Imidazolyl-Phenyl (IMP) Anions: A Modular Structure for Tuning Solubility and Coordinating Ability.

Derek I. Wozniak, Andrew J. Hicks, William A. Sabbers, and Graham E. Dobereiner

Department of Chemistry, Temple University, Philadelphia, PA 19122, United States

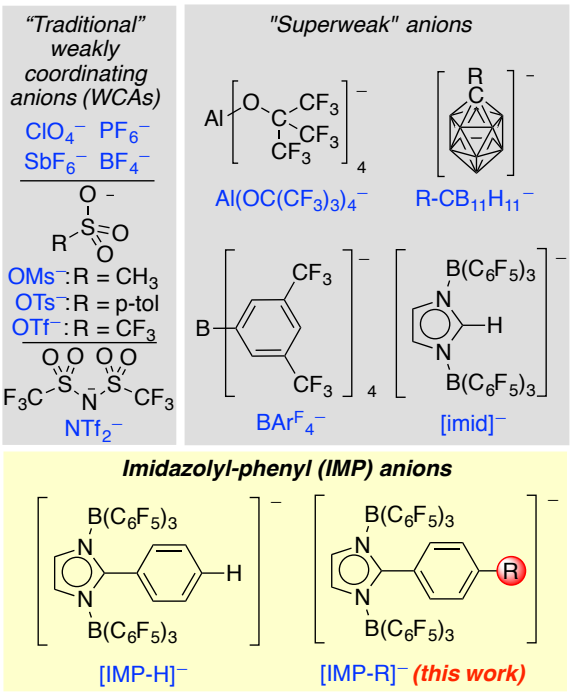
ABSTRACT: The effect of counteranion upon a cation's solution-phase reactivity depends on a subtle interplay of weak interactions. Although these effects are widely appreciated in synthesis and catalysis, probing and controlling anion-cation interactions remains a significant challenge. Here we report the synthesis, characterization and reactivity of the IMP anions, a family of anions with a coordinating ability that can be tuned for a given application. The anions are robust, compatible with both strongly basic and acidic media, suitable for isolation of unstable organometallic species, and effective as counteranions for homogeneous catalysis. IMP anions are prepared in two steps: deprotonation of substituted 2-phenylimidazoles with NaH, followed by addition of 2 equiv. $B(C_6F_5)_3$. The anions prepared feature a range of functionality, including nitro, ester, amide, amine and alcohol groups. Based on the spectroscopic properties of [Pd(IPr)(C(O)C_9H_6N)] [IMP-R], the coordinating ability of $[IMP\text{-}R]^-$ ranges between BF_4^- and $BAr^F{}_4^-$, depending on the polarity of the R group. Gold complexes of type [L-Au-L'][IMP-R] have been isolated and characterized, resulting in the first X-ray structure of a (η^2-diphenylacetylene)Au complex. [(*t*BuXPhos)Au(MeCN)][IMP-R] catalyzes [2+2] cyclization of alkenes and alkynes, as well as the hydroalkoxylation of alkynes. Unlike SbF_6^- and $BArF_4^-$, the $[IMP\text{-}H]^-$ and $[IMP\text{-}CF_3]^-$ salts are sufficiently soluble to efficiently promote cyclizations in toluene with $[(tBuXPhos)Au(MeCN)]^+$.

INTRODUCTION

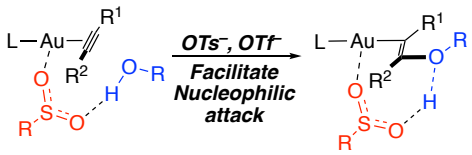
Weakly-coordinating anions (WCAs; Chart 1)[1-4] enable isolation of highly electrophilic species[5-7] and play essential roles in homogeneous catalysis.[8-10] The charge-diffuse "superweak" halogenated boranes, especially tetrakis[3,5-(bis(trifluoromethyl)phenyl]borate[11] ($BAr^F{}_4^-$), have been widely adopted thanks to their kinetic stability and facile preparation.[12-14] The weak ion pairing[15] typical of WCAs allows cations to interact with substrate without strong competition from the anion. High WCA solubility in low-polarity media[16] permits catalytic reactions to be run in non-coordinating solvents,[15, 17] further freeing sites for substrate binding. For many reactions, these effects boost activity, but anion coordination is not necessarily a hindrance to catalysis; vacant sites are really *virtual*[3] or *operationally-unsaturated*[18] sites, where weakly associated anions can protect intermediates against deactivation.[19]

Certain catalytic reactions demonstrate superior activity and selectivity in the presence of more tightly-coordinating anions.[20-26] In gold(I) catalysis, basic counteranions are thought to participate in cooperative reactions with cationic intermediates.[20-22, 25, 27-32] Toste and coworkers[33-34] have pioneered a chiral counteranion strategy for Au(I) catalysis, where chiral anions associated through ion-pairing and/or hydrogen bonding engage substrate during a stereoselectivity-determining step. Zuccaccia, Belanzoni and coworkers[20-22] and Zhdanko and Maier[25] have explored anion effects in Au-catalyzed alkyne hydroalkoxylation, finding OTs^- and OTf^- promote nucleophilic attack (Scheme 1) by hydrogen bonding with the alcohol nucleophile; more weakly-coordinating anions (SbF_6^-) are inferior hydrogen bond acceptors and are far less effective. At the other extreme, more strongly-coordinating and basic anions (OAc^-, TFA^-) bind too well to Au for facile substrate binding, and can deactive catalyst by formation of Au-OR. Here a balance in coordination ability is key to achieving the highest catalytic rates.

Chart 1. Classification of weakly coordinating anions.



Scheme 1. Proposed counteranion effect in Au-catalyzed hydroalkoxylation of alkynes.[20-21, 25]



Because anions can play multifaceted roles in catalysis,[35-37] extensive screening may be needed before an effective counteranion and solvent is identified. Stability of anion and compatibility with cation are other important considerations.[38] Just like ligands, various physical properties of anions – solubility, basicity, hydrogen bonding/proton affinity, metal affinity – can influence reaction outcomes, but unlike the myriad variants of highly modular phosphorus and carbene ligand classes, chemists instead rely almost exclusively on a collection of "traditional" anions (e.g., ClO_4^-, BF_4^-, and PF_6^-; Chart 1). These anions are smaller, less charge-diffuse, and more coordinating[39-40] than the "superweak" borates, aluminates, and carboranes, a growing family of anions[1-3, 41] with extremely low cation affinities and basicity. Superweak anions remain an area of continued synthetic activity, but these scaffolds are purposefully designed to *avoid* contact with electrophiles, and are therefore poor candidates for facilitating mechanisms such as that illustrated in Scheme 1. In exploring subtle counteranion effects by substituting one anion for another, one must therefore choose among the structurally-heterogeneous "traditional" anions, which vary dramatically in physical properties from one another.

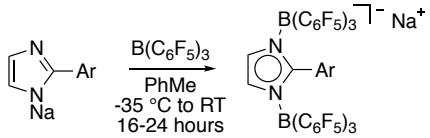
A systematic approach to tuning anion coordinating ability would be useful in empirical optimization of catalytic conditions, especially in cases where anion functionality facilitiates a key step. More broadly, controlling the hydrophobicity of counteranions permits "fine-tuning" in the rational design for synthetic routes, including construction of ionic liquids and soft (polymer) materials.[42] Another potential use is in exploring the structure/activity relationships within a mechanistic study. Computational approaches to considering ion-pairing effects have led to important insights,[43] and examination of solid-phase data provides a comparison of weakly-coordinating character.[44] However, pinpointing the role of anions in solution-phase reactions remains challenging because weak anion/cation solution interactions are difficult to measure. Several NMR techinques are available for quantification if the key resonances are observed *in situ*.[15, 45-47] Granular adjustments to anion coordinating ability could reveal potential roles of counteranion during catalysis, offering a broader understanding of underlying mechanisms.

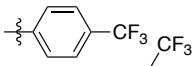
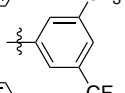
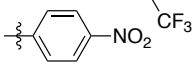
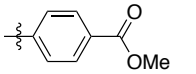
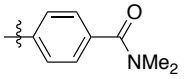
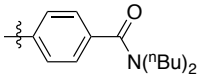
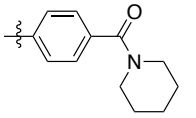
Criteria for a tunable anion scaffold include stability in strongly acidic and basic media and facile synthetic access via a general, functional group-tolerant pathway. The present work describes the synthesis and properties of an anion platform that meet these requirements. The parent of this anion family is our[35] weakly-coordinating phenylimidazole-based anion (**[IMP-H]**$^-$, Chart 1) a deriviative of the superweak [imid]$^-$ anions prepared by LaPointe, Klosin, Babb and co-workers[48-49] and part of a broader class of borane-adduct anions.[50-52] The IMP anion family is simple to synthesize, air- and moisture-stable, and features an array of installed functionalities. [IMP-R]$^-$ anions have been paired with [Pd(IPr)(C(O)C_9H_6N)]$^+$ (**1**) to assess donor abilities[35] via NMR, IR, DFT, and percent buried volume. Preliminary examination of counteranion effects have been explored in Au-catalyzed intermolecular [2+2] cyclization of phenylacetylene with α-methyl styrene as well as the Au-catalyzed alkoxylation of 3-hexyne with two different nucleophiles. We find that the choice of installed anion functionality affects the coordinating ability of the IMP anions as well as their solubility, and therefore serves as a means to cantrol the structure and reactivity of organometallic cations.

RESULTS

Synthesis and Characterization of Na[IMP-R] Salts. Deprotonation of substituted 2-phenylimidazoles or 2-phenylbenzimidazole with NaH followed by addition of $B(C_6F_5)_3$ at –35 °C yields the sodium salts of [IMP-R]$^-$ (Table 1). Benzimidazole-based **[BIMP]**$^-$ was prepared similarly (Chart 2). In our hands Li imidazolates were incompatible with $B(C_6F_5)_3$ and formed other products, but once prepared, [IMP-R]$^-$ are stable to Li^+ including in strongly basic and reducing conditions. For example, lithium aluminum hydride reduction of **Na[IMP-CO_2Me]** and **Na[IMP-DMA]** affords the benzyl alcohol- and benzyl amine-substituted anions **[IMP-CH_2OH]** and **[IMP-CH_2NMe_2]** (Chart 2).

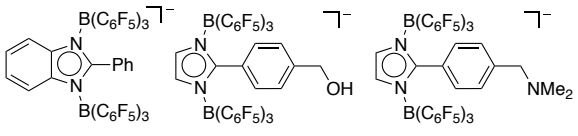
Table 1. IMP anions prepared via reaction of sodium imidazolates and $B(C_6F_5)_3$[a]



Anion	Ar	Yield (%)
[IMP-CF_3]		62%
[IMP-$(CF_3)_2$]		74%
[IMP-NO_2]		62%
[IMP-CO_2Me]		56%
[IMP-DMA]		41%
[IMP-DBA]		41%
[IMP-pipA]		77%

[a]See Experimental Section for details of synthetic procedures.

Chart 2. [BIMP]$^-$, [IMP-CH_2OH]$^-$ and [IMP-CH_2NMe_2]$^-$.



The salts are indefinitely air- and moisture-stable, and in our hands less hygroscopic than $NaBAr^{F}_4$. Recrystallization of anions from dichloromethane/tetrahydrofuran/pentane results in $Na(THF)_x$[IMP-R]. Like the parent [imid]$^-$ anion (Chart 1),[48] the bond distances of the anion's phenylimidazolato core are essentially the same as those of the parent imidazoles. For example, bond parameters of 4-(1H-imidazol-2-yl)-N,N-dimethylbenzamide are nearly identical to **Na[IMP-DMA]**; 2-(3,5-bis(trifluoromethyl)phenyl)-1H-imidazole and **Na[IMP-(CF$_3$)$_2$]** also have similar bond lengths and angles (see structure reports for each in the Supporting Information). In the obtained structures of **Na[IMP-CO$_2$Me]** (Figure 1), **Na[IMP-DMA]**, **Na[IMP-DBA]**, and **Na[IMP-pipA]**, Na^+ coordinates to the anion C═O, with Na–O bonds ranging 2.25 – 2.32 Å. **Na[IMP-CH$_2$OH]** and **Na[IMP-CH$_2$NMe$_2$]** show Na^+ coordinating to the heteroatomic (O, N) anion functionality; **Na[IMP-CH$_2$OH]** further shows a 2.659(7) Å O–H···O hydrogen bond between -CH_2OH and cocrystallized THF (Figure 1). **Na[BIMP]** demonstrates Na^+ coordination to mutually *ortho*-fluorines on one C_6F_5 ring, while **[IMP-(CF$_3$)$_2$]**$^-$ exhibits no contacts with Na^+. On the whole, X-ray analysis shows the negative charge of [IMP-R]$^-$ to be highly diffuse, such that coordination of *para*-substituents to Na^+ mimics the behavior of neutral organic molecules.

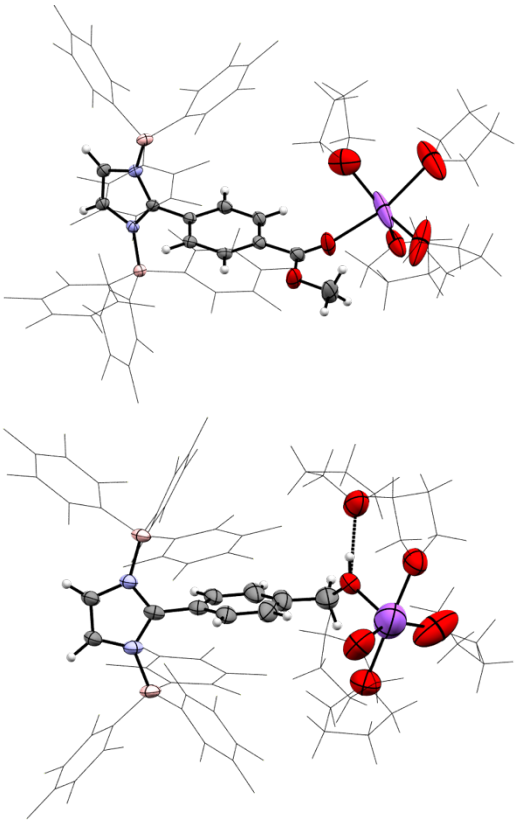
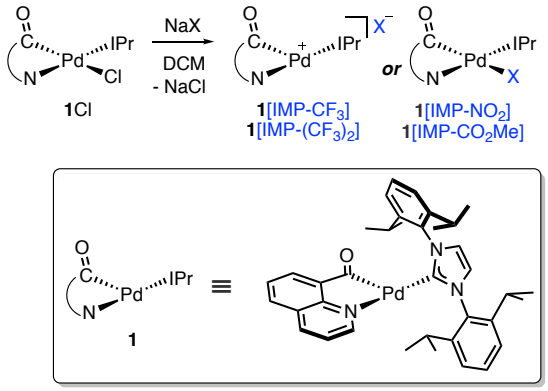


Figure 1. Thermal ellipsoid plots of **Na[IMP-CO$_2$Me]** (top) and **Na[IMP-CH$_2$OH]** (bottom). Ellipsoids shown at 50% probability. THF and C_6F_5 rings shown as wireframe for clarity. O–H···O hydrogen bond drawn with dashed line.

Assessment of [IMP-R] Coordinating Ability. Pairing of [IMP-R]$^-$ with the [Pd(IPr)(C(O)C_9H_6N)] cation (**1**) allowed us to use several metrics previously reported by our group[35] to assess donor ability in both solid and solution states. With more tightly-binding anions (e.g,. BF_4^-, OTf^-, ClO_4^-), complexes of **1** crystallize with counteranion bound in the primary coordination sphere; if the anion is sufficiently weakly-coordinating (SbF_6^-, $BAr^{F}_4^-$), IPr ispropyl groups instead will form agostic interactions to occupy the vacant site (Scheme 2). Addition of Na[IMP-R] salts to a solution of **1Cl** followed by recrystallization from dichloromethane/pentane or toluene/pentane resulted in X-ray quality crystals. Inner-sphere coordination was observed for **1[IMP-NO$_2$]** and **1[IMP-CO$_2$Me]** (Figure 2). Both anions are bound to **1** via oxygen atoms, owing to the polarity of the nitro (N–O) and ester (C–O) bonds. **1[IMP-CF$_3$]** and **1[IMP-(CF$_3$)$_2$]** instead crystallize as outer-sphere ion pairs like the prevously reported **1[IMP-H]**.[35]

Scheme 2. Synthesis of 1[IMP-R] complexes.



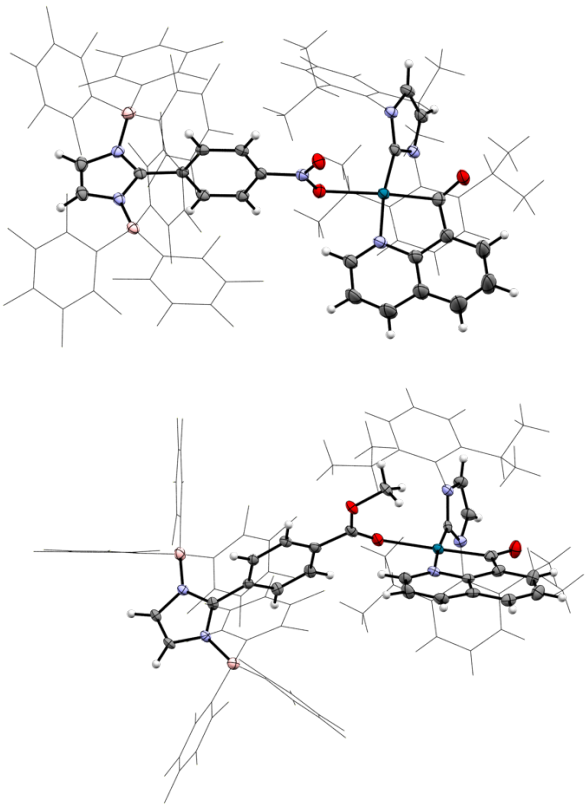


Figure 2. Crystal structures of inner-sphere **1[IMP-NO$_2$]** (top) and **1[IMP-CO$_2$Me]** (bottom) complexes. C_6F_5 rings and diisopropylphenyl substituents shown in wireframe; solvent hidden for clarity. Ellipsoids shown at 50% probability.

The lipophilicity of the $B(C_6F_5)_3$ groups is apparently insufficient to impart dichoromethane (DCM) solublility to complexes of the more basic $[IMP\text{-}R]^-$ variants. Upon adding **1**Cl to amide-containing **Na[IMP-DMA]**, **Na[IMP-DBA]**, or **Na[IMP-pipA]** in DCM, bright yellow solids rapidly precipitated, likely *O*-bound inner-sphere complexes akin to **1[IMP-CO_2Me]**. The strength of amide binding may outcompete weakly-coordinating DCM and prevent dissolution. However, the yellow solids dissolve upon addition of more coordinating solvents. When recrystallized from DCM/pentane in the presence of MeCN ion pairs can be cleanly isolated with MeCN bound in the fourth coordination site (for example, **[1(MeCN)][IMP-pipA]**, Figure 3). Solubility also complicated isolation of **1[IMP-CH_2OH]** and **1[IMP-CH_2NMe_2]**, and in these cases the compounds could not be sufficiently purified for characterization.

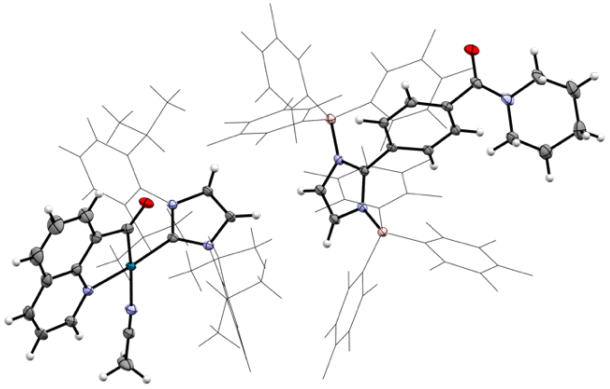


Figure 3. Crystal structure of **[1(MeCN)][IMP-pipA]**. Ellipsoids shown at 50% probability; C_6F_5 rings and diisopropylphenyl substituents shown in wireframe.

Beyond insights from solid-state structures, **1** is a useful probe of coordinating ability of anions in solution. When dissolved in DCM, anions weakly bound to **1** depart the primary coordination sphere, forming ion pairs. The IPr isopropyl methine chemical shift in ^{1}H NMR (CD_2Cl_2, 298 K) correlates with the coordinating ability of the anion: the farther upfield the shift, the less interaction there is between cation and anion.[35] Based on this benchmark, soluble **1**[IMP-R] compounds all fully dissociate in CD_2Cl_2; the cation/anion interactions of **1[IMP-NO_2]** and **1[IMP-CO_2Me]** observed in the solid state are apparently disrupted by DCM (Table 2). Since complexes **1**[IMP-R] of the amide-functionalized anions are insoluble in CD_2Cl_2 they cannot be directly compared. Instead, **1[IMP-DMA]** was dissolved in DMSO-d_6 and compared to **1**[$BAr^F{}_4$]. Although DMSO was expected to coordinate in both cases to form identical Pd environments, chemical shifts of Pd IPr and acylquinoline ligands differed substantially, suggesting **[IMP-DMA]**$^-$ retains some cation association - even in tightly-coordinating DMSO.

Solution-state IR spectroscopy also offers valuable information about the coordination environment of the Pd center; the Pd-acyl C═O stretch shifts to lower energy when a donor is bound to the coordination site *trans* to the acyl.[35] Complexes of **1** exhibited nearly identical C═O stretches in solution, consistent with weakly-associated ion pairs (Table 2). In contrast, solid-state IR suggests [IMP-R] anions range in coordinating ability. At one extreme, **[IMP-CF_3]**$^-$ is nearly as weakly coordinating as $BAr^F{}_4{}^-$; meanwhile the more tightly-coordinating anions **[IMP-DMA]**$^-$ and **[IMP-pipA]**$^-$ provide as nearly as much electron density as BF_4.

While larger in volume than all of the traditional anions in Chart 1, IMP anions are not symmetrical and their steric profile depends upon coordination mode. Percent buried volume ($\%V_{bur}$) calculations carried out on X-ray structures of **1[IMP-NO_2]** and **1[IMP-CO_2Me]** using the *SambVca2* program[53] indicate both **[IMP-NO_2]**$^-$ and **[IMP-CO_2Me]**$^-$ have a $\%V_{bur}$ below the previously-determined threshold for binding to **1** (< ~ 20%).[35] The methyl ester group imparts slightly more steric demand than the nitro group. **[IMP-NO_2]**$^-$ $\%V_{bur}$ (16.9%) is actually smaller than ClO_4^- (17.3%) when bound to **1**. Based on these calculations, the sterically demanding $B(C_6F_5)_3$ groups appear to offer only modest steric demand around the imidazolyl phenyl substituent. Coordination in the solid-state is mostly dependent on the donating character of the *para*-phenyl group.

Table 2. ^{1}H NMR Methine Chemical Shifts, Pd-Acyl C═O Frequencies, and $\%V_{bur}$ of complexes of 1

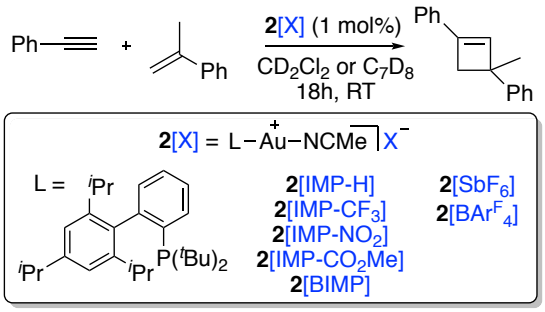
Anion	δ (ppm)	$\nu_{C=O}$, ATR-IR[a]	$\nu_{C=O}$, DCM[a]	$\%V_{bur}$
$BAr^F{}_4$[35]	2.75	1776	1760	-
IMP-CF_3	2.74	1770	1761	-
IMP-H[35]	2.75	1757	1760	-
PF_6[35]	2.75	1759	1760	-
IMP-$(CF_3)_2$	2.75	1755	1761	-
IMP-NO_2	2.76	1737	1760	16.9
IMP-CO_2Me	2.76	1729	1761	18.7
IMP-DMA	-[b]	1695	-[b]	-
IMP-pipA	-[b]	1695	-[b]	-
BF_4[35]	2.89	1689	1760	14.2
ClO_4[35]	3.12	1684	1695	17.3

[a]All frequencies in cm^{-1}. [b]Complexes are insoluble in DCM.

[IMP-R] anions in Au catalysis. To assess the stability and compatibility of $[IMP\text{-}R]^-$ in organometallic reactions, we prepared $[AuL_n][IMP\text{-}R]$ complexes and compared activity to catalysts featuring traditional anions. [*t*BuXPhosAu(MeCN)]$^+$ (**2**) shows counteranion-dependent activity in the [2+2] cyclization of α-methyl styrene and phenylacetylene; Echavarren and coworkers[54-57] found **2**[$BAr^F{}_4$] and **2**[SbF_6][56-57] to provide higher yields than more-coordinating anions (BF_4^-, PF_6^-, NTf_2^-, OTf^-).[56] Addition of Na[IMP-R] to *t*BuXPhosAuCl in a 1:1 mixture of DCM/MeCN generated the analogous **2**[IMP-R] complexes. When performed in CD_2Cl_2 (1 mol%, RT) the [2+2] cyclization of α-methyl styrene and phenylacetylene was compatible with **[IMP-CF_3]**$^-$, **[IMP-NO_2]**$^-$, and **[IMP-CO_2Me]**$^-$ anions as well as the phenylbenzimidazole-based anion **[BIMP]**$^-$ (Table 3). **2**[$BAr^F{}_4$], **2[BIMP]** and **2**[SbF_6] showed slightly better yields and reaction rates than the **2**[IMP-R] complexes (Figure 4). Moving to toluene presents a solubility challenge for conventional gold salts; even with the lipophilic *t*BuXPhos ligand, **2**[SbF_6] is completely insoluble, while **2**[$BAr^F{}_4$] is only slightly soluble. In contrast, several of the IMP-R complexes dissolve in toluene, including **2[IMP-H]**, **2[IMP-CF_3]**, **2[IMP-NO_2]** and **2[BIMP]. 2[IMP-CO_2Me]** is completely insoluble. **2[IMP-H]** and **2[IMP-CF_3]** provide good yields and rates in

cyclizations run in toluene-d_8 (Figure 5), while the more tightly-coordinating **[IMP-NO$_2$]**$^-$ shows decreased reactivity, and **[IMP-CO$_2$Me]**$^-$ fails entirely. Meanwhile the poorly-soluble **2**[BAr$^F{}_4$] provides inconsistent conversions in toluene.

Table 3. Activity of complexes 2[X] in [2+2] cyclizations.



Anion	% Yield in CD_2Cl_2 at 18h[a]	% Yield in toluene-d_8 at 18h[a]
IMP-H	46	47
IMP-CF_3	47	47
IMP-NO_2	46	37
IMP-CO_2Me	52	0
BIMP	53	35
BAr$^F{}_4$	64	23
SbF_6	54	-

[a]All yields are average of at least two trials.

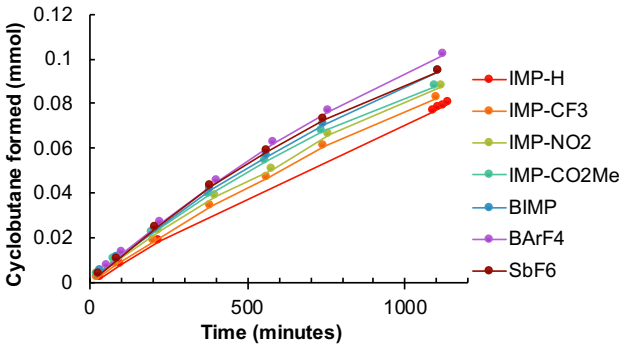


Figure 4. Reaction profile of [2+2] cyclization in dichloromethane catalyzed by **2**[X].

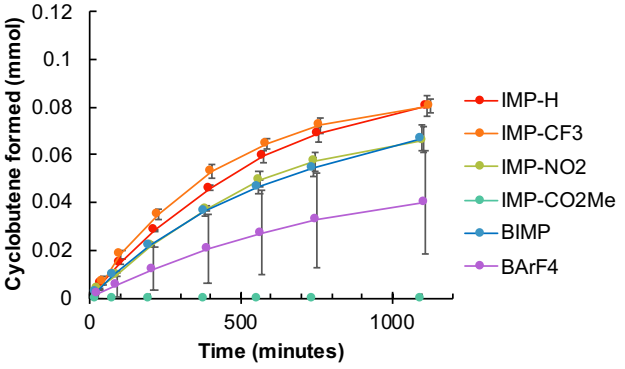
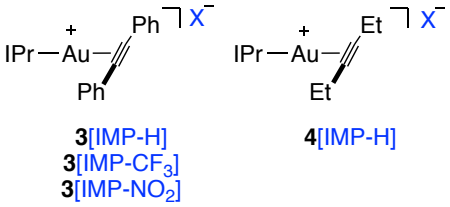


Figure 5. Reaction profile of [2+2] cyclization in toluene catalyzed by **2**[X]; error bars show standard deviation of three runs.

A second series of Au complexes (Chart 3) was prepared for the gold-catalyzed hydroalkoxylation of 3-hexyne, a reaction where basic counteranions have been proposed to play active roles in catalytic mechanisms (vide supra).[20-22,25] We believed that the variable coordinating ability of [IMP-R]$^-$ anions would allow for an exploration of the accelerating effect illustrated in Scheme 1.

Chart 3. Au complexes 3-4.



Among the complexes prepared were series **3**. The X-ray structures of **3[IMP-H]** and **3[IMP-CF$_3$]** are, to our knowledge, the first of Au complexes of diphenylacetylene. These compounds proved to be thermally unstable, decomposing at −35 °C over the course of several days. In the solid-state structure of **3[IMP-H]** the C-C≡C alkyne bond angle is significantly distored from linearity (~162°; Figure 6). Because of their rapid decomposition at cryogenic conditions we did not consider complexes **3** further in catalytic experiments. Complex **4** was stable at room temperature but in our hands solutions became bright purple during attempts at hydroalkoxylation of 3-hexyne with methanol, suggesting the formation of gold nanoparticles; the complexes were also significantly less efficient than (IPr)Au(OTs).[24]

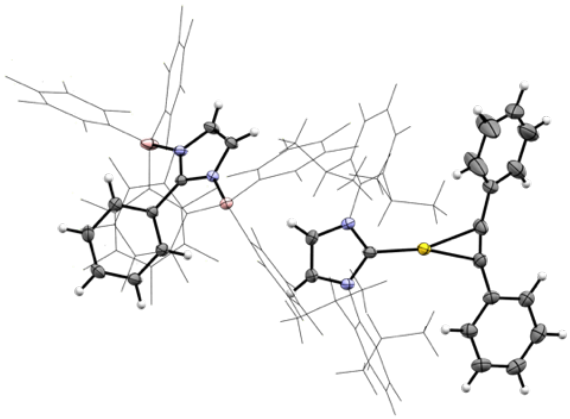
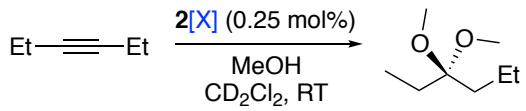


Figure 6. Thermal ellipsoid plot of **3**[IMP-H]. Ellipsoids shown at 50% probability; hydrogens hidden for clarity; diisopropylphenyl and C_6F_5 substituents shown in wireframe.

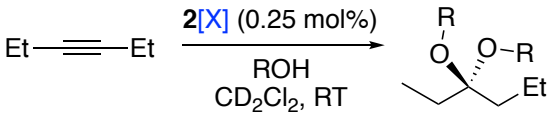
In contrast, complexes **2** were much more stable and did not generate purple solutions in the hydroalkoxylation of 3-hexyne with methanol (Table 4; Figure 7). In all cases only the ketal product was observed, consistent with general acid-catalyzed conversion of the intermediate vinyl ether.[58] The **2**[IMP-R] complexes performed comparably to **2**[BAr$^F{}_4$], suggesting [IMP-R]$^-$ is compatible with the acidic conditions generated *in situ*. We note that the *t*BuXPhos catalysts react more slowly than the corresponding IPr complexes reported by Zuccachia and coworkers.[24]

Table 4. Conversions and Turnover Numbers (TONs) for gold-catalyzed hydroalkoxylation of 3-hexyne with methanol.



Anion	% Conversion (18 h)	TON (18 h)
IMP-H	73	292
IMP-CF_3	77	308
IMP-CO_2Me	77	308
IMP-NO_2	66	264
$BAr^F{}_4$	80	320
SbF_6	88	352
OTs	70	280

Table 5. Conversions and Turnover Numbers (TONs) for gold-catalyzed hydroalkoxylation of 3-hexyne with triethyleneglycol monomethyl ether.



R = $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$

Anion	% Conversion (18 h)	TON (18 h)
IMP-H	29	58
IMP-CF_3	26	52
IMP-CO_2Me	27	52
IMP-NO_2	19	38
$BAr^F{}_4$	28	56
SbF_6	28	56
OTs	7	14

In an effort to better understand the effect of [IMP-R] anions upon catalysis, alkoxylation of 3-hexyne was attempted using the more nucleophilic triethyleneglycol monomethyl ether (Table 5, Figure 8). Consistent with previous findings of Zuccaccia and D'Amora,[22] lower turnover numbers are observed than seen with methanol, despite the stronger nucleophilicity. SbF_6^- performed slightly better than $[IMP\text{-}R]^-$ when using methanol as a nucleophile, but with the more challenging triethyleneglycol monomethyl ether, the rates were nearly identical, with the exception of the poorly-performing **[IMP-NO_2]$^-$** anion. (*t*BuXPhos)Au(OTs) performed worse than other weakly-coordinating anions tested, in contrast to the beneficial effect of OTs^- seen by Zuccaccia and coworkers for the $[(IPr)Au(3\text{-hexyne})]^+$ series of catalysts. The differences in anion influences between IPr and *t*BuXPhosAu complexes illustrate the complex interplay of factors – involving both ligand and counterion – that determines the efficiency of gold catalysts.[24]

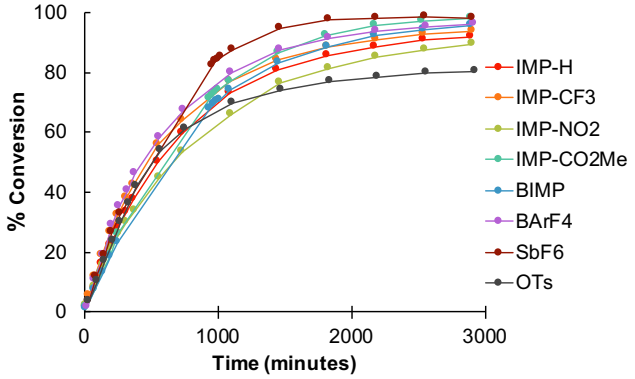


Figure 7. Reaction profile of hydroalkoxylation of 3-hexyne with methanol catalyzed by **2**[X].

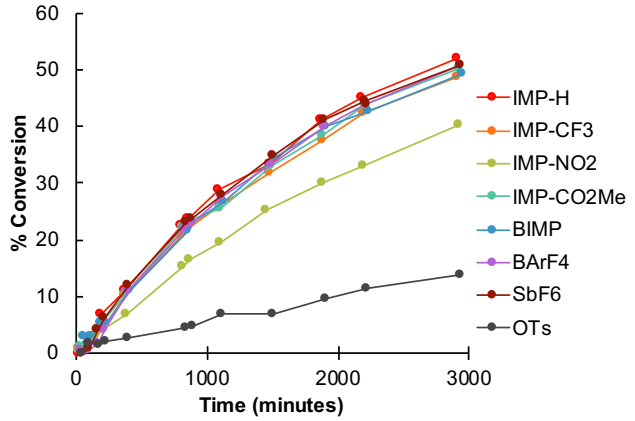


Figure 8. Reaction profile of hydroalkoxylation of 3-hexyne with triethyleneglycol monomethyl ether catalyzed by **2**[X].

DISCUSSION

Thanks to the charge-diffuse $B(C_6F_5)_3$ groups flanking both sides of the imidazole ring, the imidazolyl phenyl groups installed on the $[IMP\text{-}R]^-$ anion scaffold retain most of the characteristics of the parent phenylimidazole molecules. The IMP anion series therefore exhibits a range of properties that can be tuned by the *para*-phenyl functionality. Based on the spectroscopy of series **1** the most weakly-coordinating is **[IMP-CF_3]$^-$**, which mimics the coordinating ability of $BAr^F{}_4^-$ and performs similarly when employed in catalytic reactions of **2**. One advantage of **[IMP-H]$^-$** and **[IMP-CF_3]$^-$** is their extreme lipophilicity, as seen by the solubility of **2[IMP-CF_3]$^-$** and **2[IMP-H]$^-$** in toluene. The sheer size and inert nature of several lipophilic $[IMP\text{-}R]^-$ anions also permited the isolation of previously-unknown diphenylacetylene complexes **3**. Like other classes of "superweak" anions, the IMP anions will likely be useful in applications where extremely large, inert counteranions can provide stability against decomposition.

Anions **[IMP-NO_2]$^-$** and **[IMP-CO_2Me]$^-$** feature polar functional groups on the *para* position of the imdazolyl phenyl scaffold, enabling inner-sphere binding to transition metals in the solid-state. Based on solid-state IR measurements on **1**[IMP-R], **[IMP-NO_2]$^-$** and **[IMP-CO_2Me]$^-$** are between PF_6^- and BF_4^- in coordinating ability. In solution, Pd complexes **1[IMP-NO_2]** and **1[IMP-CO_2Me]** appear to be fully dissociated ion pairs in CD_2Cl_2. In Au catalysis in CD_2Cl_2,

2[IMP-CO_2Me] is superior to **2[IMP-NO_2]**, and approximately as active as the more weakly-coordinating **[IMP-CF_3]$^-$** and **[IMP-H]$^-$**.

The amide-functionalized **[IMP-DMA]$^-$** and **[IMP-pipA]$^-$** anions are nearly as coordinating as BF_4^- according to the solid-state IR spectra of complexes **1**. But unlike **1**[BF_4], **1[IMP-DMA]** and **1[IMP-pipA]** are insoluble in DCM. The solublity of **1[IMP-DMA]** in DMSO, and the apparent association of anion and cation in this extremely polar solvent, suggests the amide-based anions would have utility in homogeneous catalysis where very strong coordination is needed. Meanwhile, alcohol and amine-functionalizd **[IMP-CH_2OH]$^-$** and **[IMP-CH_2NMe_2]$^-$** present difficult solubility challenges, precluding a full comparison of physical properties in organometallic venues. Nonetheless, their isolation confirms that a wide range of functional groups are compatible with the IMP scaffold.

IMP anions have proven robust and compatible with Au(I) catalysis. In the [2+2] cycloaddition reaction between alkynes and alkenes, Echavarren and coworkers[56] find the rate increased with "bulkiness and softness" of the anion, $BAr^F{}_4^- > SbF_6^- > BF_4^-$. The sterically large and lipophilic **[IMP-H]$^-$** and **[IMP-CF_3]$^-$** surpisingly perform somewhat worse than $BAr^F{}_4^-$ and SbF_6^- in CD_2Cl_2 (although better in toluene due to enhanced solubility). Echavarren proposes the counteranion influences rate-determining ligand exchange to form [LAu(alkyne)]$^+$, a species in equilibrium with [LAu(MeCN)]$^+$ and an inactive digold complex. Assuming this step is rate-limiting for all counteranions examined, differences in rate may arise from other factors besides the softness of the anion. It is possible that all IMP-R anions are sufficiently "soft" to stabilize [LAu(alkyne)]$^+$ and other forces drive the equilibrium. In considering anion "softness" of the IMP scaffold, the conventional measures (size, charge diffusivity) are perhaps less critical than localized parameters (charge, steric environment) for different regions of these extremely large anions. Future work in our group will consider how to best evaluate the coordinating ability and basicity of unsymmetrical anions.

Catalysts **2**[IMP-R] are moderately effective in alkyne hydroalkoxylation, but for the R groups investigated here (H, CF_3, CO_2Me, NO_2) the substituent has only a negligible effect on activity. The ligand dependence of the anion effect illustrated in Scheme 1 has been observed previously[20] and underscores the importance of screening both anion and ligand influences during development of Au(I) catalytic methods. Ongoing work in our laboratories is exploring the use of anions featuring more basic groups in the preparation of Au complexes, since hydrogen bond acceptors are known to facilitate nucleophilic attack[58] and accelerate Au reactions where protodeauration is a turnover-limiting step.[32]

CONCLUSION

Weakly- to moderately-coordinating [IMP-R] anions have been prepared by forming $B(C_6F_5)_3$ adducts of substituted phenylimidazolates. The coordinating ability of the anions depends on the substituent present on the phenyl ring, with more Lewis-basic functionalities resulting in stronger coordination to transition metal cations. The anions are compatible with gold catalysis, including cyclizations and alkyne functionalizations. Complexes of lipophilic IMP anions **2[IMP-H]** and **2[IMP-CF_3]** perform particularly well in a very low dielectric medium (toluene). We envision that the IMP anion family will enable a rational tuning of anion coordinating ability and solubility – similar to steric and electronic tuning of ligands – thus allowing for enhanced control over catalytic reactions.

EXPERIMENTAL SECTION

General methods. Unless otherwise specified, all manipulations were performed under a dry N_2 atmosphere using standard Schlenk techniques or a Vacuum Atmospheres inert atmosphere glovebox. Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456. NMR spectra were collected on Bruker Avance III 500 and 400 MHz instruments. ^{1}H NMR chemical shifts (δ, ppm) are referenced to residual protiosolvent resonances and ^{13}C NMR chemical shifts are referenced to the deuterated solvent peak.[59] ^{19}F (fluorobenzene) and ^{31}P (phosphoric acid) NMR chemical shifts were referenced to external standards. IR spectra were collected on a Thermo Scientific Nicolet iS5 FT-IR benchtop spectrometer with either a iD5 diamond ATR or iD1 transmission accessory. Dichloromethane (DCM), tetrahydrofuran (THF), pentane, acetonitrile (MeCN), and toluene were purified using a commercial solvent purification system. All deuterated NMR solvents (Cambridge Isotope Laboratories) were dried over activated 4 Å molecular sieves for 48 h before use. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, Boulder Scientific) was purified via sublimation (100 mtorr, 90 °C) prior to use. Chloro(dimethyl sulfide) gold (I) was purchased from Strem Chemicals. All benzonitriles, aminoacetaldehyde diethyl acetal, and *t*BuXPhos were purchased from Oakwood Chemicals. Sodium hydride and 2-phenylbenzimidazole were purchased from Sigma Alrdich. 2-(4-(trifluoromethyl)phenyl)imidazole, 2-(4-nitrophenyl)imidazole, and methyl 4-(imidazol-2-yl)benzoate were prepared as reported by Zhichkin and coworkers.[60] Sodium tetrakis(3,5-bistrifuloromethyl)phenylborate ($NaBAr^F{}_4$) was prepared using the procedure of Yakelis and Bergman.[12] **1Cl** was prepared as previously reported by our group.[35] (*t*BuXPhos)AuCl and [(*t*BuXPhos)Au(NCMe)][$BAr^F{}_4$] were prepared using the procedures reported by Echavarren.[57] (IPr)AuCl was synthesized using the procedure reported by Nolan and coworkers.[61] 4-(1*H*-imidazol-2-yl)benzoic acid was synthesized according to the procedure of Hagedorn.[62] 4-(1*H*-imidazol-2-yl)benzoyl chloride was synthesized according to the patent owned by Eastman and coworkers.[63]

Sodium 2-(4-(trifluoromethyl)phenyl)imidazolide. In an inert atmosphere glovebox, a 16 mL vial was charged with 133 mg (0.625 mmol) 2-(4-(trifluoromethyl)phenyl)imidazole and 10 mL THF and cooled to −35 °C. The suspension was then stirred, and 15 mg (0.625 mmol) sodium hydride was added. The suspension was stirred for 20 hours and dried in vacuo. Yield 99% ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (d, ^3J = 7.9 Hz, 2H, aryl), 7.48 (d, ^3J = 8.1 Hz, 2H, aryl), 6.84 (s, 2H, imidazolyl).

Na[IMP-CF_3]. In an inert atmosphere glovebox, a 16 mL vial was charged with 140 mg (0.598 mmol) sodium 2-(4-(trifluoromethyl)phenyl)imidazolide and 8 mL toluene and cooled to −35 °C. This solution was stirred, and 613 mg (1.197 mmol) $B(C_6F_5)_3$ was added and stirred for 23 hours while coming to RT. The vial was removed from the glovebox and 75 mL pentane was added to precipitate the desired product as a white solid. The solid was filtered, washed with pentane, and dried in vacuo. Purification via slow diffusion of pentane into DCM/THF yielded X-ray quality crystals of the product as the

$Na(THF)_4$ salt. Yield 62%. Anal. Calc. for $NaC_{46}N_2F_{33}B_2H_6 \cdot 1.75C_4H_8O \cdot 0.25\ CH_2Cl_2$ C, 45.50 %, H, 1.47 %, N, 1.99 %, found C, 45.214 %, H, 1.829 %, N, 1.894%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.20 (s, 2H, imidazolyl), 7.02 (d, ^3J = 8.4 Hz, 2H, aryl), 6.58 (d, ^3J = 7.6 Hz, 2H, aryl). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 149.45, 147.87, 147.52, 132.62, 131.05, 130.79, 129.89, 127.13, 125.32, 125.02, 124.09. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -63.95, -126.72, -133.16, -158.80, -160.16, -164.61, -166.90. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.24. Unit cell (XRD) monoclinic P, a = 13.103(3) Å, b = 27.136(5) Å, c = 16.187(3) 372 Å, β = 92.560(3)°.

Sodium 2-(4-(nitro)phenyl)imidazolide. In an inert atmosphere glovebox, a 16 mL vial was charged with 118 mg (0.625 mmol) 2-(4-(nitro)phenyl)imidazole and 10 mL THF and cooled to −35 °C. The suspension was then stirred, and 15 mg (0.625 mmol) sodium hydride was added. The suspension was stirred for 20 hours and dried in vacuo. Yield 99% ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.03 (s, 4H, aryl), 6.95 (s, 2H, imidazolyl).

Na[IMP-NO$_2$]. In an inert atmosphere glovebox, a 16 mL vial was charged with 125 mg (0.592 mmol) sodium 2-(4-(nitro)phenyl)imidazolide and 8 mL toluene and cooled to −35 °C. This solution was stirred, and 607 mg (1.18 mmol) $B(C_6F_5)_3$ was added and stirred for 23 hours while coming to RT. The vial was removed from the glovebox and 75 mL pentane was added to precipitate the desired product as a light brown solid. The solid was filtered, washed with pentane, and dried in vacuo. Purification via slow diffusion of pentane into DCM/THF yielded X-ray quality crystals of the product as the $Na(THF)_4$ salt. Yield 62%. Anal. Calc. for $NaC_{45}N_3F_{30}B_2H_6 \cdot 1.5C_4H_8O$ C, 45.60 %, H, 1.35 %, N, 3.13 %, found C, 45.418 %, H, 1.684 %, N, 3.238%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.61 (d, ^3J = 9.1 Hz, 2H, aryl), 7.25 (d, ^4J = 3.5 Hz, 2H, aryl), 6.63 (d, ^3J = 8.1 Hz, 2H, imidazolyl). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 149.50, 147.64, 146.87, 146.31, 140.97, 138.98, 137.90, 136.51, 135.85, 131.12, 125.72, 122.16.^{19}F NMR (471 MHz, DCM-d_2) δ -126.07, -133.20, -158.60, -159.84, -164.54, -166.62. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.07.

Sodium 2-(4-(CO$_2$Me)phenyl)imidazolide. In an inert atmosphere glovebox, a 16 mL vial was charged with 202 mg (1.00 mmol) 2-(4-(CO_2Me)phenyl)imidazole and 15 mL THF and cooled to −35 °C. The suspension was then stirred, and 24 mg (1.00 mmol) sodium hydride was added. The suspension was stirred for 76 hours and dried in vacuo. Yield 99% ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.97 (d, ^3J = 8.6 Hz, 2H, aryl), 7.74 (d, ^3J = 8.6 Hz, 2H, aryl), 6.82 (s, 2H, imidazolyl), 3.79 (s, 3H C(O)CH_3).

Na[IMP-CO$_2$Me]. In an inert atmosphere glovebox, a 16 mL vial was charged with 112 mg (0.50 mmol) sodium 2-(4-(CO_2Me)phenyl)imidazolide and 8 mL toluene and cooled to −35 °C. This solution was stirred, and 512 mg (1.00 mmol) $B(C_6F_5)_3$ was added and stirred for 26 hours. The vial was removed from the glovebox and 75 mL pentane was added to precipitate the desired product as a white solid. The solid was filtered, washed with pentane, and dried in vacuo. Purification via slow diffusion of pentane into DCM/THF yielded X-ray quality crystals of the product as the $Na(THF)_4$ salt. Yield 56%. Anal. Calc. for $NaC_{47}N_2O_2F_{30}B_2H_9 \cdot 1C_4H_8O$ C, 46.40 %, H, 1.30 %, N, 2.12 %, found C, 46.214 %, H, 1.574 %, N, 2.056%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.32 (d, ^3J = 8.8 Hz, 2H, aryl), 7.23 (d, ^4J = 3.7 Hz, 2H, aryl), 6.51 (d, ^3J = 7.7 Hz, 2H, imidazolyl), 3.89 (s, 3H, C(O)CH_3). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 169.39, 149.62, 147.54, 138.67, 137.80, 136.04, 134.64, 129.92, 129.19, 128.05, 125.38.^{19}F NMR (471 MHz, CD_2Cl_2) δ -125.87, -133.25, -158.70, -160.61, -164.58, -167.08.^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.12. Unit cell (XRD) triclinic, a = 12.2126(18) Å, b = 16.759(2) Å, c = 17.209(3) Å, α = 90.069(3)°, β = 104.596(3)°, γ = 106.610(3)°.

Sodium 2-phenylbenzimidazolide. In an inert atmosphere glovebox, a 16 mL vial was charged with 194 mg (1.00 mmol) 2-phenylbenzimidazole and 10 mL THF and cooled to −35 °C. The suspension was then stirred, and 24 mg (1.00 mmol) sodium hydride was added. The suspension was stirred for 76 hours and dried in vacuo. Yield 99% ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 (dd, ^3J = 8.2, ^4J = 1.2 Hz, 2H, aryl), 7.36 – 7.30 (m, 4H, aryl), 7.19 (t, ^3J = 7.2 Hz, 1H, aryl), 6.75 (s, 2H, aryl).

Na[BIMP]. In an inert atmosphere glovebox, a 40 mL vial was charged with 223 mg (1.031 mmol) sodium 2-phenylbenziimidazolide and 8 mL toluene and cooled to −35 °C. This solution was stirred, and 1055 mg (2.062 mmol) $B(C_6F_5)_3$ was added and stirred for 27 hours. The vial was removed from the glovebox and 75 mL pentane was added to precipitate the desired product as a white solid. The solid was filtered, washed with pentane, and dried in vacuo. Purification via slow diffusion of pentane into DCM/THF yielded X-ray quality crystals. Yield 79%. Anal. Calc. for $NaC_{47}N_2O_2F_{30}B_2H_9 \cdot 2.5C_4H_8O$ C, 49.85 %, H, 1.97 %, N, 2.13 %, found C, 49.951 %, H, 1.927 %, N, 2.131%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.53 (v br s, 2H, aryl), 7.33 (v br s, 2H, aryl), 6.97 (dd, ^3J = 6.1, ^4J = 3.2 Hz, 4H, aryl), 6.81 (v br s, 1H, aryl). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 137.83, 130.90, 128.08, 127.86, 122.90, 116.12, 114.22. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -116.75, -118.86, -127.82, -129.45, -129.55, -134.05, -135.46, -136.61, -136.70, -137.57, -159.39, -159.99, -160.98, -163.86, -166.27, -167.06.^{11}B NMR (161 MHz, CD_2Cl_2) δ -7.77. Unit cell (XRD) monoclinic P, a = 15.0906(12) Å, b = 16.8592(13) Å, c = 23.0499(18) Å, β = 99.144(2)°.

4-(1H-imidazol-2-yl)-N,N-dimethylbenzamide. Under ambient conditions, a 100 mL round bottom flask was charged with 10 mL DCM and cooled to 0 °C. 1.85 mL (8.45 mmol) of 2.0 M dimethylamine in THF was added, followed by 1.18 mL of triethylamine. The solution was stirred, and 822 mg (3.382 mmol) of 4-(1H-imidazol-2-yl)benzoyl chloride•HCl was added, resulting in HCl gas evolution. The solution was stirred for 20 minutes in the ice bath and then allowed to stir overnight at room temperature. The reaction was diluted with 100 mL DCM and extracted sequentially with 15 mL saturated $NaHCO_3$, brine, and NH_4Cl. The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness under reduced pressure, resulting in a highly hygroscopic tan solid. Yield 48%. Recrystallization via slow layer diffusion of pentane into a concentrated DCM solution under N_2 atmosphere resulted in x-ray quality crystals as colorless needles. Anal. Calc. for $C_{12}H_{13}N_3O \bullet 0.1C_5H_{12} \bullet 0.1\ CH_2Cl_2$ C, 65.53 %, H, 6.28 %, N, 18.19 %, found C, 65.195 %, H, 6.544 %, N, 18.581%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.09 (s, 1H, *NH*), 7.82 – 7.75 (m, 2H, aryl), 7.35 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 2H, aryl), 7.13 (s, 2H, imdazolyl), 3.09 (s, 3H, CH_3), 2.96 (s, 3H, CH_3). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.49, 146.10, 136.33, 131.91, 127.89, 125.55, 39.75, 35.49. Unit cell (XRD) monoclinic P, a = 15.0906(12) Å, b = 16.8592(13) Å, c = 23.0499(18) Å, β = 99.144(2)°. Unit cell (XRD) orthorhombic P, a = 7.9951(13) Å, b = 14.758(2) Å, c = 21.725(4) Å.

Na[IMP-DMA]. In an inert atmosphere glovebox, a 40 mL vial was charged with 200 mg (0.930 mmol) 4-(1H-imidazol-2-

yl)-N,N-dimethylbenzamide and 4 mL THF. The suspension was stirred briefly and cooled to – 35 °C. 23 mg (0.930 mmol) of NaH was added, and the suspension was stirred while coming to room temperature and then for an addition 15 h. The reaction was dried in vacuo, yielding a beige solid. This solid was suspended in 5 mL toluene and stirred briefly before being cooled to −35 °C. 952 mg (1.860 mmol) of $B(C_6F_5)_3$ was added and the solution was stirred while coming to room temperature, and then for an additional 16 h. 30 mL of pentane was added to the reaction, resulting in a large amount of white precipitate. The reaction was removed from the glovebox, poured onto an additional 40 mL pentane, and the precipitate was filtered off, washed with hexanes, and dried in vacuo. The solid was dissolved in THF, filtered to remove insoluble impurities, and dried in vacuo. Recrystallization *via* layer diffusion of hexanes into a concentrated THF/DCM solution yielded X-ray quality crystals of the analytically pure sample; adventitious acetone was also present in the solid-state structure. Yield 41 %. Anal. Calc. for $NaC_{48}H_{12}N_3B_2F_{30}O{\cdot}1.3C_4H_8O$ C, 47.16 %, H, 1.67 %, N, 3.10 %, found C, 46.868 %, H, 1.934 %, N, 3.284%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.24 (d, ^3J = 4.3 Hz, 2H, aryl), 6.69 (d, ^3J = 8.7 Hz, 2H, aryl), 6.42 (d, ^3J = 5.6 Hz, 2H, imidazolyl), 3.01 (s, 3H, *CH*$_3$), 2.89 (s, 3H, *CH*$_3$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.72, 147.56, 136.81, 130.76, 130.35, 125.23, 125.12, 39.62, 35.53. ^{19}F NMR (471 MHz, DMSO-*d*$_6$) δ -125.42, -133.54, -158.46, -160.17, -164.38. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.37. Unit cell (XRD) monoclinic P, *a* = 13.3526(11) Å, *b* = 30.789(2) Å, *c* = 16.1477(13) Å, β = 93.240(2)°.

Na[IMP-CH$_2$OH]. In an inert atmosphere glovebox, a 40 mL vial was charged with 300 mg (0.240 mmol) **Na[IMP-CO$_2$Me]** and 20 mL THF and stirred to dissolve. The clear, light yellow solution was cooled to – 35 °C and 10 mg (0.263 mmol) $LiAlH_4$ was added. The reaction was stirred while coming to room temperature, and then for an additional 3 days. The vial was removed from the glovebox and cooled to 0 °C, at which point 1 mL H_2O, 5 drops 10% aqueous NaOH, and 15 mL diethyl ether were added sequentially. The solution was stirred while coming to room temperature and then dried over $MgSO_4$. The reaction was filtered and dried in vacuo, resulting in a pure, bright white solid. Yield 79%. Analytically pure X-ray quality crystals were obtained by layering a concentrated THF solution of the product with hexanes at room temperature. Anal. Calc. for $NaC_{46}N_2B_2F_{30}OH_9{\cdot}1.45\ C_4H_8O$ C, 46.97 %, H, 1.57 %, N, 2.11 %, found C, 46.690 %, H, 1.885 %, N, 2.217 %. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.21 (d, ^3J = 4.0 Hz, 2H, aryl), 6.72 (d, ^3J = 8.5 Hz, 2H, aryl), 6.41 (d, ^3J = 7.5 Hz, 2H, imidazolyl), 4.54 (s, 2H, Ar-*CH*$_2$-OH). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.66, 139.08, 130.23, 129.73, 126.51, 125.06, 65.61. ^{19}F NMR (471 MHz, DMSO-*d*$_6$) δ -125.42, -133.54, -158.46, -160.17, -164.38. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.37. Unit cell (XRD) triclinic, *a* = 12.7032(13) Å, *b* = 13.4507(13) Å, *c* = 20.407(2) Å, α = 91.293(2)°, β = 91.963(2)°, γ = 107.760(2)°.

Na[IMP-CH$_2$NMe$_2$]. In an inert atmosphere glovebox, a 40 mL vial was charged with 500 mg (0.3965 mmol) **Na[IMP-DMA]** and 30 mL THF and stirred to dissolve. The clear solution was cooled to −35 °C and 17 mg (0.4360 mmol) $LiAlH_4$ was added. The reaction was stirred while coming to room temperature, and then for an additional 3 days. The vial was removed from the glovebox and cooled to 0 °C, at which point 1 mL H_2O, 5 drops 10% aqueous NaOH, and 20 mL diethyl ether were added sequentially. The solution was stirred while coming to room temperature, and then dried over $MgSO_4$. The reaction was filtered and dried in vacuo, resulting in a pure, bright white solid. Yield 80%. Analytically pure X-ray quality crystals were obtained by layering a concentrated DCM/THF solution of the product with hexanes at room temperature. Anal. Calc. for $NaC_{48}N_3B_2F_{30}H_{14}{\cdot}2\ C_4H_8O$, 0.4 C_5H_{12} C, 49.05 %, H, 2.47 %, N, 2.96 %, found C, 49.03 %, H, 2.52 %, N, 2.91 %. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.25 (d, ^4J = 2.4 Hz, 2H, aryl), 6.74 (d, ^3J = 8.4 Hz, 2H, aryl), 6.43 (s, 2H, imidazolyl), 3.53 (s, 2H, Ar-*CH*$_2$-N), 2.47 (d, ^3J = 9.5 Hz, 6H, N(*CH*$_3$)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 128.95, 44.38, 22.74. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -125.68, -133.30, -158.78, -160.56, -164.60, -167.16. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.19. Unit cell (XRD) monoclinic P, *a* = 12.1872(17) Å, *b* = 19.000(3) Å, *c* = 14.971(2) Å, β = 111.618(3)°.

4-(1H-imidazol-2-yl)-N,N-dibutylbenzamide. Under ambient conditions, a 100 mL round bottom flask was charged with 40 mL DCM, 925 µL (5.5 mmol) di-*n*-butylamine, and 3 mL of triethylamine. The solution was stirred, and 1215 mg (5 mmol) of 4-(1H-imidazol-2-yl)benzoyl chloride•HCl was added, resulting in HCl gas evolution and a rapid color change from orange/yellow to brown. The reaction was allowed to stir for 20 hours, and was then diluted with 50 mL of DCM. The reaction was extracted sequentially with 5 mL saturated $NaHCO_3$, and 5 mL brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness under reduced pressure, resulting in a viscous brown oil. The oil was triturated with hexanes and dried again, resulting in a brown foam that became a solid powder when broken up. Yield 56%. HRMS (ESI) calc. for $C_{18}H_{25}N_3O$ ($[M + H]^+$): 300.2070, found 300.2077. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.67 (s, 1H, *NH*), 7.78 (d, ^3J = 8.0 Hz, 2H, aryl), 7.32 – 7.25 (m, 2H, aryl), 7.12 (s, 2H, imidazolyl), 3.53 – 3.44 (m, 2H, N-*CH*$_2$), 3.24 – 3.13 (m, 2H, N-*CH*$_2$), 1.65 (s, 2H, N-CH$_2$-*CH*$_2$), 1.54 – 1.34 (m, 4H, N-CH$_2$-*CH*$_2$ + CH$_2$-CH$_2$-*CH*$_2$), 1.17 – 1.04 (m, 2H, CH$_2$-CH$_2$-*CH*$_2$), 0.99 (t, ^3J = 7.3 Hz, 3H, *CH*$_3$), 0.77 (t, *J* = 6.6 Hz, 3H, *CH*$_3$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.64, 143.19, 137.28, 131.61, 130.60, 127.24, 125.58, 49.25, 44.98, 31.13, 30.04, 20.72, 20.14, 14.13, 13.80.

Na[IMP-DBA]. In an inert atmosphere glovebox, a 20 mL vial was charged with 299 mg (1.00 mmol) 4-(1H-imidazol-2-yl)-N,N-dibutylbenzamide and 5 mL THF. The suspension was stirred briefly and cooled to –35 °C. 24 mg (1.00 mmol) of NaH was added, and the suspension was stirred while coming to room temperature and then for an addition 23 h. The reaction was dried in vacuo, yielding a beige solid. This solid was suspended in 8 mL toluene and stirred briefly before being cooled to −35 °C. 1024 mg (2.00 mmol) of $B(C_6F_5)_3$ was added and the solution was stirred while coming to room temperature, and then for an additional 18 h. 30 mL of pentane was added to the reaction, resulting in a large amount of white precipitate. The reaction was removed from the glovebox, poured onto an additional 50 mL pentane, and the precipitate was filtered off, washed with hexanes, and dried in vacuo. Yield 46%. Recrystallization *via* layer diffusion of hexanes into a concentrated THF/DCM solution yielded X-ray quality crystals of the analytically pure sample. Anal. Calc. for $NaC_{54}H_{24}N_3B_2F_{30}O{\cdot}1.3C_4H_8O$ C, 49.41 %, H, 2.41 %, N, 2.92 %, found C, 49.652 %, H, 2.400 %, N, 3.201%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.23 (d, ^3J = 5.1 Hz, 2H, aryl), 6.63 (d, ^3J = 8.4 Hz, 2H, aryl), 6.32 (br s, 2H, imidazolyl), 3.37 (br s, 2H, N-*CH*$_2$), 3.04 (br s, 2H, N-*CH*$_2$), 1.56 (m, 2H, N-CH$_2$-*CH*$_2$), 1.24 (m, 6H, N-CH$_2$-*CH*$_2$ + CH$_2$-CH$_2$-*CH*$_2$), 0.93 (t, ^3J = 7.4 Hz, 3H, *CH*$_3$), 0.73 (t, ^3J = 7.3 Hz, 3H, *CH*$_3$). ^{13}C NMR (126 MHz,

CD_2Cl_2) δ 171.98, 138.06, 130.98, 130.02, 129.36, 128.55, 125.11, 124.30, 49.34, 45.13, 30.99, 29.61, 20.60, 19.79, 13.98, 13.49. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -125.28, -133.47, -158.45, -160.10, -164.29, -165.76. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.40. Unit cell (XRD) monoclinic P, a = 33.184(3) Å, b = 15.7566(14) Å, c = 26.172(2) Å, β = 109.217(2)°.

(4-(1H-imidazol-2-yl)phenyl)(piperidin-1-yl)methanone. Under ambient conditions, a 100 mL round bottom flask was charged with 30 mL DCM, 434 µL (4.4 mmol) piperidine, and 2.2 mL of triethylamine. The solution was stirred, and 972 mg (4 mmol) of 4-(1H-imidazol-2-yl)benzoyl chloride•HCl was added, resulting in HCl gas evolution and a rapid color change from orange/yellow to brown. The reaction was allowed to stir for 15 hours, and was then diluted with 50 mL of DCM. The reaction was extracted sequentially with 5 mL saturated $NaHCO_3$, and 5 mL brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness under reduced pressure, resulting in light brown solid. Yield 82%. Anal. Calc. for $C_{15}H_{17}n_3O{\cdot}0.1CH_2Cl_2$ C, 68.75 %, H, 6.57 %, N, 15.93 %, found C, 68.360 %, H, 6.969 %, N, 16.317%. ^1H NMR (500 MHz, CD_2Cl_2) δ 11.18 (v br s, 1H, *NH*), 7.81 – 7.75 (dd, ^3J = 8.4, ^4J = 1.8, 2H, aryl), 7.31 (d, ^3J = 8.1 Hz, 2H, aryl), 7.11 (s, 2H, imidazolyl), 3.69 (br s, 2H, N-*CH*$_2$), 3.33 (br s, 2H, N-*CH*$_2$), 1.67 (br s, 4H, N-CH$_2$-*CH*$_2$), 1.50 (br s, 2H, CH$_2$-*CH*$_2$-CH$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.23, 146.21, 136.32, 132.03, 127.62, 125.63, 49.15, 46.20, 43.52, 26.88, 26.05.

Na[IMP-pipA]. In an inert atmosphere glovebox, a 20 mL vial was charged with 255 mg (1.00 mmol) 4-((1H-imidazol-2-yl)-phenyl)(piperidin-1-yl)methanone and 5 mL THF. The suspension was stirred briefly and cooled to – 35 °C. 24 mg (1.00 mmol) of NaH was added, and the suspension was stirred while coming to room temperature and then for an addition 18 h. The reaction was dried in vacuo, yielding a brown solid. This solid was suspended in 10 mL toluene and stirred briefly before being cooled to −35 °C. 1024 mg (2.00 mmol) of $B(C_6F_5)_3$ was added and the solution was stirred while coming to room temperature, and then for an additional 17 h. 30 mL of pentane was added to the reaction, resulting in a large amount of white precipitate. The reaction was removed from the glovebox, poured onto an additional 50 mL pentane, and the precipitate was filtered off, washed with hexanes, and dried in vacuo. Yield 77%. Recrystallization *via* layer diffusion of hexanes into a concentrated THF/DCM solution yielded X-ray quality crystals of the analytically pure sample. Anal. Calc. for $NaC_{51}H_{16}N_3B_2F_{30}O{\cdot}2\ C_4H_8O$ C, 49.03 %, H, 2.23 %, N, 2.91 %, found C, 49.338 %, H, 2.435 %, N, 3.031%. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.24 (d, ^3J = 4.0 Hz, 2H, aryl), 6.67 (d, ^3J = 8.4 Hz, 2H, aryl), 6.43 (br s, 2H, imidazolyl), 3.58 (br s, 2H, 2H, N-*CH*$_2$), 3.24 – 3.19 (m, 2H, 2H, N-*CH*$_2$), 1.68 (p, ^3J = 6.2, ^3J = 5.8 Hz, 2H, N-CH$_2$-*CH*$_2$), 1.61 (dt, ^3J = 11.0, ^3J = 5.8 Hz, 2H, N-CH$_2$-*CH*$_2$), 1.52 (p, ^3J = 6.2 Hz, 2H, CH$_2$-*CH*$_2$-CH$_2$). ^{19}F NMR (471 MHz, CD_2Cl_2) δ -125.39, -133.45, -158.48, -160.12, -164.41, -166.03. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.82. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.06, 147.62, 141.42, 137.13, 130.48, 125.23, 124.87, 121.80, 49.23, 43.64, 26.58, 24.45. Unit cell (XRD) triclinic, a = 14.2164(17) Å, b = 14.4515(17) Å, c = 17.120(2) Å, α = 81.955(2)°, β = 72.302(2)°, γ = 67.813(2)°.

2-(3,5-bis(trifluoromethyl)phenyl)-1H-imidazole. This compound was synthesized using a modified version of the procedure reported by Zhichkin and coworkers.[40] Under air, a 100 mL round bottom flask was charged with 10 mL methanol and 1.68 mL (10 mmol) 3,5-bis(trifluoromethyl)benzonitrile and stirred. Sodium methoxide in methanol (25%, 1 mmol) was added and the solution was stirred at room temperature for 2 h. Aminoacetaldehyde diethyl acetal (1.45 mL, 10 mmol) and 1.2 mL glacial acetic acid were then added and the reaction was heated to 50 °C for 1 h. The reaction was cooled and diluted with 20 mL methanol, followed by addition of 5 mL 6 M HCl, and the reaction was heated to 75 °C for 5 h. After cooling, solvent was removed with a rotary evaporator, and the white residue was taken up in 30 mL 1:1 water/diethyl ether and extracted. NaOH was added to the clear aqueous layer until it attained a pH of 10; the white precipitate that formed was filtered and dried in vacuo. The aqueous filtrate was allowed to stand overnight, during which time X-ray quality crystals grew as large colorless needles. Yield 22%. HRMS (ESI) calc. for $C_{11}H_6N_2F_6$ ($[M + H]^+$): 281.0513, found 281.0512. ^1H NMR (500 MHz, DMSO-d_6) δ 13.06 (s, 1H, *NH*), 8.58 (s, 2H, aryl), 8.06 (s, 1H, aryl), 7.29 (s, 2H, aryl). ^{13}C NMR (126 MHz, DMSO-d_6) δ 143.21, 133.39, 131.77, 131.51, 131.25, 130.98, 124.83, 122.66, 121.43. ^{19}F NMR (471 MHz, DMSO-d_6) δ -61.55.

Na[IMP-(CF$_3$)$_2$]. In an inert atmosphere glovebox, a 40 mL vial was charged with 280 mg (1.0 mmol) 2-(3,5-bis(trifluoromethyl)phenyl)-1H-imidazole and 5 mL THF. The solution was stirred briefly and cooled to −35 °C. 24 mg (1.0 mmol) of NaH was added, and the suspension was stirred while coming to room temperature and then for an addition 24 h. The reaction was dried in vacuo, yielding a white solid. This solid was suspended in 8 mL toluene and stirred briefly before being cooled to −35 °C. 1024 mg (2.0 mmol) of $B(C_6F_5)_3$ was added and the solution was stirred while coming to room temperature, and then for an additional 17 h. 30 mL of pentane was added to the reaction, resulting in a large amount of white precipitate. The reaction was removed from the glovebox, poured onto an additional 40 mL pentane, and the precipitate was filtered off, washed with hexanes, and dried in vacuo. The solid was purified *via* slow diffusion of hexanes into a concentrated DCM/THF solution of the product. It should be noted that the product, while solid, is very tacky and must be kept under somewhat anhydrous conditions. Yield 74 %. Anal. Calc. for $NaC_{47}H_5N_2B_2F_{36}{\cdot}2C_4H_8O$ C, 44.93 %, H, 1.44 %, N, 1.91 %, found C, 45.070 %, H, 1.615 %, N, 1.986%. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.61 (s, 1H, aryl), 7.27 (d, ^4J = 3.5 Hz, 2H, aryl), 6.98 (s, 2H, imidazolyl).^{13}C NMR (126 MHz, CD_2Cl_2) δ 149.45, 147.45, 145.68, 131.35, 131.13, 129.58,125.73, 123.92, 123.01, 121.75, 108.53. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -64.65, -133.39, -158.63, -159.64, -164.44, -164.60, -166.85. ^{11}B NMR (161 MHz, CD_2Cl_2) δ -8.22. Unit cell (XRD) monoclinic P, a = 15.937(3) Å, b = 25.254(4) Å, c = 18.608(3) Å, β = 106.941(3)°.

1[IMP-CF$_3$]. In an inert atmosphere glovebox, a 4 mL vial was charged with 30 mg (0.048 mmol) of **1Cl**, and 2 mL of DCM and stirred to dissolve. To the bright orange solution was added 60 mg (0.048 mmol) of **Na[IMP-CF$_3$]**, and the solution immediately turned bright yellow. The reaction was allowed to stir for 2.5 h and the solution was filtered through celite, layered with pentane, and stored at −35 °C to afford X-ray quality crystals as yellow needles. Yield 81%. Anal Calc. for $PdC_{83}N_5OF_{30}B_2H_{49}{\cdot}CH_2Cl_2$ C, 51.18 %, H, 2.56 %, N, 3.55 %, found C, 51.119 %, H, 2.720 %, N, 3.488 %. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.52 (d, ^3J = 8.1 Hz, 1H, quinolyl), 8.22 (d, ^3J = 4.8 Hz, 1H, quinolyl), 8.13 (d, ^3J = 8.1 Hz, 1H, quinolyl), 7.92 (d, ^3J = 7.3 Hz, 1H, quinolyl), 7.66 – 7.60 (m, 2H, quinolyl), 7.57 (t, ^3J = 7.8 Hz, 2H, IPr aryl), 7.43 – 7.34 (m, 6H, IPr aryl + imidazolyl), 7.20 (s, 2H, IMP-CF$_3$ imidazolyl), 7.00 (d, ^3J =

8.5 Hz, 2H, IMP-CF_3 aryl), 6.58 (d, ^3J = 7.6 Hz, 2H, IMP-CF_3 aryl), 2.74 (hept, ^3J = 6.5 Hz, 4H, C*H*(CH_3)$_2$), 1.32 (d, ^3J = 6.8 Hz, 12H, CH(*CH_3*)$_2$), 1.27 (d, ^3J = 6.9 Hz, 12H, CH(*CH_3*)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.80, 146.61, 139.89, 133.84, 131.36, 129.94, 129.64, 129.37, 125.27, 124.96, 124.04, 123.90, 29.38, 25.11, 25.05. IR (thin film, cm^{-1}): ν_{CO} 1770; IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1761. Unit cell (XRD) triclinic, *a* = 14.1686(15) Å, *b* = 18.684(2) Å, *c* = 19.045(2) Å, α = 114.321(4)°, β = 98.469(4)°, γ = 107.830(4)°.

1[IMP-NO_2]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.079 mmol) of **1Cl**, and 2 mL of DCM and stirred to dissolve. To the bright orange solution was added 107 mg (0.087 mmol) of **Na[IMP-NO_2]**, and the solution immediately turned bright yellow. The reaction was allowed to stir for 16.5 h and the solution was filtered through celite, and layered with pentane. This resulted in the product oiling out; layer diffusion of hexamethyldisiloxane into DCM resulted in an analytically pure sample. Subsequent vapor diffusion of pentane into a concentrated toluene solution yielded X-ray quality crystals as yellow blocks. Yield 92%. Anal Calc. for $PdC_{81}N_6O_3F_{30}B_2H_{49}$ C, 52.52 %, H, 2.67 %, N, 4.54 %, found C, 52.473 %, H, 2.364 %, N, 4.516 %. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.52 (d, ^3J = 8.3 Hz, 1H, quinolyl), 8.21 (d, ^3J = 4.6 Hz, 1H, quinolyl), 8.17 – 8.10 (m, 1H, quinolyl), 7.92 (dd, ^3J = 7.3, ^4J = 1.0 Hz, 1H, quinolyl), 7.65 – 7.52 (m, 6H, quinolyl + IPr aryl + IMP-NO_2 aryl), 7.39 (d, ^3J = 7.8 Hz, 4H, IPr aryl), 7.36 (s, 2H, IPr imidazolyl), 7.24 (d, ^3J = 4.0 Hz, 2H, IMP-NO_2 aryl), 6.59 (d, ^3J = 7.9 Hz, 2H, IMP-NO_2 imidzolyl), 2.76 (hept, ^3J = 6.4 Hz, 4H, C*H*(CH_3)$_2$), 1.31 (d, ^3J = 6.8 Hz, 12H, CH(*CH_3*)$_2$), 1.27 (d, ^3J = 6.9 Hz, 12H, CH(*CH_3*)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 175.12, 150.78, 149.37, 147.45, 146.58, 139.87, 138.97, 137.94, 135.80, 135.54, 133.85, 133.73, 131.30, 130.91, 129.61, 129.36, 125.53, 125.09, 124.95, 123.87, 122.02, 29.33, 25.13, 24.97. IR (thin film, cm^{-1}): ν_{CO} 1737; IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1761. Unit cell (XRD) monoclinic P, *a* = 18.6043(18) Å, *b* = 26.890(3) Å, *c* = 21.779(2) Å, β = 101.862(2)°.

1[IMP-CO_2Me]. In an inert atmosphere glovebox, a 4 mL vial was charged with 61 mg (0.095 mmol) of **1Cl**, and 2 mL of DCM and stirred to dissolve. To the bright orange solution was added 100 mg (0.048 mmol) of **Na[IMP-CO_2Me]**, and the solution immediately turned bright yellow. The reaction was allowed to stir for 0.5 h and the solution was filtered through celite, layered with pentane. Recrystallization under air *via* vapor diffusion of hexanes into a concentrated DCM solution afforded X-ray quality crystals. Yield 81%. Anal Calc. for $PdC_{84}N_5O_3F_{30}B_2H_{51}$·1.5$C_4H_8O$ C, 54.36 %, H, 3.13 %, N, 3.56 %, found C, 54.694 %, H, 3.139 %, N, 3.636. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.50 (d, ^3J = 8.2 Hz, 1H, quinolyl), 8.23 (d, ^3J = 4.6 Hz, 1H, quinolyl), 8.12 (d, ^3J = 8.1 Hz, 1H, quinolyl), 7.91 (dd, ^3J = 7.3, ^4J = 1.1 Hz, 1H, quinolyl), 7.65 – 7.58 (m, 2H, quinolyl), 7.56 (m, *J* = 7.8 Hz, 3H, quinolyl + IPr aryl), 7.39 (d, ^3J = 7.8 Hz, 4H, IPr aryl), 7.37 – 7.35 (s + d, ^3J = 8.9 Hz, 2H + 2H, IPr imidazolyl + IMP-CO_2Me aryl), 7.20 (d, ^4J = 3.7 Hz, 2H, IMP-CO_2Me aryl), 6.44 (d, ^3J = 7.6 Hz, 2H, IMP-CO_2Me imidazolyl), 3.81 (s, 3H, C(O)*CH_3*), 2.76 (hept, ^3J = 6.6 Hz, 4H, C*H*(CH_3)$_2$), 1.31 (d, ^3J = 6.8 Hz, 12H, CH(*CH_3*)$_2$), 1.27 (d, ^3J = 6.8 Hz, 12H, CH(*CH_3*)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 166.42, 150.90, 149.33, 148.25, 146.60, 139.83, 133.82, 133.28, 131.32, 129.90, 129.59, 129.49, 129.33, 128.19, 125.09, 123.90, 52.57, 35.01, 34.52, 29.33, 25.63, 25.06, 23.06, 11.60. IR (thin film, cm^{-1}): ν_{CO} 1729; IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1761. Unit cell (XRD) monoclinic P, *a* = 22.722(2) Å, *b* = 18.9379(19) Å, *c* = 22.844(2) Å, β = 105.759(2)°.

1[IMP-(CF_3)$_2$]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.0786 mmol) of **1Cl**, and 1 mL of DCM and stirred to dissolve. To the bright orange solution was added 110 mg (0.0.0825 mmol) of **Na[IMP-(CF_3)$_2$]**, and the solution immediately turned bright yellow. The reaction was allowed to stir for 16 h and the solution was filtered through celite, layered with pentane, and stored at −35 °C to afford X-ray quality crystals as yellow blocks. Yield 93%. Anal. Calc. for $PdC_{84}N_5OF_{36}B_2H_{48}$ · 0.9 CH_2Cl_2 C, 50.19 %, H, 2.47 %, N, 3.45 %, found C, 50.238 %, H, 2.502 %, N, 3.360 %. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.51 (dd, ^3J = 8.4, ^4J = 1.1 Hz, 1H, quinolyl), 8.22 (d, ^3J = 4.4 Hz, 1H, quinolyl), 8.12 (dd, ^3J = 8.1, ^4J = 1.0 Hz, 1H, quinolyl), 7.90 (dd, ^3J = 7.3, ^4J = 1.1 Hz, 1H, quinolyl), 7.63 – 7.53 (m, 5H, quinolyl + IPr aryl + IMP-(CF_3)$_2$ aryl), 7.38 (d, ^3J = 7.8 Hz, 4H, IPr aryl), 7.35 (s, 2H, IPr imidazolyl), 7.25 (d, ^3J = 3.8 Hz, 2H, IMP-(CF_3)$_2$ aryl), 6.97 (s, 2H, IMP-(CF_3)$_2$ imidazolyl), 2.74 (hept, ^3J = 6.7 Hz, 4H), 1.31 (d, ^3J = 6.8 Hz, 12H), 1.26 (d, ^3J = 6.9 Hz, 12H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 174.83, 150.89, 149.38, 146.60, 145.65, 139.89, 133.83, 133.75, 131.34, 131.18, 131.05, 130.00, 129.63, 129.36, 125.70, 125.65, 125.10, 124.95, 123.93, 123.90, 122.91, 121.76, 29.36, 25.12, 25.03. Solid state IR 1755 cm^{-1}, soln. state 1761 cm^{-1}. Unit cell (XRD) triclinic, *a* = 13.652(5) Å, *b* = 16.550(6) Å, *c* = 20.994(8) Å, α = 112.393(7)°, β = 91.470(7)°, γ = 101.814(7)°.

1[IMP-DMA]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.0786 mmol) of **1Cl**, and 1 mL of DCM and stirred to dissolve. To the bright orange solution was added 104 mg (0.0.0825 mmol) of **Na[IMP-DMA]**, and the solution immediately turned bright yellow. After less than a minute of stirring, a large amount of pale yellow precipitate was observed. The reaction was allowed to stir for 16 h and the solution was filtered through a frit. The pale yellow solid and yellow filtrate were each dried in vacuo; NMR of each revealed that the solid was the desired product. Yield 85%. Anal. Calc. for $PdC_{87}N_7O_2F_{30}B_2H_{59}$ · 0.65 CH_2Cl_2 C, 52.97 %, H, 3.06 %, N, 4.93 %, found C, 53.23 %, H, 3.12 %, N, 4.65 %. ^{1}H NMR (500 MHz, DMSO-d6) δ 9.60 (dd, ^3J = 5.0, ^4J = 1.5 Hz, 1H, quinolyl), 8.69 (dd, ^3J = 8.3, ^4J = 1.4 Hz, 1H, quinolyl), 8.20 (dd, ^3J = 8.0, ^4J = 1.2 Hz, 1H, quinolyl), 7.81 – 7.73 (m, 4H, quinolyl + IPr aryl), 7.71 – 7.66 (m, 1H, quinolyl), 7.39 (t, ^3J = 7.7 Hz, 2H, IPr aryl), 7.30 – 7.21 (m, 6H, IPr aryl + IPr imidazolyl IMP-DMA aryl), 6.89 (d, ^3J = 8.5 Hz, 2H, IMP-DMA aryl), 6.26 (s, 2H, IMP-DMA imidazolyl), 3.40 – 3.33 (m, 2H, C*H*(CH_3)$_2$), 3.10 (hept, ^3J = 5.9 Hz, 2H, C*H*(CH_3)$_2$), 2.90 (s, 3H, N-*CH_3*), 2.78 (s, 3H, N-*CH_3*), 1.32 (d, ^3J = 6.6 Hz, 6H, CH(*CH_3*)$_2$), 1.19 (d, ^3J = 6.9 Hz, 6H, CH(*CH_3*)$_2$), 0.99 (dd, ^3J = 14.1, ^3J = 6.7 Hz, 12H, CH(*CH_3*)$_2$).^{1}H NMR of MeCN adduct (500 MHz, CD_2Cl_2) δ 8.52 – 8.46 (m, 2H, quinolyl), 8.04 (dd, ^3J = 8.1, ^4J = 1.1 Hz, 1H, quinolyl), 7.87 (dd, ^3J = 7.3, ^4J = 1.2 Hz, 1H, quinolyl), 7.64 – 7.57 (m, 2H, quinolyl), 7.44 (t, ^3J = 7.8 Hz, 2H, IPr aryl), 7.32 – 7.27 (m, 6H, IPr aryl + IPr imidazolyl), 7.19 (d, ^3J = 3.5 Hz, 2H, IMP-DMA aryl), 6.77 (d, ^3J = 8.7 Hz, 2H, IMP-DMA aryl), 6.36 (s, 2H, IMP-DMA imidazolyl), 3.02 (dt, ^3J = 13.2, ^3J = 6.4 Hz, 4H, C*H*(CH_3)$_2$), 2.79 (d, *J* = 9.8 Hz, 6H), 2.16 (s, 3H, MeCN *CH_3*), 1.17 (dd, ^3J = 11.9, ^3J = 6.8 Hz, 24H, CH(*CH_3*)$_2$).^{13}C NMR (126 MHz, CD_2Cl_2) δ 176.76, 170.67, 150.28, 149.52, 146.61, 139.85, 135.35, 133.34, 132.31, 130.82, 129.39, 127.40, 126.44, 125.11, 124.82, 128.28, 34.53, 28.89, 26.11, 23.57, 22.75. IR

(thin film, cm^{-1}): $\nu_{C=O}$ 1755 cm^{-1}, IR (CH_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1761 cm^{-1}.

1[IMP-pipA]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.0786 mmol) of **1Cl**, and 1 mL of DCM and stirred to dissolve. To the bright orange solution was added 108 mg (0.0.0825 mmol) of **Na[IMP-pipA]**, and the solution immediately turned bright yellow. After less than a minute of stirring, a large amount of pale yellow precipitate was observed. The reaction was allowed to stir for 16 h and the solution was filtered through a frit. The pale yellow solid and yellow filtrate were each dried in vacuo; NMR of each revealed that the solid was the desired product. Yield 79%. Recrystallization of the solid from DCM/1Cl/hexanes yielded X-ray quality crystals of the MeCN adduct. Anal. Calc. for $PdC_{90}N_7O_2F_{30}B_2H_{63} \cdot 1.45\ C_6H_{14}\ 1.35\ CH_2Cl_2$ C, 54.05 %, H, 3.86 %, N, 4.43 %, found C, 54.472 %, H, 3.392 %, N, 3.949 %. ^{1}H NMR of MeCN adduct (500 MHz, CD_2Cl_2) δ 8.54 (br s, 1H, quinolyl), 8.52 – 8.48 (m, 1H, quinolyl), 8.04 (dd, ^3J = 8.1, ^4J = 1.1 Hz, 1H, quinolyl), 7.88 (dd, ^3J = 7.3, ^4J = 1.2 Hz, 1H, quinolyl), 7.65 – 7.57 (m, 2H, quinolyl), 7.44 (t, ^3J = 7.8 Hz, 2H, IPr aryl), 7.32 – 7.27 (m, 6H, IPr aryl + IPr imidazolyl), 7.18 (d, ^3J = 3.2 Hz, 2H, IMP-pipA aryl), 6.73 (d, ^3J = 8.7 Hz, 2H, IMP-pipA aryl), 6.34 (br s, 2H, IMP-pipA imidazolyl), 3.43 (br s, 2H, N-CH_2), 3.09 (br s, 2H, N-CH_2), 3.02 (hept, ^3J = 7.0 Hz, 4H, CH(CH_3)$_2$), 2.16 (s, 3H, MeCN CH_3), 1.52 (s, 2H, N-CH_2-CH_2), 1.34 (s, 4H, N-CH_2-CH_2+ , CH_2-CH_2-CH_2), 1.19 (d, ^3J = 6.7 Hz, 12H, CH(CH_3)$_2$), 1.16 (d, ^3J = 6.8 Hz, 12H, CH(CH_3)$_2$).^{13}C NMR (126 MHz, CD_2Cl_2) δ 176.78, 169.37, 150.36, 149.55, 148.44, 141.22, 139.93, 137.19, 135.40, 132.27, 130.80, 130.10, 129.79, 129.40, 129.32, 128.54, 127.33, 126.12, 125.13, 124.82, 123.16, 35.02, 34.53, 29.45, 28.88, 26.15, 25.64, 24.68, 23.51, 22.75, 20.82, 3.51. IR (thin film, cm^{-1}): $\nu_{C=O}$ 1755 cm^{-1}, IR (CH_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1761 cm^{-1}. Unit cell (MeCN adduct) (XRD) triclinic, a = 15.857(3) Å, b = 19.087(4) Å, c = 19.142(4) Å, α = 115.371(3)°, β = 106.919(3)°, γ = 99.963(4)°.

2[IMP-H]. In an inert atmosphere glovebox, a 4 mL vial was charged with 61 mg (0.094 mmol) *t*BuXPhosAuCl and 2 mL of 1:1 DCM:MeCN, and stirred to dissolve. 123 mg (0.1036 mmol) **Na[IMP-H]** was added to the vial and the solution was stirred for 21 h. The solution was then dried in vacuo, dissolved in 2 mL of DCM, filtered through celite, layered with pentane, and stored at −35 °C. The product crystallized as a colorless solid, yield 68%. Anal. Calc. for $AuPC_{76}N_3F_{30}B_2H_{55}$•1.7 CH_2Cl_2 C, 47.27 %, H, 2.98 %, N, 2.13 %, found C, 47.670 %, H, 2.571 %, N, 2.012. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.89 (td, ^3J = 9.0, ^3J = 8.4, ^4J = 1.6 Hz, 1H, P-aryl), 7.67 – 7.57 (m, 2H, P-aryl), 7.36 – 7.30 (m, 1H, P-aryl), 7.16 (br s, 4H, P-aryl + IMP-H aryl), 7.04 (tt, ^3J = 7.5, ^4J =1.1 Hz, 1H, IMP-H imidazolyl), 6.71 (t, ^3J = 8.0 Hz, 2H, IMP-H aryl), 6.39 – 6.31 (m, 2H, IMP-H imidazolyl), 2.95 (hept, ^3J = 7.0 Hz, 1H, Ar-CH(CH_3)$_2$), 2.33 (hept + s, ^3J = 6.7 Hz, 5H, Ar-CH(CH_3)$_2$ + MeCN CH_3), 1.42 (d, ^3J = 16.3 Hz, 18H, P-C(CH_3)$_3$), 1.33 (d, ^3J = 6.9 Hz, 6H, Ar-CH(CH_3)$_2$), 1.26 (d, ^3J = 6.8 Hz, 6H, Ar-CH(CH_3)$_2$), 0.93 (d, J = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 150.20, 149.57, 147.78, 135.25, 134.57, 131.98, 129.15, 128.86, 128.67, 127.98, 124.69, 124.65, 122.28, 39.15, 38.93, 34.44, 31.38, 31.34, 31.31, 26.15, 23.22. ^{31}P NMR (203 MHz, CD_2Cl_2) δ 58.32.

2[IMP-CF$_3$]. In an inert atmosphere glovebox, a 4 mL vial was charged with 47 mg (0.0696 mmol) *t*BuXPhosAuCl and 2 mL of 1:1 DCM:MeCN, and stirred to dissolve. 100 mg (0.104 mmol) **Na[IMP-CF$_3$]** was added to the vial and the solution was stirred for 17 h. The solution was then dried in vacuo, dissolved in 2 mL of DCM, filtered through celite, layered with hexamethyldisiloxane, and stored at −35 °C. The product crystallized as a colorless solid, yield 67%. Anal. Calc. for $AuPC_{77}N_3F_{33}B_2H_{54}$·1.5 CH_2Cl_2 C, 46.56 %, H, 2.84 %, N, 2.07 %, found C, 46.000 %, H, 2.723 %, N, 2.320%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.89 (td, ^3J = 8.9, ^3J = 8.4, ^4J = 1.5 Hz, 1H, P-aryl), 7.66 – 7.57 (m, 2H, P-aryl), 7.33 (ddd, ^3J = 7.3, ^3J = 4.9, ^4J = 1.8 Hz, 1H, P-aryl), 7.20 (s, 2H, IMP-CF_3 aryl), 7.17 (s, 2H, P-aryl), 7.01 (d, ^3J = 8.4 Hz, 2H, IMP-CF_3 aryl), 6.58 (d, ^3J = 7.7 Hz, 2H, IMP-CF_3 imidazolyl), 2.95 (hept, ^3J = 6.7 Hz, 1H, Ar-CH(CH_3)$_2$), 2.32 (hept + s, ^3J = 6.7 Hz, 5H, Ar-CH(CH_3)$_2$ + MeCN CH_3), 1.42 (d, ^3J = 16.3 Hz, 18H, P-C(CH_3)$_3$), 1.33 (d, ^3J = 6.9 Hz, 6H, Ar-CH(CH_3)$_2$), 1.26 (d, ^3J = 6.8 Hz, 6H, Ar-CH(CH_3)$_2$), 0.93 (d, ^3J = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.80, 135.27, 131.99, 129.93, 127.99, 125.28, 122.29, 39.17, 38.95, 34.45, 31.40, 31.35, 26.15, 24.34, 23.24.^{31}P NMR (202 MHz, CD_2Cl_2) δ 58.48. Unit cell (XRD) monoclinic P, a = 11.2277(11) Å, b = 21.034(2) Å, c = 17.1640(18) Å, β = 98.416(2)°.

2[IMP-NO$_2$]. In an inert atmosphere glovebox, a 4 mL vial was charged with 61 mg (0.094 mmol) tBuXPhosAuCl and 2 mL of 1:1 DCM:MeCN, and stirred to dissolve. 128 mg (0.104 mmol) **Na[IMP-NO$_2$]** was added to the vial and the solution was stirred for 18 h. The solution was then dried in vacuo, dissolved in 2 mL of DCM, filtered through celite, layered with pentane, and stored at −35 °C. The product crystallized as a colorless solid, yield 69%. Anal. Calc. for $AuPC_{76}N_4F_{30}B_2H_{54}O_2$•0.85$CH_2Cl_2$, 47.41 %, H, 2.88 %, N, 2.88 %, found C, 47.851 %, H, 2.437 %, N, 3.010 %. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.92 – 7.86 (m, 1H, P-aryl), 7.66 – 7.56 (m + d, ^3J = 9.3, 2H + 2H, P-aryl + IMP-NO_2 aryl), 7.33 (ddd, ^3J = 7.3, ^3J = 4.9, ^4J = 1.5 Hz, 1H, P-aryl), 7.24 (d, ^3J = 3.7 Hz, 2H, IMP-NO_2 aryl), 7.16 (s, 2H, P-aryl), 6.60 (d, ^3J = 8.0 Hz, 2H, IMP-NO_2 imidazolyl), 2.95 (hept, ^3J = 7.0 Hz, 1H, Ar-CH(CH_3)$_2$), 2.33 (hept + s, ^3J = 6.7 Hz, 3H + 2H, Ar-CH(CH_3)$_2$ + MeCN CH_3), 1.44 (s, 9H, P-C(CH_3)$_3$), 1.40 (s, 9H, P-C(CH_3)$_3$), 1.33 (d, ^3J = 6.9 Hz, 6H, Ar-CH(CH_3)$_2$), 1.26 (d, ^3J = 6.8 Hz, 6H, Ar-CH(CH_3)$_2$), 0.93 (d, J = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 150.20 , 147.78, 147.39, 146.65, 134.58, 132.00, 130.86, 127.98, 126.00, 125.55, 125.51, 122.28, 122.04, 39.16, 38.93, 34.44, 31.38, 31.34, 26.14, 24.33,23.23. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 58.46.

2[IMP-CO$_2$Me]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.0803 mmol) *t*BuXPhosAuCl, and 2 mL of 1:1 DCM:MeCN, and stirred to dissolve. 100 mg (0.104 mmol) **Na[IMP-CO$_2$Me]** was added to the vial and the solution was stirred for 24 h. The solution was then dried in vacuo, dissolved in 2 mL of DCM, filtered through celite, layered with pentane, and stored at −35 °C. The product crystallized as a colorless solid, yield 51%. Anal. Calc. for $AuPC_{78}N_3F_{30}B_2O_2H_{54}$ C, 49.63 %, H, 3.04 %, N, 2.23 %, found C, 49.614 %, H, 3.077 %, N, 2.089%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.92 – 7.86 (m, 1H, P-aryl), 7.61 (dddd, ^3J = 15.0, ^3J = 7.4, ^3J = 5.4, ^4J = 3.7 Hz, 2H, P-aryl), 7.38 – 7.31 (d + m, ^3J = 9.08, 2H + 1H, IMP-CO_2Me aryl + P-aryl), 7.20 (d, ^3J = 3.6 Hz, 2H, IMP-CO_2Me aryl), 7.16 (s, 2H, P-aryl), 6.44 (s, 2H, IMP-CO_2Me imidazolyl), 3.84 (s, 3H, IMP-CO_2CH_3), 2.94 (hept, ^3J = 7.0 Hz, 1H, Ar-CH(CH_3)$_2$), 2.33 (hept + s, ^3J = 6.3 Hz, 2H+ 3H, Ar-CH(CH_3)$_2$ + MeCN CH_3), 1.42 (d, ^3J = 16.3 Hz, 18H, P-C(CH_3)$_3$), 1.33 (d, ^3J = 6.9 Hz, 6H, Ar-CH(CH_3)$_2$), 1.26 (d, ^3J = 6.8 Hz, 6H, Ar-CH(CH_3)$_2$), 0.93 (d, ^3J = 6.6 Hz, 6H, Ar-

CH(CH_3)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.77, 135.24, 131.98, 128.15, 122.28, 52.61, 39.15, 34.44, 31.33, 26.14, 24.33, 23.22. ^{31}P NMR (203 MHz, CD_2Cl_2) δ 58.32. Unit cell (XRD) monoclinic P, a = 11.4352(19) Å, b = 20.494(3) Å, c = 17.462(3) Å, β = 98.794(4)°.

2[BIMP]. In an inert atmosphere glovebox, a 4 mL vial was charged with 61 mg (0.094 mmol) *t*BuXPhosAuCl and 2 mL of 1:1 DCM:MeCN, and stirred to dissolve. 129 mg (0.1036 mmol) **Na[BIMP]** was added to the vial and the solution was stirred for 24 h. The solution was then dried in vacuo, dissolved in 2 mL of DCM, filtered through celite, layered with pentane, and stored at −35 °C. The product crystallized as a colorless solid, yield 83%. Anal Calc. for $AuPC_{80}N_3F_{30}B_2H_{59}\cdot 0.5CH_2Cl_2$ C, 50.24 %, H, 3.14 %, N, 2.18 %, found C, 50.528 %, H, 2.965 %, N, 2.154. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.92 – 7.87 (m, 1H, P-aryl), 7.67 – 7.57 (m, 2H, P-aryl), 7.53 (br s, 2H, BIMP aryl), 7.33 (ddd, ^3J = 7.3, ^3J = 3.4, ^4J = 1.6 Hz, 4H, BIMP aryl), 7.17 (s, 2H, P-aryl), 6.96 (m, 2H, P-aryl + BIMP aryl), 6.80 (br s, 1H, BIMP aryl), 2.94 (hept, ^3J = 7.2 Hz, 1H, Ar-CH(CH_3)$_2$), 2.40 – 2.19 (hept + s, ^3J = 6.3 Hz, 5H, Ar-CH(CH_3)$_2$ + MeCN CH_3), 1.42 (d, ^3J = 16.3 Hz, 18H, P-C(CH_3)$_3$), 1.33 (d, ^3J = 6.9 Hz, 6H, Ar-CH(CH_3)$_2$), 1.26 (d, ^3J = 6.8 Hz, 6H, Ar-CH(CH_3)$_2$), 0.93 (d, ^3J = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 180.71, 150.23, 147.81, 137.88, 135.22, 134.59, 132.02, 127.93, 122.90, 122.30, 116.13, 39.18, 38.95, 31.36, 26.16, 24.34, 23.24. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 58.48. Unit cell (XRD) monoclinic P, a = 11.2277(11) Å, b = 21.034(2) Å, c = 17.1640(18) Å, β = 98.416(2)°. Unit cell (XRD) triclinic, a = 15.447(3) Å, b = 17.053(3) Å, c = 18.040(3) Å, α = 67.410(3)°, β = 82.920(4)°, γ = 84.125(4)°.

3[IMP-H]. In an inert atmosphere glovebox, a 4 mL vial was charged with 26 mg (0.0425 mmol) IPrAuCl, 60 mg (0.319 mmol) diphenylacetylene, and 60 mg (0.04675 mmol) **Na[IMP-H]**. DCM (2 mL) was added and the reaction immediately began to turn purple, likely due to formation of gold nanoparticles. The reaction was stirred for 7 minutes, at which time it was filtered through celite, layered with pentane, and placed in the freezer, resulting in the formation of colorless X-ray quality crystals. Yield 45%. Anal. Calc. for $AuC_{86}N_4F_{30}B_2H_{57}\bullet 2\ CH_2Cl_2$ C, 50.22 %, H, 2.92 %, N, 2.66 %, found C, 50.397 %, H, 2.522 %, N, 2.683. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66 (t, ^3J = 7.8 Hz, 2H, IPr aryl), 7.49 (t, ^3J = 8.2 Hz, 2H, diphenylacteylene aryl), 7.45 (s, 2H, IPr imidazolyl), 7.36 (d, ^3J = 7.8 Hz, 4H, IPr aryl), 7.27 (t, ^3J = 7.9 Hz, 4H, diphenylacetylene aryl), 7.17 (d, ^4J = 2.9 Hz, 2H, IMP-H aryl), 7.06 – 7.01 (m, 1H, IMP-H aryl), 6.94 – 6.89 (m, 4H, diphenylacetylene aryl), 6.71 (t, ^3J = 8.0 Hz, 2H, IMP-H aryl), 6.36 (d, ^3J = 7.4 Hz, 2H, IMP-H imidazolyl), 2.48 (hept, ^3J = 6.9 Hz, 4H, CH(CH_3)$_2$), 1.24 (d, ^3J = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.13 (d, ^3J = 6.9 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.27, 133.23, 132.37, 132.29, 132.06, 129.77, 129.17, 128.66, 127.40, 125.28, 125.20, 117.45, 89.81, 29.31, 24.67, 24.14. Unit cell (XRD) triclinic, a = 13.708(2) Å, b = 18.136(3) Å, c = 18.494(3) Å, α = 113.739(3)°, β = 97.758(3)°, γ = 99.532(3)°.

3[IMP-CF$_3$]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.08 mmol) IPrAuCl, 72 mg (0.40 mmol) diphenylacetylene, and 100 mg (0.08 mmol) **Na[IMP-CF$_3$]**. DCM (2 mL) was added and the reaction immediately began to turn purple, likely due to formation of gold nanoparticles. The reaction was stirred for 2 minutes, at which time it was filtered through celite, layered with pentane, and placed in the freezer, resulting in the formation of colorless X-ray quality crystals. Yield 96%. Anal. Calc. for $AuC_{87}N_4F_{33}B_2H_{56}\bullet 0.5\ C_5H_{12}$ C, 52.72 %, H, 2.82 %, N, 2.80 %, found C, 52.891 %, H, 2.860 %, N, 2.877. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66 (t, ^3J = 7.8 Hz, 2H, IPr aryl), 7.49 (t, ^3J = 8.2 Hz, 2H, diphenylacetylene aryl), 7.45 (s, 2H, IPr imidazolyl), 7.36 (d, ^3J = 7.8 Hz, 4H, IPr aryl), 7.27 (t, ^3J = 7.9 Hz, 4H, diphenylacetylene aryl), 7.19 (d, ^4J = 2.6 Hz, 2H, IMP-CF$_3$ aryl), 7.00 (d, ^3J = 8.4 Hz, 2H, IMP-CF$_3$ aryl), 6.94 – 6.90 (m, 4H, diphenylacetylene aryl), 6.58 (d, ^3J = 7.9 Hz, 2H, IMP-CF$_3$ imidazolyl), 2.48 (hept, ^3J = 6.9 Hz, 4H, CH(CH_3)$_2$), 1.24 (d, ^3J = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.13 (d, ^3J = 6.9 Hz, 12H, CH(CH_3)$_2$).^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.27, 133.38, 132.30, 129.77, 125.20, 73.85, 29.32, 24.68, 24.17. Unit cell (XRD) triclinic, a = 15.320(11) Å, b = 18.411(14) Å, c = 19.587(18) Å, α = 62.891(19)°, β = 67.043(13)°, γ = 89.683(14)°.

3[IMP-NO$_2$]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.08 mmol) IPrAuCl, 72 mg (0.40 mmol) diphenylacetylene, and 99 mg (0.08 mmol) **Na[IMP-NO$_2$]**. DCM (2 mL) was added and the reaction immediately began to turn purple, likely due to formation of gold nanoparticles. The reaction was stirred for 2 minutes, at which time it was filtered through celite, layered with pentane, and placed in the freezer, resulting in the formation of colorless crystals. Yield 72%. Anal. Calc. for $AuC_{86}N_5F_{30}B_2H_{56}O_2$ C, 52.17 %, H, 2.85 %, N, 3.54 %, found C, 52.389 %, H, 2.757 %, N, 3.666. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.67 (d, ^3J = 7.9 Hz, 2H, IPr aryl), 7.58 (d, ^3J = 9.1 Hz, 2H, IMP-NO$_2$ aryl), 7.50 (t, ^3J = 7.0 Hz, 2H, diphenylacetylene aryl), 7.46 (s, 2H, IPr imidazolyl), 7.36 (d, ^3J = 7.8 Hz, 4H, IPr aryl), 7.30 – 7.24 (m, 4H, diphenylacetylene aryl), 7.23 (d, ^3J = 4.1 Hz, 2H, IMP-NO$_2$ aryl), 6.94 – 6.90 (m, 4H, diphenylacetylene aryl), 6.58 (d, ^3J = 8.0 Hz, 2H, IMP-NO$_2$ imidazolyl), 2.48 (hept, ^3J = 7.0 Hz, 4H, CH(CH_3)$_2$), 1.24 (d, ^3J = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.13 (d, ^3J = 6.9 Hz, 12H, CH(CH_3)$_2$).^{13}C NMR (126 MHz, CD_2Cl_2) δ 175.07, 146.27, 132.30, 130.79, 129.77, 125.20, 121.99, 29.32, 24.68, 24.17.

4[IMP-H]. In an inert atmosphere glovebox, a 4 mL vial was charged with 50 mg (0.08 mmol) IPrAuCl, 14 µL (0.12 mmol) 3-hexyne, and 2 mL of DCM, and stirred to dissolve. **Na[IMP-H]** (106 mg, 0.09 mmol) was added, and the reaction immediately turned purple, indicating the formation of gold nanoparticles. The reaction was stirred for half an hour, filtered through celite, layered with pentane, and placed in the glovebox freezer, resulting in the formation of colorless X-ray quality crystals. Yield 90%. Anal. Calc. for $AuC_{78}N_4F_{30}B_2H_{54}$ C, 51.03 %, H, 2.96 %, N, 3.05 %, found C, 50.920 %, H, 2.809 %, N, 2.970. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.58 (t, ^3J = 7.8 Hz, 2H, IPr aryl), 7.44 (s, 2H, IPr imidazolyl), 7.38 (d, ^3J = 7.8 Hz, 4H, IPr aryl), 7.17 (d, ^4J = 2.8 Hz, 2H, IMP-H aryl), 7.05 – 7.01 (m, 1H, IMP-H aryl), 6.71 (t, ^3J = 8.0 Hz, 2H, IMP-H aryl), 6.36 (d, ^3J = 7.2 Hz, 2H, IMP-H imidazolyl), 2.51 (hept, ^3J = 7.0 Hz, 4H, CH(CH_3)$_2$), 2.25 – 2.18 (m, 4H, C≡C-CH_2), 1.28 (dd, ^3J = 9.3, ^3J = 6.9 Hz, 24H, CH(CH_3)$_2$), 0.61 (t, J = 7.5 Hz, 6H, C≡C-CH$_2$-CH_3). Unit cell (XRD) monoclinic P, a = 12.184(6) Å, b = 19.349(10) Å, c = 33.546(17) Å, β = 96.835(9)°.

***t*BuXPhos)AuOTs.** In an inert atmosphere glovebox, a 4 mL vial was charged with 53 mg (0.081 mmol) *t*BuXPhosAuCl and 1 mL of DCM and stirred to dissolve. 25 mg (0.089 mmol) AgOTs was added to the vial and the reaction was stirred for 17 hours. The solution was filtered through celite and layered with pentane, but the resulting product is too soluble to recrystallize in this method. The solution was dried in vacuo, and was

determined to be pure by NMR, yield 90%. Anal Calc. for $AuPC_{80}N_3F_{30}B_2H_{59}$ C, 54.54 %, H, 6.61 %, N, 0 %, found C, 54.371 %, H, 6.391 %, N, 0.018. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.87 (td, ^3J = 8.1, ^4J = 1.4 Hz, 1H, P-aryl), 7.64 (d, ^3J = 8.1 Hz, 2H, OTs aryl), 7.57 – 7.48 (m, 2H, P-aryl), 7.34 – 7.30 (m, 1H, P-aryl), 7.18 (d, ^3J = 8.0 Hz, 2H, OTs aryl), 7.06 (s, 2H, P-aryl), 2.78 (hept, ^3J = 6.8 Hz, 1H, Ar-C*H*$(CH_3)_2$), 2.36 (s, 3H, OTs *CH*$_3$), 2.29 (hept, ^3J = 6.6 Hz, 2H, Ar-C*H*$(CH_3)_2$), 1.36 (s, 9H, P-C(*CH*$_3$)$_3$), 1.33 (s, 9H, P-C(*CH*$_3$)$_3$), 1.24 (dd, ^3J = 13.5, ^3J = 6.9 Hz, 12H, Ar-CH(*CH*$_3$)$_2$), 0.90 (d, ^3J = 6.6 Hz, 6H, Ar-CH(*CH*$_3$)$_2$). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 150.41, 148.34, 146.51, 135.10, 134.40, 130.95, 129.06, 127.02, 126.69, 121.94, 38.77, 38.54, 34.50, 31.26, 26.35, 24.07, 22.98, 21.44. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 57.19.

General procedure for [2+2] cycloadditions. An 1800 μL CD_2Cl_2 or toluene-d_8 stock solution of 0.00169 mmol **2**[X] and 51 mg (0.3 mmol) of 1,3,5-trimethoxybenzene (internal standard) was prepared in an inert atmosphere glovebox. 44 μL (0.338 mmol) α-methylstyrene and 19 μL (0.169 mmol) phenyl acetylene were each added to three NMR tubes. 600 μL of catalyst stock solution was then added to each tube. The tubes were capped, shaken, and removed from the glovebox, and spectra were recorded at regular intervals. Yields are calculated based on ratios of integrations of product versus internal standard.

General procedure for alkyne hydroalkoxylations. Gold catalyst (0.0022 mmol) and 1,3,5,-trimethoxybenzene (7 mg, 0.044 mmol) were weighed into vials in an inert atmosphere glovebox, capped, and removed. To each vial was added 400 μL CD_2Cl_2, 100 μL (0.88 mmol) 3-hexyne, and 1.76 mmol nucleophile sequentially. The vials were capped and shaken, and the solutions were transferred to NMR tubes. Spectra were recorded at regular intervals and yields were calculated based on ratios of integrations of product versus internal standard (trimethoxybenzene).

ASSOCIATED CONTENT

Supporting Information

Supporting Information:

NMR spectra and IR spectra for all new compounds (PDF)
Crystal structure reports for all X-ray structures (PDF)

Accession Codes

CCDC 1919818-1919840 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

* E-mail: dob@temple.edu

ORCID

Graham E. Dobereiner: 0000-0001-6885-2021

Notes

The authors declare no competing financial interest.

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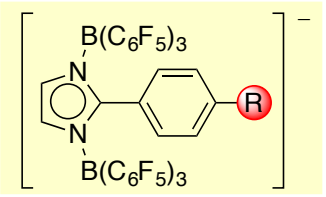
Imidazolyl-phenyl (IMP) anions



$[IMP\text{-}R]^-$

Tunable platform for controlling coordinating ability

R = H, CF_3, NO_2, CO_2Me, $CONR_2$...