.

We postulate that the extraordinary activity of this system might be due in part to the proximity of the anionic $CB_{11}Cl_{11}^-$ group to the Au center during catalysis. This proximity may lead to electrostatic stabilization of the positively charged reaction intermediates. Analogously, the charge on the carborane substituent may also act as an electrostatic tether to prevent phosphine dissociation and subsequent catalyst decomposition. For large-scale applications of homogenous gold catalysis or catalysis with systems based on other precious metals, highly active and efficient catalysts, such as complexes **3**, must be available. Many transition-metal-catalyzed processes involve cationic intermediates that might benefit from the use of ligands containing a $CB_{11}Cl_{11}^-$ or related substituent. We are currently designing other ligand families that use halogenated carba-*closo*-dodecaborate substituents, as well as expanding on the phosphine system outlined above for use with different transition metals.

Experimental Section

For complete experimental details, see the Supporting Information. CCDC 909516 (**2**), 909517 (**3**$_{\mathbf{(THT)}}$), and 909518 (**3**$_{\mathbf{(LiCl)}}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: November 13, 2012
Revised: January 18, 2013

Keywords: carborane anions · gold · homogeneous catalysis · hydroamination · phosphanes

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