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New Phosphine-Functionalized NHC Ligands: Discovery of an Effective Catalyst for the Room-Temperature Amination of Aryl Chlorides with Primary and Secondary Amines

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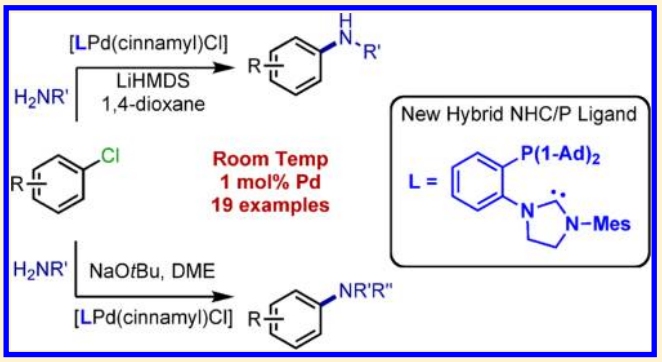
Supporting Information

ABSTRACT: We report convenient and high-yielding syntheses of new phosphine-functionalized dihydroimidazolium salts and demonstrate their utility as ligand precursors for Buchwald–Hartwig amination. Several examples of the general formula [1-Mes-3-{2-(PR_2)phenyl}imidazolidin-2-ylium][BF_4] have been prepared, where phosphines of varying steric and electronic properties (R = Ph (**9**), Cy (**10**), 1-Ad (**11**)) are tethered by an *o*-phenylene group. The synthesis was not adaptable to *N*-aryl groups other than mesityl, giving unexpected phosphonium salt species instead. The synthesis was adapted to flexible benzyl-linked variants of the formula [1-Ar-3-{2-(PCy_2)benzyl}imidazolidin-2-ylium][BF_4], which allowed more steric variation of the dihydroimidazolium *N*-aryl group (Ar = Mes (**21**), Dipp (**22**)). A preliminary study of these hybrid NHC/P ligands in Buchwald–Hartwig amination catalysis (in situ precatalyst formation) revealed **11** to be the most active of the series. Premixing the isolated free NHC ligand 1-Mes-3-{2-(PAd_2)phenyl}imidazolidin-2-ylidene (**23**) with [Pd(cinnamyl)Cl]$_2$ provided a highly active precatalyst that performed well at room temperature and 1 mol % catalyst loading. The system was shown to have an unprecedented ability to arylate both primary alkylamines (monoarylation) and secondary dialkylamines with aryl chlorides at room temperature. Electron-rich and -poor aryl and heteroaryl halides, as well as those featuring *ortho* substitution, were well tolerated, while substrates featuring both primary and secondary amine groups were selectively arylated at the NH_2 position. Furthermore, a preliminary examination of performance in ammonia arylation and acetone α-arylation showed promising results, giving good conversion and high selectivity for monoarylation in both cases.



INTRODUCTION

Late-transition-metal catalysis plays a central role in modern chemical synthesis, in facilitating otherwise challenging or impossible bond-forming reactions at low loadings and with high activity and selectivity.[1] Indeed, it is not an overstatement to say that late-metal catalysis has revolutionized the way in which chemists think about constructing organic molecules on benchtop and industrial scales, enabling the streamlined synthesis of many target molecules under mild conditions without the need for stoichiometric reagents, protecting groups, or preactivated substrates.[1] In this regard, the continued development of late-transition-metal catalysis can be viewed as contributing positively toward the establishment of more sustainable chemical protocols. While the early development of late-transition-metal catalysis involved the study of complexes featuring relatively simple ancillary coligands (e.g., PPh_3), the ability of more elaborate ligand sets to provide vastly improved catalytic performance has been demonstrated in diverse applications. Such observations have given rise to the burgeoning domain of ancillary ligand design within the field of late-transition-metal catalysis.

Our recent research efforts have been directed in part toward palladium-catalyzed C–N cross-coupling (i.e., Buchwald–Hartwig amination, BHA), which has emerged as a broadly useful methodology for the construction of aniline derivatives.[2] Early pioneering work by the groups of Buchwald and Hartwig focused primarily on monodentate phosphine as well as simple bis(phosphine) ligands.[2a,b] In the ensuing years, important advances in the field by these and other research groups have come from the development and/or application of more intricately designed bidentate ligands that enhance catalytic performance. In particular, practical catalysts for BHA can largely be attributed to the development of biaryl monophosphine ligands by Buchwald that exhibit κ^2P,C-bidentate ligation[3] (including ^{t}BuBrettPhos),[4] and use of κ^2P,P-bis(phosphine) ligands by Hartwig,[2b] including the JosiPhos family of ligands (Figure 1).[5] Recent work from our group has built upon this foundation through the development of the DalPhos family of ligands, which include potentially heterobidentate P,N (e.g., Mor-DalPhos, Figure 1)[6] and P,O (e.g.,

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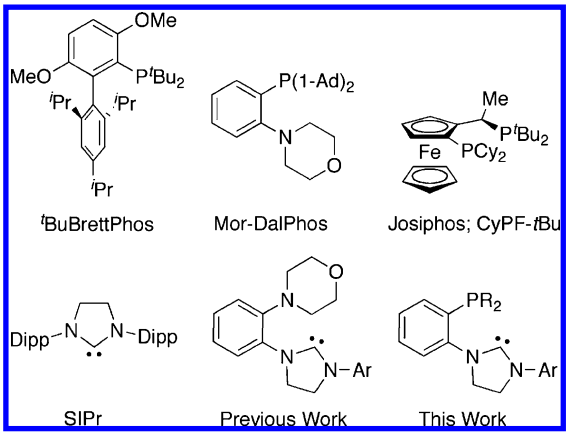

Figure 1. Selection of phosphine and NHC ligands employed in Buchwald–Hartwig amination catalysis and functionalized NHC ligands employed in previous studies and in this study.

OTips-DalPhos)[7] variants that have proven useful in a range of challenging BHA applications.

N-heterocyclic carbenes (NHCs) represent a complementary class of ancillary ligands that have proven to be particularly effective in BHA chemistry. Of particular importance are the (NHC)Pd(cinnamyl)Cl precatalyst complexes developed by Nolan and co-workers, where the NHC is the saturated monodentate SIPr (Figure 1)[8] or alternatively the more sterically encumbered IPr*.[9] These catalysts are notable for excellent performance in the arylation of secondary amine and primary aniline substrates at room temperature and/or low catalyst loadings. Additionally, Organ and co-workers have developed the highly active PEPPSI precatalysts featuring an unsaturated monodentate NHC coligand, such as IPr or IPent.[10] These catalysts also offer excellent performance in the arylation of secondary amines and primary anilines and are notable for their ease of preparation and handling. Despite the established utility of (hetero)bidentate phosphine-based ancillary ligands (vide supra), a careful survey of the literature reveals that the application of conceptually related heterobidentate NHCs has received relatively little attention in BHA chemistry.

In this context, we were motivated to examine analogous heterobidentate NHC ligands for application in BHA chemistry. Encouraged by the remarkable reactivity properties exhibited by catalysts featuring Mor-DalPhos, we recently developed a heterobidentate ligand variant featuring an NHC in place of the phosphorus donor group.[11] However, these morpholino-tethered NHC ligands performed rather poorly in BHA in comparison with both their monodentate NHC counterparts and Mor-DalPhos. The high lability of the Pd–N(morpholino) bond and the accompanying diminished steric demands of the ligand represent possible sources of poor performance.

In the present study, we have adapted our approach by targeting related phosphine-functionalized NHC ligands (Figure 1). We reasoned that the improved ligating ability of a phosphine relative to an amine would enforce a rigid chelate geometry, reminiscent of bis(phosphines) and related ligands. The resulting increase in steric hindrance could contribute in part to facilitating C–N bond-forming reductive elimination, which often represents the rate-limiting step in BHA chemistry. This research direction is also inspired by the development of [Pd(NHC)(PR$_3$)] complexes by Cazin and Nolan, which have shown new reactivity profiles and many useful applications in catalysis.[12]

Although no such phosphine-functionalized NHC ligands have been applied in BHA, various examples have been synthesized for use in other applications. Among these are a number of examples with different linkers between the NHC and phosphine groups, including designs with alkyl,[13] benzyl,[14] anthracene,[15] and phenylene[16] linkers, as well as some chiral examples,[17] and recently a directly linked *N*-phosphanyl NHC.[18] Additionally, there are examples of hybrid pincer-type ligands containing both types of donor groups.[19] It is notable that the vast majority of these phosphine-functionalized NHC ligands incorporate a diphenylphosphino donor fragment; the application of bulkier and more electron rich phosphines in this capacity remains underexplored.

Herein we report the synthesis and characterization of two types of phosphine-functionalized dihydroimidazolium salts, in which the two groups are linked by either an *o*-phenylene or a benzyl group. The unexpected formation of unusual new types of phosphonium salts is also reported. Notably, a variant that incorporates a bis(1-adamantyl)phosphino donor group is shown to give highly active catalysts for BHA, resulting in the first single-ligand catalyst system capable of room-temperature amination of unactivated aryl chlorides involving both primary and secondary alkylamines.

RESULTS AND DISCUSSION

Dihydroimidazolium Salt Syntheses. As an extension of our previous work on morpholine-functionalized NHC ligands,[11] we have chosen to pursue a directly analogous ligand design in which an *o*-phenylene group rigidly links the phosphine and NHC donors. A series of NHC–phosphine ligands of this type have been prepared previously by Zhou and co-workers.[16] However, the reported synthetic route is low-yielding and inconvenient and is limited to diphenylphosphino derivatives. We therefore sought to develop a more convenient and flexible synthetic route similar to what we developed previously for the synthesis of morpholino-functionalized NHC ligands.[11] Such morpholine-functionalized NHC ligands are prepared from *o*-bromoiodobenzene, whereby the ligand is generated through two palladium-catalyzed C–N cross-coupling steps. Adapting this methodology to the phosphine-functionalized NHCs sought after herein requires the installation of the diamine moiety in the first step, even though its presence in the second step creates a potential chemoselectivity challenge (i.e., inter-/intramolecular C–N versus intermolecular C–P bond formation). Installation of the diamine was accomplished easily using the conditions for selective cross-coupling of dihalogenated benzenes established by Jørgensen and co-workers,[20] giving **1**–**3** in high yield and purity within 30 min (Scheme 1).

Our preliminary examination of the C–P cross-coupling step focused initially on the *N*-mesityl diamine **1**. Under standard C–P cross-coupling conditions, both PPh$_2$ and PCy$_2$ groups could be selectively installed with negligible formation of competing C–N intermolecular or intramolecular cross-coupling products, giving compounds **4** and **5**, respectively. In the case of P(1-Ad)$_2$ installation, some minor products, presumed to be due to undesired C–N coupling, were formed. Nonetheless, under our standard conditions, compound **6** was isolated in 62% yield. We then examined the cyclization step using the established protocol employing triethyl orthoformate as the precarbenic unit.[21] With no precautions to exclude air

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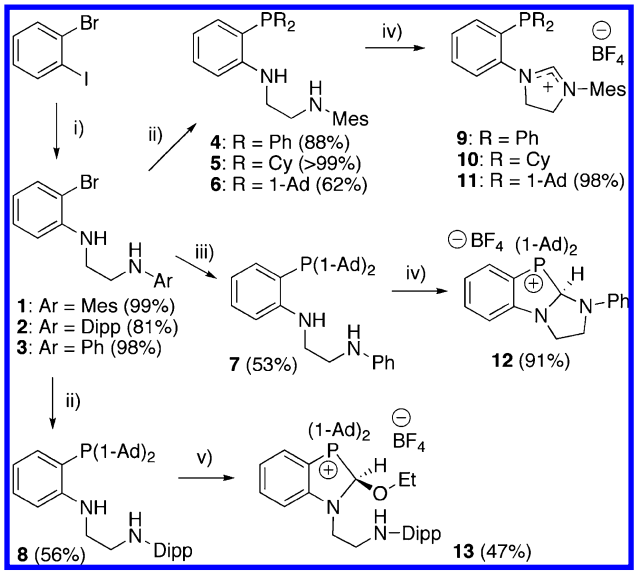
Scheme 1. Three-Step Synthesis of Dihydroimidazolium Salts 9–11 and Phosphonium Salts 12 and 13[a]



[a]Conditions: (i) 1.05 equiv of *N*-aryl-1,2-diaminoethane, 1.4 equiv of NaO*t*Bu, 0.5 mol % of $Pd_2(dba)_3$, 2 mol % of Xantphos, toluene ([ArI] = 1 M), 110 °C, 30 min; (ii) 2 mol % of $Pd(OAc)_2$, 2.4 mol % of DiPPF, toluene ([ArBr] = 0.25 M), 1/1/1.4 ArCl/HPR_2/NaO*t*Bu; (iii) 2 mol % of $Pd(OAc)_2$, 2.4 mol % of DiPPF, 1,4-dioxane ([ArBr] = 0.25 M), 1/1/1.4 ArCl/$HP(1\text{-Ad})_2$/Cs_2CO_3; (iv) $CH(OEt)_3$, 1.2 equiv of NH_4BF_4, 110-120 °C, 0.5–1 h; (v) $CH(OEt)_3$, 1.2 equiv of NH_4BF_4, 80 °C, 10 min.

and moisture from the reaction, the three dihydroimidazolium salts **9**–**11** were isolated in high yield. The ^{31}P NMR chemical shifts are indicative of neutral phosphines (**9**, −18.2 ppm; **10**, −16.5 ppm; **11**, 14.2 ppm), while new aromatic peaks corresponding to the dihydroimidazole C2 position were observed in the ^1H NMR spectra (7.74–7.82 ppm). Compound **11** was isolated in very high purity, while **9** and **10** were isolated in ca. 80% purity, as determined by integration of the ^{31}P NMR spectra, with minor byproducts exhibiting downfield chemical shifts around δ 25 and 39, respectively. Performing this cyclization step under an atmosphere of N_2 gave the same result, ruling out phosphine oxide formation as the source of these impurities. As such, we attribute the impurities observed in the synthesis of **9** and **10** as likely corresponding to the formation of a phosphonium salt, analogous to **12** and **13** (vide infra).

Given the superior yield and purity of the $P(1\text{-Ad})_2$ variant **11** in the cyclization reaction, we sought to prepare further derivatives featuring this bulky phosphine group. We found the less bulky precursor **7** to be inaccessible under our standard P–C coupling conditions, giving instead the tetrahydroquinoxaline product of intramolecular amination. By modifying the conditions (Cs_2CO_3, 1,4-dioxane), the desired phosphine **7** was obtained in 53% yield. Standard cyclization conditions then cleanly afforded a new compound (**12**) in high yield, but with NMR signatures that deviated significantly from those of the *N*-mesityl variant **11**. Specifically, the ^{31}P NMR chemical shift of the *N*-phenyl species **12** (δ 36.2) is downfield of the bulkier *N*-mesityl analogue, while the newly installed CH functionality is shifted upfield to δ 6.61 in the ^1H NMR spectrum. Notably, this latter proton resonance exhibited a P–H coupling constant of 24.3 Hz, indicating a close proximity of the phosphine moiety. Single-crystal X-ray diffraction studies revealed **12** to be the phosphonium salt depicted in Scheme 1 and Figure 2.

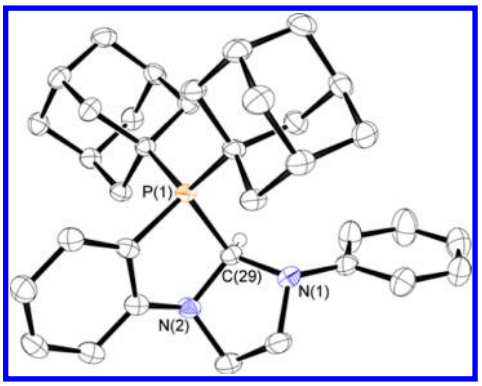


Figure 2. Molecular structure of the cation of **12** with most H atoms omitted and ellipsoids drawn at the 50% probability level.

Evidently, the reduced steric hindrance of this system versus that of **11** enabled nucleophilic attack of the phosphino group at the C2 site of the dihydroimidazolium after cyclization had occurred. The newly formed P–C bond is in the range expected for a single bond (P(1)–C(29) = 1.895(1) Å), while the N–C bond lengths also indicate single-bond character (N(2)–C(29) = 1.479(2) Å; N(1)–C(29) = 1.464(2) Å), rather than the bond order of 1.5 expected for a dihydroimidazolium species. These metrical data along with spectroscopic data support the assignment of this compound as a phosphonium salt. This unique compound represents, to our knowledge, the first example of a β-diamino phosphonium salt. This potential precursor to unique phosphorus ylides, such as those studied by Bertrand and co-workers,[22] remains an interesting avenue for future exploration.

We then attempted to synthesize a bulkier variant of **11** containing an *N*-Dipp (Dipp = 2,6-diisopropylphenyl) group. Installation of the $P(1\text{-Ad})_2$ moiety was readily achieved, giving **8** in moderate yield. However, the standard conditions employed previously for cyclization to the dihydroimidazolium salt consistently gave a mixture of two major products in approximately a 1:1 ratio. One of these features a ^{31}P NMR resonance consistent with the desired dihydroimidazolium salt (δ 14.2), while the ^{31}P NMR resonance of the other appears at δ 32.3, suggesting a phosphonium salt. Longer reaction times or higher reaction temperatures did not change the ratio of products significantly; however, we found that a lower temperature and shorter reaction time gave only the latter compound, which was identified as the phosphonium salt **13** by determination of the X-ray structure (Figure 3). This product, which retains one ethoxy group from the orthoformate, presumably results from nucleophilic attack of the phosphine at the orthoformate carbon at an intermediate stage of the cyclization, thereby blocking the already sterically hindered amine from undergoing conversion to the target dihydroimidazolium salt. All C–heteroatom bonds are in the single-bond range, again indicating a +5 oxidation state of the phosphorus and phosphonium salt character (P(1)–C(27) = 1.876(2) Å; N(1)–C(27) = 1.446(2) Å; O(1)–C(27) = 1.416(2) Å). To our knowledge, **13** represents the first example of a β-amino-β-alkoxy phosphonium salt.

Given the novelty of phosphonium salt **13**, we chose to demonstrate the generality of this synthesis for simpler variants not containing the dangling NHDipp group. To this end, the

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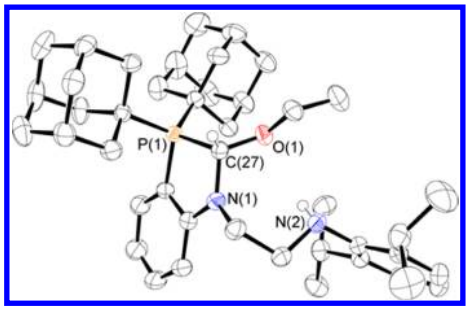
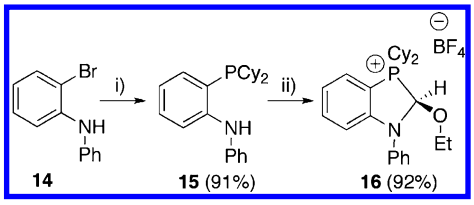


Figure 3. Molecular structure of the cation of **13** with most H atoms omitted and ellipsoids drawn at the 50% probability level.

phosphine precursor **15** was prepared using our established synthetic methodology from the diarylamine **14** (Scheme 2).

Scheme 2. Synthesis of the Phosphonium Salt 16[a]



[a]Conditions: (i) 2 mol % of $Pd(OAc)_2$, 2.4 mol % of DiPPF, toluene ([ArBr] = 0.25 M), 1/1/1.4 ArCl/$HPCy_2$/NaO*t*Bu; (ii) $CH(OEt)_3$, 1.2 equiv of NH_4BF_4, 110 °C, 20 min.

Treating this with acid and triethyl orthoformate under standard cyclization conditions gave **16**, a simplified analogue of the phosphonium salt **13**. Spectroscopic characteristics of this compound are similar to **13**, with a downfield signal in the ^{31}P NMR spectrum at δ 39.5. The connectivity within this compound was verified by determination of the X-ray crystal structure (Figure 4). The metrical parameters found in **16** (P(1)−C(25) = 1.857(2) Å; N(1)−C(25) = 1.453(3) Å; O(1)−C(25) = 1.409(3) Å) are similar to those of **13**, albeit with a noticeable reduction in the P−C distance of 0.019(4) Å that can be attributed to the reduced steric repulsion from the smaller PCy_2 group in **16**.

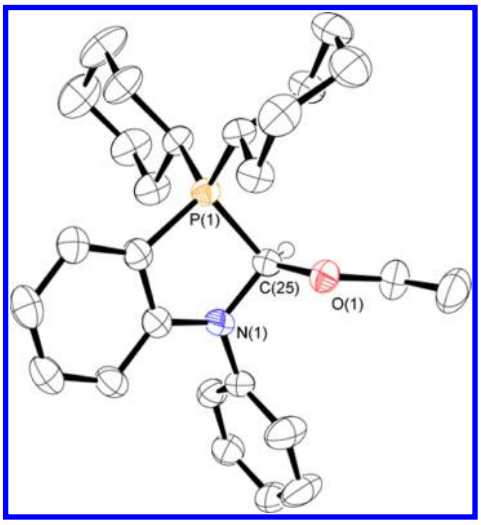
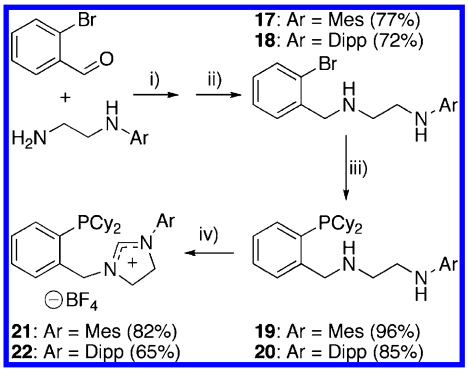


Figure 4. Molecular structure of the cation of **16**, with most hydrogen atoms omitted and ellipsoids drawn at the 50% probability level.

Having established that our synthetic route to phosphine-functionalized dihydroimidazolium salts is not highly amenable to steric variation at the *N*-aryl group, we sought to prepare variants with greater separation between the phosphine and dihydroimidazolium groups, by employing a benzyl linker. Although Zhou and co-workers have disclosed a similar ligand framework, the report featured an unsaturated NHC and is limited to PPh_2 donor fragments.[14b] Our synthetic route to such ligands is depicted in Scheme 3.

Scheme 3. Synthesis of the Phosphine-Functionalized Dihydroimidazolium Salts 21 and 22[a]



[a]Conditions: (i) 1.0 equiv of *N*-aryl-1,2-diaminoethane, toluene, room temperature, 1 h; (ii) 2.0 equiv of $NaBH_4$, anhydrous EtOH, room temperature, 19 h; (iii) 2 mol % of $Pd(OAc)_2$, 2.4 mol % of DiPPF, toluene ([ArBr] = 0.25 M), 1/1.1/1.4 ArCl/$HPCy_2$/NaO*t*Bu; (iv) N_2 atmosphere, $CH(OEt)_3$, 1.2 equiv of NH_4BF_4, 110 °C, 15 min.

Starting from 2-bromobenzaldehyde, the diamine precursors **17** and **18** were prepared via reductive amination in moderate yield. The PCy_2 group was efficiently installed by using the standard Pd-catalyzed coupling methodology, providing **19** and **20** in excellent yield. Unfortunately, the bulkier $P(1\text{-Ad})_2$ variants could not be prepared in an analogous manner, which we attribute to a high susceptibility of the benzylamine site to intermolecular arylation under the reaction conditions.

Under our standard benchtop conditions, attempts to cyclize either **19** or **20** to the corresponding dihydroimidazolium salts gave an intractable mixture of products. However, when the reaction flask was purged of oxygen by sparging the reaction mixture with N_2 prior to heating under dynamic N_2 flow, the desired dihydroimidazolium salts **21** and **22** could be obtained. It should be noted that a short reaction time was necessary to prevent phosphonium salt formation, where heating at 110 °C for 15 min was found to be optimal. The X-ray crystal structure of **21** was obtained (Figure 5), thereby confirming the identity of this expected dihydroimidazolium salt in the solid state.

Catalytic Studies. With these new phosphine-functionalized saturated NHC precursors in hand, we sought to determine their potential utility as ancillary ligands in the BHA of aryl chlorides. We chose to restrict our survey to the five dihydroimidazolium salts **9**−**11**, **21**, and **22**. The initial screening study was conducted with deprotonation and complexation of the NHC precursors carried out in situ (see the Experimental Section for more details), in order to identify the most promising candidate for more careful examination. Coupling between chlorobenzene and a representative series of amines (octylamine, aniline, and morpholine) was surveyed, and the results of this preliminary study are given in Table 1. In a comparison of the structurally related series **9**−**11**, it is

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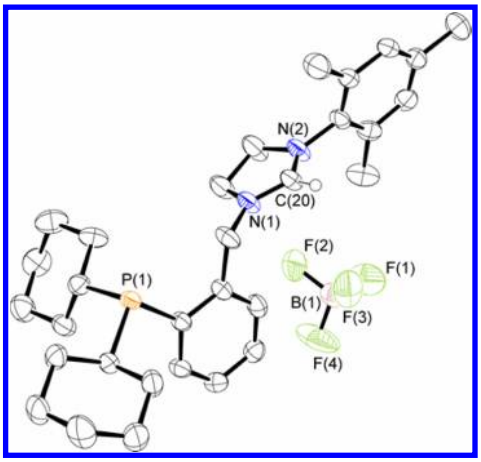
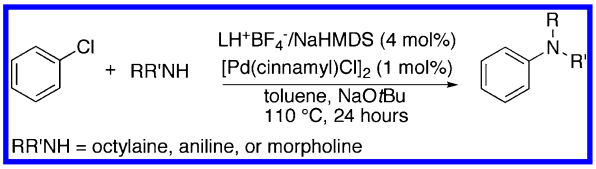


Figure 5. Molecular structure of **21**, with most hydrogen atoms omitted and ellipsoids drawn at the 50% probability level.

Table 1. Preliminary BHA Screening of Palladium Catalysts Generated in Situ from Newly Prepared Dihydroimidazolium Salts[a]



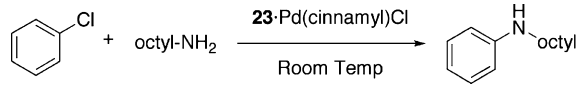
	GC yield (%)		
$LH^+BF_4^-$	octylamine	aniline	morpholine
9	0	2	3
10	16	75	33
11	20	91	8
21	14	59	50
22	6	64	20

[a]Reagents and conditions: PhCl (0.25 mmol), amine (0.3 mmol), NaO*t*Bu (0.35 mmol), toluene (0.5 mL). Yields determined from GC data, calibrated using authentic samples and employing dodecane as an internal standard.

evident that the nature of the phosphine significantly alters the catalytic properties. The least bulky and less donating PPh_2 variant exhibits virtually no activity, while going to the slightly bulkier and more electron rich PCy_2 derivative provides a significant enhancement, giving 75% yield in the arylation of aniline. The more sterically encumbered $P(1\text{-Ad})_2$ variant **11** proved better still, giving 91% yield in the arylation of aniline. Neither of the more flexible analogues **21** and **22** performed better than **11** for the arylation of primary amines, although **21** gave the best result for arylation of morpholine, albeit at only 50% yield. On the basis of these observations, we selected **11** for a more detailed study.

Prior to initiating further catalytic studies, we carried out a preliminary survey of the coordination chemistry of this new ligand system. The dihydroimidazolium salt **11** could be readily deprotonated with NaHMDS to cleanly generate the corresponding phosphine-functionalized free NHC **23** in high yield. This compound exhibits somewhat broadened resonances in the ^1H, ^{31}P, and ^{13}C NMR spectra. The ^{31}P NMR signature is shifted downfield by approximately 5 ppm to δ 19.5 (C_6D_6) relative to **11**, which may indicate a weak interaction between the phosphine and carbene groups (i.e., phosphorus ylide character). However, the appearance of a broad peak in the ^{13}C NMR spectrum at δ 245.1 is consistent with a primarily NHC character for this compound. Mixing **23**, a colorless compound, with $[Pd(cinnamyl)Cl]_2$ (a yellow compound with low solubility in THF) in precisely a 1:1 ratio of ligand to metal in THF gave initially a light red solution, which gradually changed to a very dark red-brown over the course of approximately 30 min. The resulting material, which is presumed to be composed of species of the additive general formula **23**·Pd(cinnamyl)Cl, was isolated after 1 h by removal of volatiles under vacuum. This material proved not to be composed of a single, well-defined species on the basis of solution NMR data; rather, the ^1H NMR spectrum is very broad and featureless. However, the catalytic performance of this precatalyst mixture proved to be vastly superior to in situ precatalyst generation. With a catalyst loading of 2 mol % (toluene, NaO*t*Bu), it was observed that coupling between chlorobenzene and octylamine proceeded rapidly at ambient temperature, giving 85% yield after 15 min and >99% yield within 3 h, with complete monoarylation selectivity (Table 2).

Table 2. Optimization of Conditions for Arylation of Octylamine with Chlorobenzene[a]



amt of Pd (mol %)	solvent	base	GC yeld (%)
2	toluene	NaO*t*Bu	>99[b]
1	toluene	NaO*t*Bu	84
0.5	toluene	NaO*t*Bu	45
0.1	toluene	NaO*t*Bu	7
0.5	DME	NaO*t*Bu	72
0.5	1,4-dioxane	NaO*t*Bu	83
0.5	toluene	KO*t*Bu	69
0.5	DME	KO*t*Bu	22
0.5	1,4-dioxane	KO*t*Bu	63
0.5	DME	LiHMDS	46
0	1,4-dioxane	LiHMDS	92

[a]Reagents and conditions: PhCl (0.25 mmol), amine (0.3 mmol), base (0.35 mmol), solvent (0.5 mL), 24 h. Yields determined from GC data, calibrated using authentic samples and using dodecane as an internal standard. [b]Reaction time 3 h.

The conversions were considerably reduced at lower catalyst loading, to only 45% at 0.5 mol %. Therefore, we optimized conditions at this catalyst loading and found that the best yields were obtained in 1,4-dioxane solvent using LiHMDS base, which gave a yield of 92%.

It is well established that catalyst systems that are highly active and selective for monoarylation of primary alkylamines tend to function poorly for the arylation of secondary amines.[5g,23] In this context, we examined the arylation of morpholine using the precatalyst mixture **23**·Pd(cinnamyl)Cl under ambient-temperature conditions. This reaction proved to be slow in comparison to the octylamine reaction, giving only 56% yield after 3 h using 2 mol % catalyst loading. Therefore, optimization of conditions for arylation of morpholine was performed (Table 3). Optimal conditions proved to be DME solvent and NaO*t*Bu base, giving a 99% yield in only 1 h at ambient temperature.

Having established conditions for room-temperature arylation of these two distinct classes of amines using **23**·Pd(cinnamyl)Cl, we then studied the performance of this

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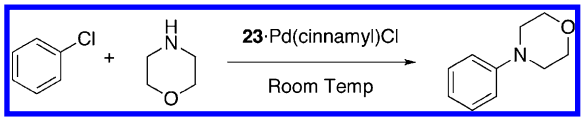
Table 3. Optimization of Conditions for Arylation of Morpholine with Chlorobenzene[a]

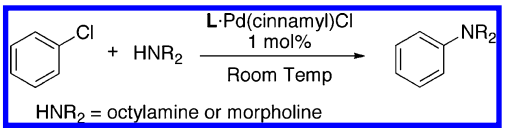


solvent	base	yime (h)	GC yield (%)
toluene	NaO*t*Bu	3	56
THF	NaO*t*Bu	3	58
DME	NaO*t*Bu	1	99
1,4-dioxane	NaO*t*Bu	3	31
N,*N*-DMF	NaO*t*Bu	3	79
DME	KO*t*Bu	1	5
DME	NaHMDS	1	85

[a]Reagents and conditions: 2 mol % Pd, PhCl (0.25 mmol), morpholine (0.3 mmol), base (0.35 mmol), solvent (0.5 mL). Yields determined from GC data, calibrated using authentic samples and employing dodecane as an internal standard.

catalyst system in direct comparison to a representative series of commercially available ligands. These include examples known to be highly effective in the arylation of primary amines (Mor-DalPhos,[6] CyPF-*t*Bu[5]) or secondary amines (SIPr),[8] as well as BippyPhos, which has shown utility for arylation of both primary and secondary amines.[24] Additionally, we have included Buchwald's biaryl ligand *t*BuBrettPhos, which performs extremely well in a broad range of challenging C−N and C−O cross-coupling reactions.[4] All ligands were treated in the same manner as **23**, whereby premixing the ligand with $[Pd(cinnamyl)Cl]_2$ in THF for 1 h, followed by solvent evaporation, was undertaken to give the precatalyst mixtures. BHA reactions were then carried out at ambient temperature, with GC yields determined at 1 and 24 h reaction times (Table 4). For arylation of octylamine, we found that **23**, Mor-DalPhos, and CyPF-*t*Bu all performed well, giving high conversions of 95% or greater after 24 h. The NHC-phosphine ligand **23** gave the most rapid conversion, reaching 98% after only 1 h. SIPr provided high conversion also but suffered poor selectivity, generating appreciable quantities of diarylation product. For the arylation of morpholine, only SIPr and **23** performed well, where SIPr reached quantitative yield in less than 1 h, while **23** reached 93% yield in 1 h and 99% after 24 h. Notably, within this series of ligands, only **23** afforded a catalyst capable of highly efficient arylation of both octylamine and morpholine at room temperature.

Table 4. Comparison between the Phosphine-Functionalized NHC Ligand 23 and Representative Commercially Available Ligands in the Arylation of Morpholine and Octylamine



	octylamine GC yield (%)[a]		morpholine GC yield (%)[b]	
ligand	1 h	24 h	1 h	24 h
23	98	>99	93	99
Mor-DalPhos	87	>99	31	47
SIPr	15	76[c]	100	
CyPF-*t*Bu	13	95	0	3
BippyPhos	13	22	52	53
*t*BuBrettPhos	2	12	0	0

[a]Reagents and (standard) conditions: 1 mol % Pd, PhCl (0.25 mmol), HNR_2 (0.3 mmol), LiHMDS (0.35 mmol), 1,4-dioxane (0.5 mL). Calibrated GC yields. [b]Reagents and conditions: 1 mol % Pd, PhCl (0.25 mmol), HNR_2 (0.3 mmol), NaO*t*Bu (0.35 mmol), DME (0.5 mL). Calibrated GC yields. [c]Reaction gives complete consumption of aryl chloride and 3:1 ratio of monoarylation to diarylation.

No previous reports utilizing Pd(NHC)(cinnamyl)Cl or PEPPSI have demonstrated a single catalyst that can accommodate both of these classes of substrates at ambient temperature. In particular, these catalyst types readily arylate secondary amines or primary anilines at ambient temperature, while primary alkylamines require elevated temperatures and/or the use of ortho-substituted aryl halides.[8−10] The coupling of simple unhindered alkylamines with sterically unbiased and unactivated aryl chlorides is notably absent from these reports. Conversely, Hartwig has shown the JosiPhos system to be highly effective for (hetero)arylation of primary amines at very low catalyst loadings, while the system is ineffective for arylation of secondary amines under similar conditions.[5] The CyPF-*t*Bu/$Pd[P(o\text{-}Tol)_3]_2$ system is highly active for amination of aryl tosylates at room temperature;[5f] however, the only reported use of JosiPhos for amination of a (hetero)aryl chloride at room temperature employed CyPF-*t*Bu/$Pd(OAc)_2$, which coupled octylamine and 2-chloropyridine in high yield within 5 h.[5f] Buchwald's BrettPhos ligand has also displayed excellent performance in monoarylation of primary amines with aryl chlorides, as demonstrated using methylamine as substrate,[25] but this too is ineffective for BHA with secondary amines. On the basis of these observations we conclude that **23** offers an unprecedented ability to accommodate primary and secondary amine substrates in BHA at room temperature.

Encouraged by the unique ability of this new phosphine-functionalized NHC to enable the selective room-temperature BHA of both octylamine and morpholine, we sought to further explore the scope of this system for the arylation of primary (Table 5) and secondary amines (Table 6). Unhindered primary alkylamines were all coupled efficiently with chlorobenzene (**24a−c**) using the optimized room-temperature catalytic conditions. The arylation of methylamine was conducted using only 1.4 equiv of the amine, with 96% isolated yield achieved, and no diarylation product was observed. Arylation of a dialkylhydrazine to give **24d** was effective only with the use of NaO*t*Bu base. Bulkier alkylamines were not as well tolerated, giving low to moderate yields of cross-coupling products (**24e**,**f**) at room temperature. Efficient room-temperature arylation of aniline (**24g**) demonstrates the applicability of this protocol for unhindered arylamines, while the sterically demanding $DippNH_2$ could only be arylated at 65 °C, providing a good yield of **24h**. The amination of activated aryl chlorides with octylamine proved extremely facile at ambient temperature. Amination of 2-chloropyridine went to completion in less than 1 min and gave rise to a noticeable exotherm within seconds of amine addition. An isolated yield of 91% was achieved using the standard conditions, which was improved to 96% with the use of NaO*t*Bu base. At a catalyst loading of 0.25 mol %, 60% of the 2-chloropyridine substrate is consumed after 60 s (calibrated GC), corresponding to a turnover frequency (TOF) of ca. 14000 h^{-1}. To our knowledge, this represents the highest TOF reported at room temperature for the arylation of octylamine or any similar nucleophilic primary alkylamine. For comparison, this is roughly 2 orders of magnitude faster than the coupling of the same substrates using

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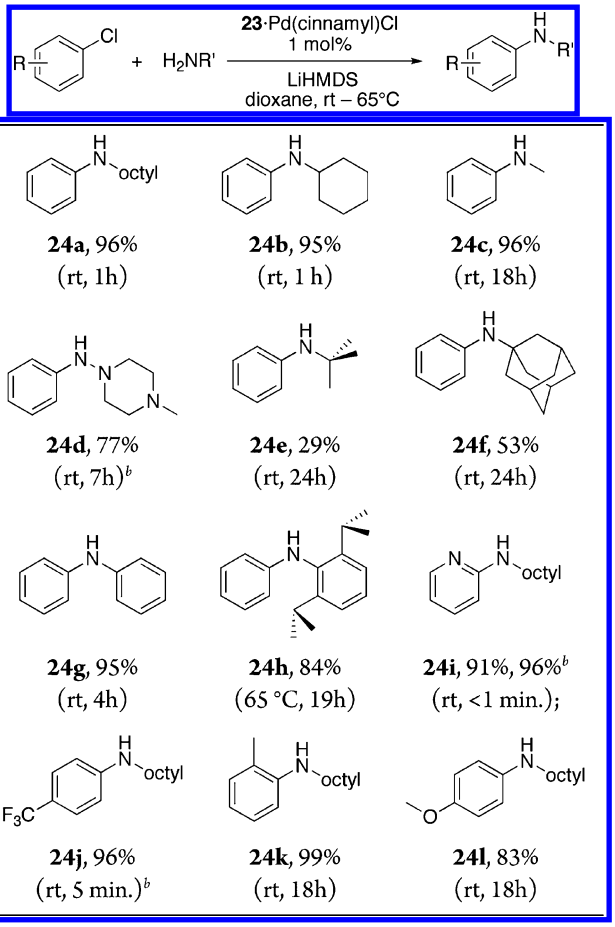
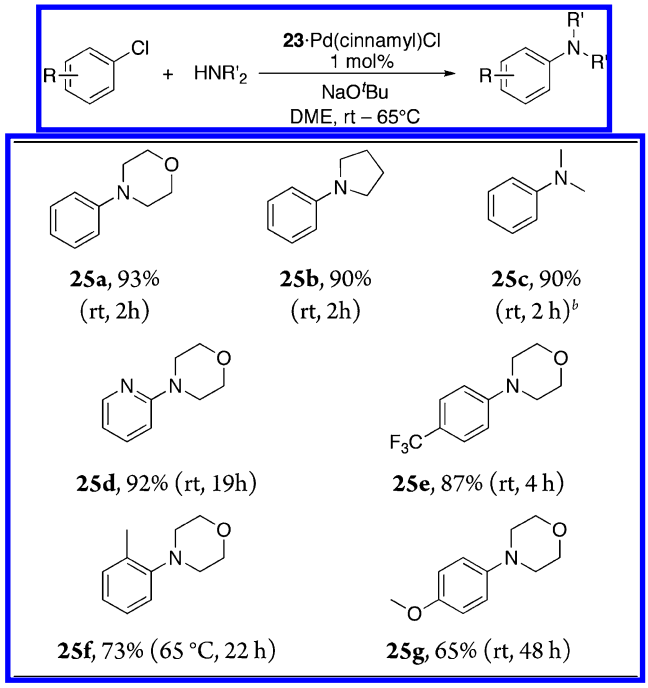
Table 5. Amination of (Hetero)aryl Chlorides with Primary Amines under Mild Conditions[a]



[a]Reagents and (standard) conditions: (hetero)aryl halide (1.0 mmol), H_2NR (1.2 mmol), LiHMDS (1.4 mmol), 1,4-dioxane (2 mL). Isolated yields; average of two runs. Temperature and unoptimized reaction time indicated in parentheses. [b]The base is NaO*t*Bu (1.4 mmol).

Table 6. Amination of (Hetero)aryl Chlorides with Secondary Dialkylamines under Mild Conditions[a]



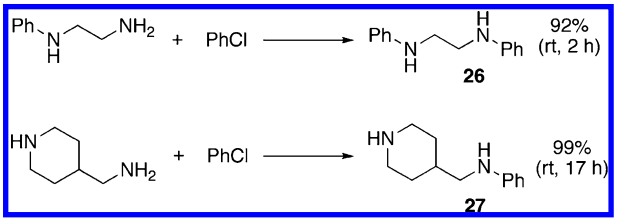
[a]Reagents and (standard) conditions: (hetero)aryl halide (1.0 mmol), HNR_2 (1.2 mmol), NaO*t*Bu (1.4 mmol), DME (2 mL). Temperature and unoptimized reaction time indicated in parentheses. Isolated yields; average of two runs. [b]Used 1.4 equiv of $HNMe_2$ as a 2 M solution in THF.

the JosiPhos/$Pd(OAc)_2$ system.[5e] Amination of the activated 4-chlorobenzotrifluoride by using **23**·Pd(cinnamyl)Cl gave only hydrodehalogenation with LiHMDS base but was similarly facile when NaO*t*Bu base was employed, providing **24j** in 96% yield in less than 5 min. Additionally, the system tolerates ortho substitution (**24k**) as well as electronic deactivation (**24l**).

A narrow scope of secondary amines was also examined using **23**·Pd(cinnamyl)Cl as the precatalyst. Small cyclic and acyclic secondary amines are coupled efficiently under the standard conditions (**25a–c**). The arylation of dimethylamine was performed similarly to that of methylamine, whereby a 2 M THF solution was employed using only 1.4 equiv of the amine. Interestingly, amination of activated aryl chlorides with morpholine did not provide the same rate enhancement seen for amination with octylamine, although high yields of coupling products were obtained (**25d,e**). Furthermore, ortho substitution (**25f**) and electronic deactivation (**25g**) were not as well tolerated with secondary amines. Amination of 2-chlorotoluene required heating to 65 °C for 22 h to provide a 73% yield of **25f**, while amination of 4-chloroanisole proceeded slowly at room temperature, giving a moderate yield of **25g** after 48 h.

In additional to the cross-coupling experiments discussed above, we have taken a preliminary look at some more challenging substrates to demonstrate the chemoselectivity of the **23**·Pd(cinnamyl)Cl precatalyst system. In particular, two substrates bearing both a primary and secondary amine functional group were subjected to arylation employing the optimized conditions for primary amines (Scheme 4); in both cases the system was completely selective for amination at the primary amine site.

Scheme 4. Room-Temperature Chemoselectivity Studies Demonstrating Selectivity for Primary over Secondary Amines[a]



[a]Conditions: PhCl (1.0 mmol), amine (1.2 mmol), LiHMDS (1.4 mmol). Temperature and unoptimized reaction time indicated in parentheses.

The selective monoarylation of ammonia[5b,6] and the mono-α-arylation of acetone[26] with the unactivated and sterically unbiased aryl halides and pseudohalides remain highly challenging transformations, for which only a handful of catalyst systems have proven effective. We therefore undertook a preliminary examination of the performance of **23**·Pd-

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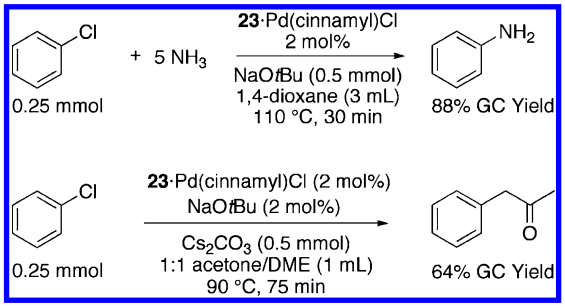
(cinnamyl)Cl in these challenging cross-coupling reactions (Scheme 5). The system proved highly effective for amination

Scheme 5. Selective Monoarylation of Ammonia and Acetone



of chlorobenzene with ammonia, giving an 88% yield of monoarylation product and 13:1 product ratio of mono- to diarylation products, as determined by GC analysis. This yield and selectivity is competitive with those of Mor-DalPhos, and ammonia monoarylation therefore represents an interesting potential application of this ligand that is deserving of further study. It was also found that the system performed well in the mono-α-arylation of acetone with chlorobenzene, whereby a GC yield of 64% was achieved. Notably, this is the first example of an NHC-based catalyst system exhibiting a high selectivity for monoarylation in either of these transformations.

CONCLUSION

In summary, a straightforward and high-yielding three-step method for the preparation of phosphine-functionalized dihydroimidazolium salts has been established. The bulkiest example, which incorporated a bis(1-adamantyl)phosphine donor group (**11**), proved most promising for application in Buchwald–Hartwig amination catalysis. This new ligand demonstrates unprecedented activity for the monoarylation of primary nucleophilic alkylamines, as well as the ability to couple alternative amine classes (i.e., primary alkyl- and arylamines, secondary dialkylamines) at ambient temperature. The **23**·Pd(cinnamyl)Cl catalyst system also exhibits chemoselectivity, with a demonstrated preference for primary over secondary amines. Such selectivity is further highlighted by the excellent performance in a preliminary examination of the monoarylation of both ammonia and acetone. This is the first example of a bidentate NHC-phosphine system ligand with high activity in Buchwald–Hartwig amination, and we believe that these findings show this class of ligands to be promising and worthy of further consideration by other researchers in the field. Our continuing studies in this area will examine the utility of phosphine-functionalized NHC ligands in other challenging metal-catalyzed reactions and will aim to gain an improved understanding of the coordination chemistry of this new ligand system.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all manipulations were conducted under an inert N_2 atmosphere of dinitrogen using standard Schlenk methods or within an mBraun glovebox apparatus, using glassware that was oven-dried at 120 °C and evacuated while hot prior to use. Toluene, benzene, hexanes, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. THF, 1,4-dioxane, and DME were dried over Na/benzophenone, distilled, and stored over 4 Å molecular sieves. Benzene-d_6 (Cambridge Isotopes) was degassed by using at least three repeated freeze–pump–thaw cycles and stored over 4 Å molecular sieves for 24 h prior to use. Other deuterated solvents ($CDCl_3$, DMSO-d_6) were used with air- and moisture-stable compounds and were used as received. *N*-(2,4,6-Trimethylphenyl)-1,2-ethanediamine,[27] *N*-(2,6-diisopropylphenyl)-1,2-ethanediamine,[27] *N*-(2-bromophenyl)morpholine,[28] and $[Pd(cinnamyl)Cl]_2$[29] were prepared according to literature procedures. All other materials were obtained from commercial sources (Sigma-Aldrich, Alfa Aesar, Strem) and used without further purification. NMR spectra were collected on a Bruker spectrometer at a frequency of 500 MHz for ^1H and 126 MHz for ^{13}C experiments, at ambient temperature, and referenced to residual solvent signals. Peak assignments were made with the aid of COSY, DEPT-135, and HSQC experiments. Mass spectrometric data were acquired by Mr. Xiao Feng (Mass Spectrometry Laboratory, Dalhousie University). Single-crystal X-ray diffraction data were collected by Dr. Robert McDonald and Dr. Michael Ferguson (X-ray Crystallography laboratory, University of Alberta).

Synthesis and Characterization. *Synthesis of N¹-{2-bromophenyl}-N²-Mes-1,2-ethanediamine (**1**).* $Pd_2(dba)_3$ (46 mg, 0.05 mmol), Xantphos (116 mg, 0.2 mmol), NaO*t*Bu (1.34 g, 14 mmol), and 10 mL of toluene were combined in a 20 dram catalysis vial. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. Bromoiodobenzene (2.83 g, 1.28 mL, 10 mmol) and *N*-mesityl-1,2-diaminoethane (1.87 g, 10.5 mmol) were then injected using a syringe. The resulting reaction mixture was heated to 110 °C with vigorous stirring for 30 min. After it was cooled, the mixture was filtered through a bed of silica, which was then washed down with CH_2Cl_2 (40 mL). Removal of solvent and prolonged drying in vacuo afforded the product as a beige crystalline solid in >99% yield (3.32 g, 9.96 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.9, 1.5 Hz, 1H, 3-Ph), 7.20 (td, J = 7.7, 1.3 Hz, 1H, 5-Ph), 6.86 (s, 2H, *m*-Mes), 6.68 (dd, J = 8.2, 1.3 Hz, 1H, 4-Ph), 6.61 (td, J = 7.6, 1.3 Hz, 1H, 6-Ph), 4.79 (t, J = 5.0 Hz, 1H, N*H*), 3.38 (q, J = 5.6 Hz, 2H, CH_2), 3.24 (dd, J = 6.5, 5.0 Hz, 2H, NHCH_2), 3.10 (s, 1H, N*H*), 2.29 (s, 6H, *o*-CH_3 Mes), 2.25 (s, 3H, *p*-CH_3 Mes). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 145.1, 142.8, 132.6 (3-Ph), 132.0, 130.4, 129.6 (*m*-Mes), 128.6 (5-Ph), 118.1 (4-Ph), 111.5 (6-Ph), 110.2, 47.5 (CH_2), 44.3 (CH_2), 20.7 (*p*-CH_3 Mes), 18.4 (*m*-CH_3 Mes). HRMS (ESI/[M + H]$^+$): calcd for $C_{17}H_{22}BrN_2$ 333.0961, found 333.0956.

*Synthesis of N¹-{2-bromophenyl}-N²-Dipp-1,2-ethanediamine (**2**).* This was prepared similarly to **1** from bromoiodobenzene (1.41 g, 5.00 mmol) and *N*-2,6-diisopropylphenyl-1,2-diaminoethane (1.10 g, 5.0 mmol). Purification by flash chromatography (10/1 hexanes/EtOAc) afforded a pale yellow oil, which crystallized upon standing for several hours. Yield: 81% (1.51 g, 4.03 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, J = 7.9, 1.5 Hz, 1H, 3-Ph), 7.20 (td, J = 7.7, 1.3 Hz, 1H, 5-Ph), 7.11 (ov m, 3H, *m*+*p*-Dipp), 6.71 (dd, J = 8.2, 1.3 Hz, 1H, 6-Ph), 6.61 (td, J = 7.6, 1.3 Hz, 1H, 4-Ph), 4.90 (t, J = 5.4 Hz, 1H, N*H*), 3.46 (q, J = 5.5 Hz, 2H, CH_2), 3.29 (sp, J = 6.9 Hz, 2H, $CH(CH_3)_2$), 3.17 (t, J = 5.6 Hz, 2H, CH_2), 3.11 (br s, 1H, N*H*), 1.22 (d, J = 6.9 Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 144.9, 143.1, 142.6, 132.6 (3-Ph), 128.6 (5-Ph), 124.4 (*p*-Dipp), 123.7 (*m*-Dipp), 118.2 (4-Ph), 111.6 (6-Ph), 110.2, 50.4 (CH_2), 44.2 (CH_2), 27.8 ($CH(CH_3)_2$), 24.5 ($CH(CH_3)_2$). HRMS (ESI/[M + H]$^+$): calcd for $C_{20}H_{28}BrN_2$ 375.1430, found 375.1413.

*Synthesis of N¹-{2-bromophenyl}-N²-Ph-1,2-ethanediamine (**3**).* This was prepared similarly to **1** from bromoiodobenzene (1.41 g, 5.00 mmol) and *N*-phenyl-1,2-diaminoethane (695 mg, 5.10 mmol). Filtration of the reaction mixture through a bed of silica and removal of volatiles in vacuo afforded the title compound as a light yellow-orange oil in 98% yield (1.43 g, 2.48 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, J = 7.9 Hz, 1H, 3-Ph), 7.26–7.17 (ov m, 3H, *m*-NPh + 5-Ph), 6.78 (t, J = 7.3 Hz, 1H, 6-Ph), 6.72–6.67 (ov m, 3H, *o*+*p*-NPh), 6.63 (t, J = 7.6 Hz, 1H, 4-Ph), 4.53 (br s, 1H, N*H*), 3.89 (br s, 1H, N*H*), 3.48–3.42 (ov m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 147.9, 144.9, 132.7 (3-Ph), 129.5 (*m*-Ph), 128.6 (5-Ph), 118.3 (4-Ph), 118.0 (6-Ph), 113.2 (*o*-Ph), 111.6 (*p*-Ph), 110.2, 43.24

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(CH_2), 43.10 (CH_2). HRMS (ESI/[M + H]$^+$): calcd for $C_{14}H_{16}BrN_2$ 291.0491, found 291.0493.

*Synthesis of N^1-{2-(PPh$_2$)phenyl}-N^2-Mes-1,2-ethanediamine (**4**).* $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and DiPPF (10 mg, 0.024 mmol) were combined in a 2 dram catalysis vial with 4 mL of toluene. After the mixture was stirred for 5 min, NaO*t*Bu was added (135 mg, 1.4 mmol), followed by diphenylphosphine (186 mg, 1.0 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. Compound **1** (333 mg, 1.00 mmol) was added via syringe. The vial was then heated to 110 °C with vigorous stirring for 21 h, at which point complete conversion was confirmed by ^{1}H and ^{31}P NMR of an aliquot of the reaction mixture. The cooled reaction mixture was then filtered through a bed of silica and washed down with CH_2Cl_2 (20 mL). The solution was concentrated, and the resulting crude material was purified by flash chromatography (5/1 hexanes/EtOAc), giving the product as a yellow oil in 88% yield (388 mg, 0.885 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35−7.32 (ov m, 10H, *o*+*m*+*p*-PPh_2), 7.27 (ddd, J = 8.2, 7.2, 1.6 Hz, 1H, 4-Ph), 6.80−6.78 (ov m, 3H, 6-Ph + *m*-Mes), 6.71 (dd, J = 8.2, 5.2 Hz, 1H, 3-Ph), 6.67 (t, J = 7.4 Hz, 1H, 5-Ph), 5.12 (br q, J = 6.4 Hz, 1H, N*H*), 3.33 (br q, J = 5.4 Hz, 2H, CH_2), 3.10 (dd, J = 6.4, 4.8 Hz, 2H, CH_2), 2.22 (s, 3H, *p*-CH_3 Mes), 2.11 (s, 6H, *o*-CH_3 Mes). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.2 (d, J = 18.1 Hz), 143.0, 135.6 (d, J = 7.3 Hz), 134.6 (d, J = 1.9 Hz, 6-Ph), 133.8 (d, J = 8.8 Hz, *m*-PPh_2), 131.8, 130.8 (4-Ph), 130.4, 129.5 (*m*-Mes), 128.9 (*p*-PPh_2), 128.7 (d, J = 7.1 Hz, *o*-PPh_2), 119.8 (d, J = 7.3 Hz), 117.7 (d, J = 1.8 Hz, 5-Ph), 110.5 (d, J = 2.2 Hz, 3-Ph), 47.6 (CH_2), 44.5 (CH_2), 20.7 (*p*-CH_3 Mes), 18.3 (*o*-CH_3 Mes). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ −22.0 (s). HRMS (ESI/[M + H]$^+$): calcd for $C_{29}H_{32}N_2P$ 439.2298, found 439.2282.

*Synthesis of N^1-{2-(PCy$_2$)phenyl}-N^2-Mes-1,2-ethanediamine (**5**).* This was prepared similarly to **4** from **1** (1.00 g, 3.00 mmol) and dicyclohexylphosphine (615 mg, 3.1 mmol). After a 17 h reaction time, filtration of the cooled reaction mixture through a bed of silica and removal of volatiles in vacuo gave the title compound as a light red oil in high purity and >99% yield (1.348 g, 2.99 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25−7.19 (m, 2H, 4-Ph + 6-Ph), 6.83 (s, 2H, *m*-Mes), 6.69 (td, J = 7.4, 1.0 Hz, 1H, 5-Ph), 6.65 (dd, J = 8.2, 4.9 Hz, 1H, 3-Ph), 5.67 (br s, 1H, N*H*), 3.34 (br m, 2H, CH_2), 3.18 (t, J = 5.7 Hz, 3H, CH_2), 2.26 (s, 6H, *o*-CH_3 Mes), 2.24 (s, 3H, *p*-CH_3 Mes), 1.96−1.86 (ov m, 4H, Cy), 1.77 (m, 2H, Cy), 1.71−1.56 (br ov m, 6H, Cy), 1.32−1.05 (ov m, 10H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.9 (d, J = 18.7 Hz), 143.3, 133.4 (6-Ph), 131.6, 130.2 (4-Ph), 129.5 (*m*-Mes), 117.0 (d, J = 13.6 Hz), 116.5 (5-Ph), 110.3 (3-Ph), 48.0 (NCH_2), 44.8 (NCH_2), 33.1 (d, J = 9.1 Hz, CH Cy), 30.6 (d, J = 16.2 Hz, CH_2 Cy), 28.9 (d, J = 7.1 Hz, CH_2 Cy), 27.3 (d, J = 12.8 Hz, CH_2 Cy), 27.1 (d, J = 8.0 Hz, CH_2 Cy), 26.5 (CH_2 Cy), 20.7 (*p*-CH_3 Mes), 18.5 (*o*-CH_3 Mes); one quaternary carbon signal associated with the Mes group is not observed. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ −26.6. HRMS (ESI/[M + H]$^+$): calcd for $C_{29}H_{44}N_2P$ 451.3237, found 451.3237.

*Synthesis of N^1-{2-(PAd$_2$)phenyl}-N^2-Mes-1,2-ethanediamine (**6**).* *Condition A.* This procedure is similar to that used to prepare **4**, from **1** (333 mg, 1.0 mmol) and bis(1-adamantyl)phosphine (302 mg, 1.0 mmol). Purification by flash chromatography (20/1 hexanes/EtOAc) provided the compound as a light yellow powder in 62% yield.

Condition B. $Pd(OAc)_2$ (9.0 mg, 0.04 mmol) and DiPPF (20 mg, 0.048 mmol) were combined in a 2 dram catalysis vial with 1,4-dioxane (8 mL). After the mixture was stirred for 5 min, Cs_2CO_3 (912 mg, 2.8 mmol) was added, followed by **1** (667 mg, 2.0 mmol) and bis(1-adamantyl)phosphine (605 mg, 2.0 mmol). The reaction mixture was heated to 120 °C for 72 h, followed by the workup procedure described for condition A. This provided the title compound in 66% yield (734 mg, 1.32 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 7.8 Hz, 1H, 6-Ph), 7.22 (t, J = 7.8 Hz, 1H, 4-Ph), 6.83 (s, 2H, *m*-Mes), 6.68−6.63 (ov m, J = 7.1 Hz, 2H, 3-Ph + 5-Ph), 6.11 (dt, J = 13.1, 6.3 Hz, 1H, N*H*), 3.34 (q, J = 5.7 Hz, 2H, CH_2), 3.23 (s, 1H, N*H*), 3.18 (t, J = 5.8 Hz, 2H, CH_2), 2.27 (s, 6H, *o*-CH_3), 2.24 (s, 3H, *p*-CH_3), 2.03−1.96 (ov m, 6H, Ad), 1.93−1.87 (ov m, 12H, Ad), 1.68 (s, 12H, Ad). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 154.8 (d, J = 20.3 Hz), 143.4 (s), 136.8 (d, J = 2.3 Hz, 6-Ph), 131.5 (s), 130.4 (s, 4-Ph), 130.1 (s), 129.5 (s, *m*-Mes), 116.3 (d, J = 16.2 Hz), 115.4 (s, 5-Ph), 110.2 (d, J = 2.9 Hz, 3-Ph), 48.2 (s, NCH_2), 44.7 (s, NCH_2), 41.8 (d, J = 11.4 Hz, CH_2 Ad), 37.1 (d, J = 18.1 Hz, CH_2 Ad), 37.0 (s, quaternary Ad), 28.9 (d, J = 9.0 Hz, CH Ad), 20.7 (*p*-CH_3 Mes), 18.6 (*o*-CH_3 Mes). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 3.3 (s). HRMS (ESI/[M + H]$^+$): calcd for $C_{37}H_{52}N_2P$ 555.3863, found 555.3873.

*Synthesis of N^1-{2-(PAd$_2$)phenyl}-N^2-Ph-1,2-ethanediamine (**7**).* This compound was prepared similarly to **6** (Condition B) from **3** (580 mg, 2.0 mmol). Flash chromatography (20/1 hexanes/EtOAc) provided the compound as a white powder in 53% yield (547 mg, 1.07 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (dt, J = 7.6, 2.0 Hz, 1H, 6-Ph), 7.23 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H, 4-Ph), 7.19−7.15 (m, 2H, *m*-NPh), 6.72−6.65 (ov m, 3H, *p*-NPh + 3-Ph + 5-Ph), 6.62−6.60 (m, 2H, *o*-NPh), 5.99 (dt, J = 13.1, 6.4 Hz, 1H, N*H*), 3.92 (s, 1H, N*H*), 3.43 (q, J = 5.8 Hz, 2H, NCH_2), 3.35 (t, J = 5.3 Hz, 2H, NCH_2), 1.99−1.97 (m, 6H, Ad), 1.90 (m, 12H, Ad), 1.67 (s, 12H, Ad). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 154.3 (d, J = 20.3 Hz), 148.2 (s), 136.9 (d, J = 2.6 Hz, 6-Ph), 130.4 (s, 4-Ph), 129.4 (s, *m*-NPh), 117.6 (s), 116.6 (d, J = 15.4 Hz), 115.7 (s), 113.1 (s, *p*-NPh), 110.8 (d, J = 2.7 Hz, 3-Ph), 43.4 (d, J = 1.3 Hz, NCH_2), 42.8 (s, NCH_2), 41.8 (d, J = 11.3 Hz, CH_2 Ad), 37.1 (d, J = 17.8 Hz, quaternary Ad), 37.0 (s, CH_2 Ad), 28.9 (d, J = 8.9 Hz, CH Ad). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 3.2 (s). HRMS (ESI/[M + H]$^+$): calcd for $C_{34}H_{46}N_2P$ 513.3393, found 513.3414.

*Synthesis of N^1-{2-(PAd$_2$)phenyl}-N^2-Dipp-1,2-ethanediamine (**8**).* This compound was prepared similarly to **4** from **2** (375 mg, 1.0 mmol) and bis(1-adamantyl)phosphine (302 mg, 1.0 mmol). Purification by flash chromatography gave the compound as a light yellow powder in 56% yield (334 mg, 0.56 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dt, J = 7.5, 2.0 Hz, 1H, 6-Ph), 7.23 (t, J = 7.7 Hz, 1H, 4-Ph), 7.12−7.06 (ov m, 3H, *m*+*p*-Dipp), 6.70−6.65 (ov m, 2H, 5-Ph + 3-Ph), 6.20 (dt, J = 13.0, 6.2 Hz, 1H, NH), 3.39−3.32 (ov m, 4H, NCH_2 + CH(CH_3)$_2$), 3.22 (s, 1H, N*H*), 3.13 (t, J = 5.6 Hz, 2H, NCH_2), 2.06−1.96 (ov m, 6H, Ad), 1.91 (ov m, 12H, Ad), 1.68 (br s, 12H, Ad), 1.25 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 154.8 (d, J = 20.1 Hz), 143.0 (s), 142.9 (s), 136.7 (d, J = 2.5 Hz, 6-Ph), 130.3 (s, 4-Ph), 123.9 (s, *p*-Dipp), 123.6 (s, *m*-Dipp), 116.3 (d, J = 16.3 Hz), 115.4 (5-Ph), 110.4 (d, J = 2.8 Hz, 3-Ph), 51.2 (NCH_2), 44.9 (s, NCH_2), 41.7 (d, J = 11.6 Hz, CH_2 Ad), 37.0 (d, J = 18.3 Hz, quaternary Ad), 36.9 (CH_2 Ad), 28.8 (d, J = 8.7 Hz, CH Ad), 27.6 (CH(CH_3)$_2$), 24.5 (CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 3.4 (s). HRMS (ESI/[M + H]$^+$): calcd for $C_{40}H_{58}N_2P$ 597.4332, found 597.4358.

*Synthesis of [1-Mes-3-{2-(PPh$_2$)phenyl}imidazolidin-2-ylium][BF$_4$] (**9**).* In air, compound **4** (365 mg, 0.832 mmol), NH_4BF_4 (105 mg, 1.0 mmol), 3 mL of $CH(OEt)_3$, and a stir bar were combined in a 2 dram vial. The open vial was heated to 120 °C for 1 h with vigorous stirring, resulting in the formation of a yellow oil which separated from the reaction mixture. After the mixture was cooled to ambient temperature, the solvent was decanted from the oil and 4 mL of diethyl ether was added. Stirring for 1 h provided a fine white powder, which was collected by filtration and washed with additional diethyl ether (2 × 2 mL). The product was taken up in CH_2Cl_2 and filtered. Removal of volatiles from the resulting clear solution afforded a white powder in 94% yield. Examination of the material by NMR revealed it to be ∼80% pure by integration of ^{31}P NMR resonances. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (ddd, J = 7.9, 4.4, 1.0 Hz, 1H, 3-Ph), 7.74 (d, J = 1.6 Hz, 1H, NCHN$^+$), 7.56 (td, J = 7.7, 1.5 Hz, 1H, 4-Ph), 7.39 (ov m, J = 7.8 Hz, 7H, *o*+*p*-PPh_2 + 5-Ph), 7.22 (td, J = 8.0, 1.5 Hz, 4H, *m*-PPh_2), 6.94−6.92 (m, 3H, 6-Ph + *m*-Mes), 4.55 (dd, J = 12.2, 9.4 Hz, 2H, NCH_2), 4.28 (dd, J = 12.2, 9.4 Hz, 2H, NCH_2), 2.28 (s, 3H, *p*-CH_3 Mes), 2.26 (s, 6H, *m*-CH_3 Mes). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.1 (d, J = 4.3 Hz, NCHN$^+$), 140.6 (s), 138.6 (d, J = 22.3 Hz), 135.4 (s), 134.6 (s, 6-Ph), 134.4 (d, J = 15.3 Hz), 134.0 (d, J = 8.1 Hz), 133.8 (d, J = 19.6 Hz, *m*-PPh_2), 131.6 (s, 4-Ph), 130.7 (s, 5-Ph), 130.0 (s, *m*-Mes), 130.0 (d, J = 7.0 Hz, *o*-PPh_2), 129.3 (d, J = 7.2 Hz, *p*-PPh_2), 128.0 (d, J = 1.8 Hz, 3-Ph), 53.0 (d, J = 5.9 Hz, NCH_2), 51.7 (s, NCH_2), 21.0 (s, *p*-CH_3 Mes), 17.5 (*o*-CH_3 Mes). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ −18.2 (s).

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*Synthesis of [1-Mes-3-{2-(PCy_2)phenyl}imidazolidin-2-ylium][BF_4] (**10**).* This was prepared similarly to **11** (see below) from **5** (318 mg, 0.706 mmol), with a reaction time of 15 min. The product was obtained as a white powder in 94% yield (365 mg, 0.666 mmol), which was determined to be approximately 80% pure by integration of ^{31}P NMR resonances. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (ddd, J = 8.0, 3.9, 1.2 Hz, 1H, 3-Ph), 7.80 (d, J = 2.7 Hz, 1H, NC*H*N$^+$), 7.59 (dt, J = 7.6, 1.7 Hz, 1H, 6-Ph), 7.54 (td, J = 7.7, 1.4 Hz, 1H, 4-Ph), 7.47 (td, J = 7.5, 1.2 Hz, 1H, 5-Ph), 6.99 (d, J = 0.4 Hz, 2H, *m*-Mes), 4.69 (dd, J = 12.3, 9.3 Hz, 2H, NCH_2), 4.44 (dd, J = 12.2, 9.4 Hz, 2H, NCH_2), 2.44 (s, 6H, *m*-CH_3 Mes), 2.32 (s, 3H, *p*-CH_3 Mes), 1.87−1.65 (ov m, 10H, Cy), 1.46−1.30 (ov m, 4H, Cy), 1.18−1.06 (ov m, 6H, Cy), 0.98−0.89 (ov m, 2H, Cy). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.6 (d, J = 7.4 Hz, NCHN$^+$), 141.7 (d, J = 23.2 Hz), 140.8 (s), 135.7 (s), 134.2 (d, J = 3.8 Hz, 6-Ph), 131.9 (d, J = 23.3 Hz), 131.6 (s, 4-Ph), 130.2 (s), 130.1 (s, *m*-Mes), 129.7 (s, 5-Ph), 127.3 (d, J = 3.0 Hz, 3-Ph), 54.3 (d, J = 6.2 Hz, NCH_2), 51.6 (s, NCH_2), 34.2 (d, J = 11.3 Hz, C*H* Cy), 30.8 (d, J = 17.2 Hz, CH_2 Cy), 29.4 (d, J = 7.3 Hz, CH_2 Cy), 26.9 (d, J = 13.0 Hz, CH_2 Cy), 26.8 (d, J = 8.2 Hz, CH_2 Cy), 26.1 (s, CH_2 Cy), 21.1 (s, *p*-CH_3 Mes), 18.0 (d, J = 4.0 Hz Hz, *p*-CH_3 Mes). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ −16.5 (s).

*Synthesis of [1-Mes-3-{2-(PAd_2)phenyl}imidazolidin-2-ylium][BF_4] (**11**).* In air, compound **6** (1.55 g, 2.79 mmol) and NH_4BF_4 (351 mg, 3.35 mmol) were combined in a 4 dram vial. A 10 mL portion of $CH(OEt)_3$ was added, and the open vial was heated to 110 °C with vigorous stirring for 30 min. The resulting white precipitate was collected by filtration and washed copiously with diethyl ether (5 × 5 mL). The product was taken up in CH_2Cl_2 and filtered through a sintered glass frit. Solvent was removed from the resulting clear solution, providing the product as a beige powder in 98% yield (1.79 g, 2.74 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89−7.86 (m, 2H, 3-Ph + 6-Ph), 7.82 (d, J = 3.2 Hz, 1H, NC*H*N$^+$), 7.58 (td, J = 7.7, 1.1 Hz, 1H, 4-Ph), 7.46 (td, J = 7.6, 1.2 Hz, 1H, 5-Ph), 7.00 (s, 2H, *m*-Mes), 4.72 (dd, J = 12.3, 9.3 Hz, 2H, NCH_2), 4.43 (dd, J = 12.2, 9.4 Hz, 2H, NCH_2), 2.48 (s, 6H, *o*-CH_3 Mes), 2.32 (s, 3H, *p*-CH_3 Mes), 1.92−1.90 (m, 12H, Ad), 1.83−1.81 (m, 6H, Ad), 1.66 (m, 12H, Ad). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.2 (d, J = 7.0 Hz), 142.4 (d, J = 25.2 Hz), 140.8 (s), 137.4 (d, J = 2.0 Hz, 6-Ph), 135.9 (s), 131.9 (s, 4-Ph), 130.7 (d, J = 28.5 Hz), 130.4 (s), 130.2 (s, *m*-Mes), 128.7 (s, 5-Ph), 127.7 (d, J = 3.1 Hz, 3-Ph), 54.3 (d, J = 5.8 Hz, NCH_2), 51.6 (s, NCH_2), 42.2 (d, J = 11.4 Hz, CH_2 Ad), 37.6 (d, J = 21.3 Hz, quaternary Ad), 36.7 (s, CH_2 Ad), 28.7 (d, J = 9.0 Hz, C*H* Ad), 21.2 (s, *p*-CH_3 Mes), 18.1 (s, *o*-CH_3 Mes). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 14.2 (s).

*Synthesis of Phosphonium Salt **12**.* This was prepared similarly to **11** from **7**, giving the phosphonium salt compound in 91% yield (243 mg, 0.91 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (t, J = 7.3 Hz, 1H, 5-Ph), 7.70 (t, J = 7.9 Hz, 1H, 4-Ph), 7.42 (dd, J = 8.8, 7.3 Hz, 2H, *m*-NPh), 7.29 (dd, J = 8.3, 3.4 Hz, 1H, 3-Ph), 7.25 (td, J = 7.6, 2.9 Hz, 1H, 6-Ph), 7.10−7.04 (ov m, 3H, *o*+*p*-NPh), 6.61 (d, J = 24.2 Hz, 1H, PC*H*$^+$), 3.97 (t, J = 6.8 Hz, 2H, NCH_2), 3.76 (td, J = 6.8, 1.6 Hz, 2H,, NCH_2), 2.21−2.18 (m, 6H, Ad), 2.05−1.98 (m, 12H, Ad), 1.74−1.68 (m, 12H, Ad). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.4 (d, J = 15.6 Hz), 144.1 (s), 136.3 (s, 4-Ph), 132.6 (s, 5-Ph), 130.1 (s, *m*-NPh), 123.6 (d, J = 8.1 Hz, 6-Ph), 122.9 (s, *p*-NPh), 117.6 (d, J = 5.7 Hz, 3-Ph), 117.3 (s, *o*-NPh), 88.6 (br s, PCH$^+$), 51.9 (s, NCH_2), 51.3 (d, J = 3.5 Hz, NCH_2), 42.7 (d, J = 14.9 Hz, quaternary Ad), 38.2 (s, CH_2 Ad), 35.7 (s, CH_2 Ad), 27.9 (d, J = 9.1 Hz, C*H* Ad). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 36.2 (s).

*Synthesis of Phosphonium Salt **13**.* In air, diamine compound **8** (50 mg, 0.084 mmol) was combined with NH_4BF_4 (10 mg, 0.095 mmol), 1 mL of $CH(OEt)_3$, and a stir bar in a 1 dram vial. The open vial was heated to 80 °C with vigorous stirring for 10 min. The resulting white precipitate was separated by decanting and then washed with diethyl ether (3 × 2 mL). The powder was taken up in CH_2Cl_2 and filtered through a sintered-glass frit, and the volatiles were removed to provide 13 mg of the title compound. The collected supernatant and washings were left to stand for 24 h, which resulted in the crystallization of an additional 16 mg of material, giving a combined yield of 47% (29 mg, 0.039 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (t, J = 7.9 Hz, 1H, 5-Ph), 7.49 (t, $^3J_{HH}$ = $^3J_{PH}$ = 7.5 Hz, 1H, 3-Ph), 7.09−7.03 (m, 3H, *o*+*m*-Dipp), 6.96 (td, J = 7.5, 3.5 Hz, 1H, 4-Ph), 6.86 (dd, J = 8.5, 3.4 Hz, 1H, 6-Ph), 6.19 (d, J = 4.0 Hz, 1H, PC*H*$^+$), 4.35−4.29 (m, 1H, OCH_2), 4.17−4.07 (m, 1H, OCH_2), 3.92−3.77 (m, 2H, NCH_2), 3.27 (sp, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 3.18−3.06 (m, 2H, NCH_2), 2.51−2.49 (m, 3H, Ad), 2.22−2.17 (m, 6H, Ad), 2.11 (s, 10H, Ad), 1.91−1.83 (m, 3H, Ad), 1.79 (br s, 6H, Ad), 1.76−1.67 (m, 3H, Ad), 1.30 (t, J = 7.0 Hz, 3H, OCH$_2$CH_3), 1.20 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.17 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.0 (d, J = 8.3 Hz), 143.1 (s), 142.6 (s), 136.9 (d, J = 1.2 Hz, 5-Ph), 131.7 (d, J = 4.4 Hz, 3-Ph), 124.2 (s, *p*-Dipp), 123.6 (s, *m*-Dipp), 119.6 (d, J = 10.1 Hz, 4-Ph), 110.7 (d, J = 6.5 Hz, 6-Ph), 97.6 (d, J = 71.3 Hz), 90.7 (d, J = 63.7 Hz, PCH$^+$), 69.4 (d, J = 4.3 Hz, OCH$_2$), 49.9 (s, NCH_2), 49.0 (d, J = 6.2 Hz, NCH_2), 43.4 (d, J = 24.7 Hz, quaternary Ad), 41.0 (d, J = 26.2 Hz, quaternary Ad), 37.2 (d, J = 2.6 Hz, CH_2 Ad), 36.9 (d, J = 2.5 Hz, CH_2 Ad), 35.9 (s, CH_2 Ad), 35.4 (s, CH_2 Ad), 27.9 (d, J = 9.7 Hz, C*H* Ad), 27.7 (d, J = 9.4 Hz, C*H* Ad), 27.6 (s, CH(CH_3)$_2$), 24.5 (s, CH(CH_3)$_2$), 24.4 (s, CH(CH_3)$_2$), 15.6 (s, OCH$_2$CH_3). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 32.3 (s).

*Synthesis of 2-Bromo-N-phenylbenzenamine (**14**).* This was prepared similarly to **1** from bromoiodobenzene (566 mg, 2.0 mmol) and aniline (186 mg, 2 mmol). After a reaction time of 15 min at 110 °C, the reaction mixture was cooled to ambient temperature, filtered through a bed of silica, and washed down with DCM (10 mL). Removal of volatiles afforded the title compound as a light yellow liquid in 97% yield (482 mg, 1.94 mmol). NMR data closely match previously reported values for this compound.[30] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (dd, J = 8.0, 1.5 Hz, 1H), 7.35−7.31 (m, 2H), 7.26 (dd, J = 8.2, 1.5 Hz, 1H), 7.19−7.15 (m, 3H), 7.05 (tt, J = 7.4, 1.1 Hz, 1H), 6.75 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 6.10 (br s, 1H).

*Synthesis of 2-Dicyclohexylphosphino-N-phenylbenzenamine (**15**).* This was prepared similarly to **4** from **14** (248 mg, 1.0 mmol) and dicyclohexylphosphine (198 mg, 1.0 mmol), with a reaction time of only 30 min at 110 °C. Purification by flash chromatography (20/1 hexanes/EtOAc) gave the product as a light yellow solid in 91% yield (333 mg, 0.91 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (ddd, J = 7.6, 2.8, 1.5 Hz, 1H, 6-Ph), 7.30−7.25 (m, 3H, 3-Ph + *m*-NPh), 7.21 (td, J = 7.7, 1.4 Hz, 1H, 4-Ph), 7.16 (br d, J = 11.1 Hz, 1H, N*H*), 7.13 (dd, J = 8.5, 1.0 Hz, 2H, *o*-NPh), 6.94 (tt, J = 7.3, 1.1 Hz, 1H, *p*-NPh), 6.87 (td, J = 7.4, 1.2 Hz, 1H, 5-Ph), 1.93 (tq, J = 11.8, 2.9 Hz, 2H, Cy), 1.88−1.85 (m, 2H, Cy), 1.77−1.73 (m, 2H, Cy), 1.71−1.61 (m, 6H, Cy), 1.34−1.03 (m, 10H, Cy). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.2 (d, J = 18.3 Hz), 143.2 (s), 133.5 (s, 6-Ph), 129.6 (s, 4-Ph), 129.3 (s, *m*-NPh), 121.4 (s, *p*-NPh), 120.5 (d, J = 12.8 Hz), 119.6 (s, 5-Ph), 119.1 (s, *o*-NPh), 115.7 (s, 3-Ph), 32.9 (d, J = 9.4 Hz, Cy CH), 30.5 (d, J = 16.2 Hz, Cy CH$_2$), 28.8 (d, J = 6.8 Hz, Cy CH$_2$), 27.4 (d, J = 12.5 Hz, Cy CH$_2$), 27.1 (d, J = 7.9 Hz, Cy CH$_2$), 26.5 (s, Cy CH$_2$). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ −24.4 (s). HRMS (ESI/[M + H]$^+$): calcd for $C_{24}H_{32}NP$ 366.2345, found 366.2339.

*Synthesis of Phosphonium Salt **16**.* In air, compound **15** (258 mg, 0.706 mmol) was combined with NH_4BF_4 (89 mg, 0.85 mmol), 3 mL of $CH(OEt)_3$, and a stir bar in a 4 dram vial. The open vial was heated to 110 °C with vigorous stirring for 20 min, at which point an orange oil was observed to have separated. Upon cooling, 5 mL of diethyl ether was added to encourage complete precipitation. The supernatant was decanted, and the oil was washed with diethyl ether (3 × 2 mL). The resulting solid material was taken up in CH_2Cl_2 and filtered. Evaporation of the solvent afforded 267 mg of the product as a light yellow powder. The collected supernatant and washings were left to stand for 24 h, resulting in crystallization of a further 64 mg of product, giving a combined yield of 92% (331 mg, 0.650 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (t, $^3J_{HH}$ = $^3J_{PH}$ = 7.9 Hz, 1H, 3-Ph), 7.50−7.44 (ov m, 3H, 5-Ph + *m*-NPh), 7.41−7.35 (m, 3H, *o*+*p*-NPh), 6.99 (td, J = 7.5, 3.4 Hz, 1H, 4-Ph), 6.64 (dd, J = 8.5, 3.4 Hz, 1H, 6-Ph), 6.17 (d, J = 1.9 Hz, 1H, PC*H*$^+$), 3.88 (dq, J = 9.3, 7.1 Hz, 1H, OCH_2CH$_3$), 3.48 (dq, J = 9.1, 7.1 Hz, 1H, OCH_2CH$_3$), 3.33−3.25 (m, 1H, Cy), 2.92 (qt, J = 13.3, 2.9 Hz, 1H, Cy), 2.30−2.27 (m, 1H, Cy), 2.16−2.05 (m, 3H, Cy), 1.98−1.94 (m, 2H, Cy), 1.86−1.66 (m, 7H, Cy), 1.55 (qt, J =

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13.0, 3.1 Hz, 1H, Cy), 1.46−1.34 (m, 3H, Cy), 1.28 (qt, J = 13.0, 3.3 Hz, 1H, Cy), 1.14−1.10 (m, 1H, Cy), 1.05 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.01−0.91 (m, 1H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 155.3 (d, J = 10.2 Hz), 139.2 (d, J = 7.3 Hz), 136.8 (s, 5-Ph), 132.1 (d, J = 5.0 Hz, 3-Ph), 130.5 (s, m-NPh), 128.5 (s, p-NPh), 127.7 (s, o-NPh), 120.7 (d, J = 10.3 Hz, 4-Ph), 112.0 (d, J = 7.4 Hz, 6-Ph), 98.1 (d, J = 74.0 Hz), 89.4 (d, J = 71.5 Hz, PCH^+), 70.1 (d, J = 5.9 Hz, OCH_2CH_3), 30.4 (d, J = 6.0 Hz, Cy CH), 30.1 (d, J = 2.4 Hz, Cy CH), 26.8 (d, J = 3.9 Hz, Cy CH_2), 26.7 (d, J = 8.8 Hz, Cy CH_2), 26.6 (d, J = 8.5 Hz, Cy CH_2), 26.4 (d, J = 3.7 Hz, Cy CH_2), 25.8 (d, J = 4.6 Hz, Cy CH_2), 25.6 (d, J = 14.2 Hz, Cy CH_2), 25.5 (s, Cy CH_2), 25.3 (d, J = 4.2 Hz, Cy CH_2), 25.2 (s, Cy CH_2), 25.1 (d, J = 13.6 Hz, Cy CH_2), 15.4 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 39.5 (s).

Synthesis of N¹-(2-bromobenzyl)-N²-Mes-ethane-1,2-diamine (17). 2-Bromobenzaldehyde (2.77 g, 15.0 mmol) was combined with *N*-mesityl-1,2-diaminoethane (2.67 g, 15.0 mmol) in 60 mL of toluene and stirred at ambient temperature for 1 h. The mixture was then dried with sodium sulfate and filtered, and the volatiles were removed under reduced pressure, giving the crude imine condensation product as a pale yellow oil. This material was dissolved in 60 mL of anhydrous ethanol, and sodium borohydride (1.14 g, 30 mmol) was added slowly with stirring over approximately 15 min. After the reaction mixture was stirred for 19 h, it was quenched with 60 mL of water and extracted with CH_2Cl_2 (3 × 60 mL). The combined organic extracts were dried with sodium sulfate, filtered, and evaporated to dryness under reduced pressure, giving the desired compound as a light brown oil in 77% yield (4.032 g, 12.1 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 1H, 6-Ph), 7.41 (dd, J = 7.6, 1.4 Hz, 1H, 3-Ph), 7.31 (t, J = 7.5 Hz, 1H, 4-Ph), 7.15 (td, J = 7.6, 1.5 Hz, 1H, 5-Ph), 6.84 (s, 2H, m-Mes), 3.93 (s, 2H, $PhCH_2$), 3.08 (t, J = 5.6 Hz, 2H, NCH_2), 2.85 (t, J = 5.6 Hz, 2H, NCH_2), 2.29 (s, 6H, o-CH_3 Mes), 2.25 (s, 3H, p-CH_3 Mes). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 143.8 (s), 139.3 (s), 132.9 (s, 6-Ph), 131.2 (s), 130.3 (s, 3-Ph), 129.7 (s), 129.5 (s, m-Mes), 128.7 (s, 5-Ph), 127.5 (s, 4-Ph), 124.1 (s), 53.6 (s, $PhCH_2$), 49.2 (s, NCH_2), 48.3 (s, NCH_2), 20.7 (s, p-CH_3 Mes), 18.6 (s, o-CH_3 Mes). HRMS (ESI/$[M + H]^+$): calcd for $C_{18}H_{24}BrN_2$ 347.1117, found 347.1115.

Synthesis of N¹-(2-bromobenzyl)-N²-Dipp-ethane-1,2-diamine (18). This was prepared similarly to **17** from 2-bromobenzaldehyde (2.77 g, 15.0 mmol) and *N*-2,6-diisopropylphenyl-1,2-diaminoethane (3.305 g, 15.0 mmol), giving the product in 72% yield (4.203 g, 10.8 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 1H, 3-Ph), 7.47 (dd, J = 7.6, 1.2 Hz, 1H, 6-Ph), 7.34 (t, J = 7.1 Hz, 1H, 5-Ph), 7.17 (td, J = 7.7, 1.4 Hz, 1H, 4-Ph), 7.14−7.07 (m, 3H, m+p-Dipp), 3.98 (s, 2H, $PhCH_2$), 3.37 (sp, J = 6.8 Hz, 2H, $CH(CH_3)_2$), 3.05 (dd, J = 6.4, 4.7 Hz, 2H, NCH_2), 2.94 (dd, J = 6.5, 4.6 Hz, 2H, NCH_2), 1.27 (d, J = 6.9 Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 143.6 (s), 142.5 (s), 139.3 (s), 132.9 (s, 3-Ph), 130.2 (s, 6-Ph), 128.7 (s, 4-Ph), 127.5 (s, 5-Ph), 124.0 (s), 123.7 (s, p-Dipp), 123.6 (s, m-Dipp), 53.5 (s, $PhCH_2$), 51.2 (s, NCH_2), 49.1 (s, NCH_2), 27.7 (s, $CH(CH_3)_2$), 24.4 (s, $CH(CH_3)_2$). HRMS (ESI/$[M + H]^+$): calcd for $C_{21}H_{30}BrN_2$ 389.1587, found 389.1580.

Synthesis of N¹-(2-(PCy₂)benzyl)-N²-Mes-ethane-1,2-diamine (19). $Pd(OAc)_2$ (13.5 mg, 0.06 mmol, 2 mol %) and DiPPF (30 mg, 0.072 mmol, 2.4 mol %) were combined in a 4 dram vial with 6.0 mL of toluene stirred for 5 min. NaO*t*Bu (0.4036 g, 4.2 mmol), dicyclohexylphosphine (0.7112 mL, 3.3 mol), and 6 mL of additional toluene were then added. The mixture was sealed with a cap containing a PTFE septum, the vial was removed from the glovebox, and **17** (1.051 g, 3.0 mmol) was injected with a syringe. The mixture was heated to 110 °C with stirring for 23 h. After it was cooled, the reaction mixture was then filtered through a bed of silica, which was washed down with 20 mL of 10/1 CH_2Cl_2/MeOH, and concentrated under reduced pressure. Purification by flash chromatography (20/1 CH_2Cl_2/MeOH) afforded the product as a light orange oil in 96% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, J = 7.5 Hz, 1H, 3-Ph), 7.40 (dd, J = 7.0, 3.7 Hz, 1H, 6-Ph), 7.32 (t, J = 7.1 Hz, 1H, 5-Ph), 7.27 (t, J = 7.3 Hz, 1H, 4-Ph), 6.83 (s, 2H, m-Mes), 4.10 (s, 2H, $PhCH_2$), 3.06 (t, J = 5.7 Hz, 2H, NCH_2), 2.82 (t, J = 5.7 Hz, 2H, NCH_2), 2.29 (s, 6H, o-CH_3 Mes), 2.25 (s, 3H, p-CH_3 Mes), 1.97−1.91 (ov m, 4H, Cy), 1.84−1.45 (ov m, 8H, Cy), 1.36−1.00 (ov m, 10H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 147.1 (d, J = 24.5 Hz), 144.0 (s), 133.8 (d, J = 20.0 Hz), 133.0 (d, J = 3.4 Hz, 3-Ph), 131.0 (s), 129.8 (s), 129.7 (d, J = 6.5 Hz, 6-Ph), 129.4 (s, m-Mes), 128.8 (s, 5-Ph), 126.5 (s, 4-Ph), 52.6 (d, J = 21.3 Hz, $PhCH_2$), 49.1 (s, NCH_2), 48.4 (s, NCH_2), 34.1 (d, J = 12.1 Hz, CH Cy), 30.7 (d, J = 17.1 Hz, CH_2 Cy), 29.2 (d, J = 8.1 Hz, CH_2 Cy), 27.3 (d, J = 12.3 Hz, CH_2 Cy), 27.2 (d, J = 7.6 Hz, CH_2 Cy), 26.5 (s, CH_2 Cy), 20.7 (s, p-CH_3 Mes), 18.6 (s, o-CH_3 Mes). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ −16.2 (s). HRMS (ESI/$[M + H]^+$): calcd for $C_{30}H_{46}N_2P$ 465.3393, found 465.3384.

Synthesis of N¹-(2-(PCy₂)benzyl)-N²-Dipp-ethane-1,2-diamine (20). This was prepared similarly to **19** from **18** (1.168 g, 3.00 mmol), giving the compound as a light orange oil, which crystallized upon standing to give a light orange crystalline solid in 85% yield (1.292 g, 2.55 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J = 8.1 Hz, 1H, 3-Ph), 7.41 (dd, J = 7.3, 3.8 Hz, 1H, 6-Ph), 7.32 (t, J = 7.2 Hz, 1H, 5-Ph), 7.26 (t, J = 7.0 Hz, 1H, 4-Ph), 7.10−7.02 (m, 3H, m+p-Dipp), 4.10 (s, 2H, $PhCH_2$), 3.34 (sp, J = 6.8 Hz, 2H, $CH(CH_3)_2$), 2.99 (t, J = 5.6 Hz, 2H, NCH_2), 2.85 (t, J = 5.6 Hz, 2H, NCH_2), 1.95−1.90 (m, 4H, Cy), 1.78−1.51 (m, 8H, Cy), 1.36−1.26 (m, 2H, Cy), 1.23 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.18−0.98 (m, 8H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 143.8 (s), 142.6 (s), 133.8 (d, J = 19.4 Hz), 133.1 (s, 3-Ph), 133.1 (s), 129.6 (d, J = 6.1 Hz, 6-Ph), 128.8 (s, 5-Ph), 126.6 (s, 4-Ph), 123.6 (s, m-Dipp), 123.6 (s, p-Dipp), 52.7 (d, J = 21.9 Hz, $PhCH_2$), 51.4 (s, NCH_2), 49.1 (s, NCH_2), 34.1 (d, J = 12.1 Hz, CH Cy), 30.8 (d, J = 17.2 Hz, CH_2 Cy), 29.2 (d, J = 8.0 Hz, CH_2 Cy), 27.7 (s, $CH(CH_3)_2$), 27.3 (d, J = 12.5 Hz, CH_2 Cy), 27.2 (d, J = 8.1 Hz, CH_2 Cy), 26.5 (s, CH_2 Cy), 24.5 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ −16.3 (s). HRMS (ESI/$[M + H]^+$): calcd for $C_{33}H_{52}N_2P$ 507.3863, found 507.3852.

Synthesis of [1-Mes-3-{2-(PCy₂)benzyl}imidazolidin-2-ylium][BF₄] (21). In air, compound **20** (0.500 g, 1.08 mmol) was combined with ammonium tetrafluoroborate (0.124 g, 1.18 mmol) and 3 mL of triethyl orthoformate in a 2 dram vial. The vial was sealed, and the reaction mixture was sparged with N_2 for 15 min. Under a constant flow of N_2, the vial was heated to 110 °C with vigorous stirring for 15 min at 110 °C. After the mixture was cooled, the resulting precipitate was collected on a sintered-glass frit and washed with diethyl ether (3 × 2 mL). The product was then dissolved in CH_2Cl_2, filtered, and dried under reduced pressure, resulting in a light yellow powder in a yield of 82% (498 mg, 0.89 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.55−7.47 (ov m, 2H), 7.41−7.37 (ov m, 2H), 6.91 (s, 2H), 5.14 (s, 2H), 4.15−4.04 (m, 4H), 2.27 (s, 6H), 2.26 (s, 3H), 1.96−1.82 (ov m, 4H), 1.80−1.45 (ov m, 8H), 1.34−0.87 (ov m, 10H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 157.9 (d, J = 4.6 Hz, $NCHN^+$), 140.4 (s), 138.4 (d, J = 24.4 Hz), 135.6 (s), 135.3 (d, J = 22.4 Hz), 133.7 (d, J = 3.3 Hz, 5-Ph), 131.6 (d, J = 5.5 Hz, 3-Ph), 130.6 (s), 130.0 (s, Ph), 130.0 (s, m-Mes), 129.1 (s, Ph), 51.2 (d, J = 22.0 Hz, $PhCH_2$), 51.1 (s, NCH_2), 48.5 (d, J = 1.4 Hz, NCH_2), 33.4 (d, J = 11.5 Hz, CH Cy), 30.4 (d, J = 16.7 Hz, CH_2 Cy), 28.9 (d, J = 7.1 Hz, CH_2 Cy), 27.1 (d, J = 12.5 Hz, CH_2 Cy), 27.0 (d, J = 7.4 Hz, CH_2 Cy), 26.3 (s, CH_2 Cy), 21.1 (s, p-CH_3 Mes), 17.9 (s, m-CH_3 Mes). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ −16.2 (s).

Synthesis of [1-Dipp-3-{2-(PCy₂)benzyl}imidazolidin-2-ylium][BF₄] (22). This was prepared similarly to **21** from **20** (300 mg, 0.593 mmol), affording the dihydroimidazolium salt product in 65% yield (233 mg, 0.385 mmol). ^1H NMR (500 MHz, DMSO-d_6): δ 9.08 (s, 1H, $NCHN^+$), 7.68−7.62 (m, 1H), 7.53−7.49 (m, 3H), 7.48−7.43 (m, 1H), 7.38 (d, J = 7.8 Hz, 2H, m-Dipp), 5.10 (s, 2H, $PhCH_2$), 4.13 (t, J = 10.8 Hz, 2H, NCH_2), 3.92 (t, J = 10.8 Hz, 2H, NCH_2), 2.99 (sp, J = 6.8 Hz, 2H, $CH(CH_3)_2$), 2.02 (t, J = 11.4 Hz, 2H, Cy), 1.91 (d, J = 12.1 Hz, 2H, Cy), 1.78−1.47 (m, 8H, Cy), 1.38−1.29 (m, 2H, Cy), 1.25 (d, J = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.23 (d, J = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.22−1.15 (m, 2H, Cy), 1.14−0.99 (m, 4H, Cy), 0.98−0.88 (m, 2H, Cy). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 159.0 (s, $NCHN^+$), 146.4 (s), 139.0 (d, J = 24.5 Hz), 134.7 (d, J = 23.0 Hz), 133.5 (d, J = 2.7 Hz), 130.8 (s), 130.3 (s), 130.1 (d, J = 5.1 Hz), 129.6 (s), 128.6 (s), 124.7 (s, m-Dipp), 53.2 (s, NCH_2), 50.3 (d, J = 24.3 Hz,

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Table 7. Crystal Data and Refinement Details for 12, 13, 16, and 21

	12	13	16	21
empirical formula	$C_{35}H_{44}BF_4N_2P$	$C_{43}H_{62}BF_4N_2OP$	$C_{27}H_{37}BF_4NOP$	$C_{31}H_{44}BF_4N_2P$
formula wt	610.50	740.73	509.36	562.46
temp (K)	173(2)	173(2)	173(2)	173(2)
wavelength (Å)	1.54178	1.54178	0.71073	1.54178
cryst syst	monoclinic	triclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$Pbca$
a (Å)	11.3006(2)	10.63530(10)	8.6050(5)	12.8487(4)
b (Å)	19.9760(3)	13.9417(2)	14.4373(8)	13.8907(4)
c (Å)	13.2786(2)	14.0006(2)	21.6605(12)	34.2663(9)
α (deg)	90	100.1680(10)	90	90
β (deg)	90.0860(10)	100.5580(10)	90	90
γ (deg)	90	97.8890(10)	90	90
V (Å^3)	2997.52(8)	1977.63(4)	2690.9(3)	6115.8(3)
Z	4	2	4	8
ρ_{calcd} (Mg m^{-3})	1.353	1.244	1.257	1.222
μ (mm^{-1})	1.259	1.059	0.150	1.187
cryst size (mm^3)	0.52 × 0.18 × 0.14	0.23 × 0.20 × 0.11	0.53 × 0.20 × 0.14	0.39 × 0.22 × 0.03
θ range (deg)	4.00−70.20	3.27−70.09	1.70−26.37	2.58−70.25
no. of rflns collected	54617	61462	46620	174379
no. of indep rflns (R(int))	5509 (0.0381)	7080 (0.0303)	5486 (0.0498)	5775 (0.1560)
GOF on F^2	1.043	1.057	1.062	1.013
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0398	R1 = 0.0448	R1 = 0.0414	R1 = 0.0510
	wR2 = 0.1071	wR2 = 0.1266	wR2 = 0.1098	wR2 = 0.1320
R indices (all data)[a]	R1 = 0.0410	R1 = 0.0478	R1 = 0.0500	R1 = 0.0678
	wR2 = 0.1083	wR2 =0.1297	wR2 = 0.1160	wR2 = 0.14480
largest peak, hole (e Å^{-3})	0.557, −0.386	0.454, −0.521	0.625, −0.338	0.505, −0.381

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$, where $P = (F_o^2 + 2F_c^2)/3$.

$PhCH_2$), 48.0 (s, NCH_2), 32.6 (d, J = 12.1 Hz, CH Cy), 29.9 (d, J = 16.9 Hz, CH_2 Cy), 28.5 (d, J = 7.8 Hz, CH_2 Cy), 27.9 (s, $CH(CH_3)_2$), 26.5 (d, J = 12.4 Hz, CH_2 Cy), 26.3 (d, J = 7.7 Hz, CH_2 Cy), 26.0 (s, CH_2 Cy), 24.8 (s, $CH(CH_3)_2$), 23.8 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (202 MHz, DMSO-d_6): δ −17.0 (s).

*1-Mes-3-{2-(PAd$_2$)phenyl}imidazolidin-2-ylidene (**23**).* The dihydroimidazolium salt **11** (800 mg, 1.23 mmol) was combined with 1 equiv of NaHMDS (225 mg, 1.23 mmol) in a 4 dram vial. An 8 mL portion of THF was added, and the resulting mixture was stirred at ambient temperature for 1 h. The reaction mixture was then filtered through Celite and concentrated to approximately 0.5 mL. Addition of pentane (5 mL) precipitated the product as a beige solid. This was decanted, washed with pentane (3 × 3 mL), and dried in vacuo, yielding 578 mg of the product as a beige powder. A further 62 mg of material crystallized from the collected washings upon standing for 24 h, giving a total yield of 92% (640 mg, 1.13 mmol). ^1H NMR (500 MHz, C_6D_6): δ 7.86 (d, J = 7.3 Hz, 1H, 6-Ph), 7.70 (br s, 1H, 3-Ph), 7.21 (t, J = 7.4 Hz, 1H, 4-Ph), 7.14 (t, J = 7.4 Hz, 1H, 5-Ph), 6.83 (s, 2H, m-Mes), 4.18 (br m, 2H, NCH_2), 3.49 (br m, 2H, NCH_2), 2.40 (s, 6H, o-CH_3 Mes), 2.15−2.09 (ov m, 15H, p-CH_3 Mes + Ad), 1.87 (br s, 6H, Ad), 1.63 (br s, 12H, Ad). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 245.1 (br s, NCN), 137.1 (s, 6-Ph), 136.3 (s), 130.1 (s, 4-Ph), 130.0 (d, J = 4.3 Hz, 3-Ph), 129.4 (s, m-Mes), 125.2 (br s, 5-Ph), 54.5 (d, J = 19.0 Hz, NCH_2), 51.8 (s, NCH_2), 42.6 (d, J = 13.0 Hz, CH_2 Ad), 37.6 (d, J = 25.2 Hz, quaternary Ad), 37.3 (s, CH_2 Ad), 29.3 (d, J = 8.5 Hz, CH Ad), 21.1 (s, p-CH_3 Mes), 18.6 (s, o-CH_3 Mes). Four quaternary aromatic carbon resonances are not observed due to the broad resonances associated with this compound. A broad $C_{carbene}$ peak at 245.1 is only observed upon the application of substantial line broadening to improve the signal to noise ratio. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 19.5 (s).

Details of Catalytic Studies. *Procedure for Preliminary Screening Studies (Table 1).* The dihydroimidazolium salt (0.01 mmol, 4 mol %) and NaHMDS (0.01 mmol, 1.8 mg) were combined in a 1 dram catalysis vial with a stir bar and 0.50 mL of toluene. The mixture was stirred for 5 min, and then $[Pd(cinnamyl)Cl]_2$ (0.0025 mmol, 1.3 mg, 1 mol %) was added. After the mixture was stirred for an additional 5 min, NaOtBu (0.35 mmol), PhCl (0.25 mmol), and amine (0.3 mmol) were added sequentially. The vial was sealed with a cap containing a PTFE septum, removed from the glovebox, and heated to 110 °C with vigorous stirring. After 24 h, the reaction mixture was cooled to ambient temperature and an aliquot was removed, filtered through silica with CH_2Cl_2, and analyzed by GC.

Representative Procedure for Preparation of Precatalyst Mixtures. Freshly prepared NHC-P compound **23** (400 mg, 0.708 mmol) was dissolved in 4 mL of THF. The resulting colorless solution was added dropwise to a rapidly stirred suspension of $[Pd(cinnamyl)Cl]_2$ in THF over a 10 min period, giving initially a light red solution. Stirring was continued for 1 h, and over this time the solution gradually became very dark red. Removal of solvent in vacuo gave the precatalyst mixture **23**·Pd(cinnamyl)Cl as a red powder.

Procedure for Arylation of Primary Amines (Table 5). A 0.0050 M stock solution of precatalyst mixture **23**·Pd(cinnamyl)Cl was prepared by dissolving 32.8 mg of the precatalyst in 8.00 mL of 1,4-dioxane. Stock solutions were freshly prepared as required and used within 1 h. A 2.00 mL portion of the stock solution was added to a 1 dram catalysis vial containing LiHMDS (234 mg, 1.4 mmol), and the mixture was stirred for 5 min. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The aryl halide and primary amine were then added sequentially using a syringe, and the reaction mixture was stirred at ambient temperature (65 °C for **24h**). Upon completion of the reaction, the mixture was filtered through a bed of silica and washed through with CH_2Cl_2. Removal of volatiles gave the arylamine product, which was purified by flash chromatography in silica if necessary. Reported isolated yields are an average of two runs. In some instances, the procedure was modified with the use of NaOtBu base (135 mg, 1.4 mmol), as noted in Table 5.

Procedure for Arylation of Secondary Amines (Table 6). A 0.0050 M stock solution of precatalyst mixture **23**·Pd(cinnamyl)Cl was prepared by dissolving 32.8 mg of the precatalyst in 8.00 mL of DME. Then 2.00 mL of freshly prepared stock solution was added to a 1 dram catalysis vial containing NaOtBu (135 mg, 1.4 mmol) and the

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mixture was stirred for 5 min. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The aryl halide and secondary amine were then added sequentially using a syringe, and the reaction mixture was stirred at ambient temperature (65 °C for **25f**). Upon completion, the reaction mixture was filtered through a bed of silica and washed through with CH_2Cl_2. Removal of volatiles gave the arylamine product, which was purified by flash chromatography if necessary. Reported isolated yields are an average of two runs.

Procedure for Monoarylation of Ammonia. Using a modification of the literature procedure,[6g] 4.1 mg of the precatalyst mixture **23**·Pd(cinnamyl)Cl (0.005 mmol, 2 mol %) was combined in a 1 dram catalysis vial with NaO*t*Bu (48.1 mg, 0.50 mmol) and 0.5 mL of 1,4-dioxane. The mixture was stirred for 5 min, and chlorobenzene (25.4 μL, 0.25 mmol) was added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. A 2.5 mL portion of a 0.5 M solution of ammonia in 1,4-dioxane (1.25 mmol, 5 equiv) was added with a syringe. The vial was heated to 110 °C with stirring for 30 min, at which time the reaction was complete. Calibrated GC analysis, with calibration using authentic samples and measurements relative to dodecane as an internal standard, was used to determine the yield of product and the ratio of monoarylation to diarylation.

Procedure for Mono-α-arylation of Acetone. Using a modification of the general procedure,[26e] 4.1 mg of the precatalyst mixture **23**·Pd(cinnamyl)Cl (0.005 mmol, 2 mol %) was combined in a 1 dram catalysis vial with a catalytic amount of NaO*t*Bu and 0.5 mL of DME. After the mixture was stirred for 5 min, Cs_2CO_3 (163 mg, 0.5 mmol), chlorobenzene (25.4 μL, 0.25 mmol), and 0.50 mL of dry acetone were added. The vial was sealed, removed from the glovebox, and heated to 90 °C for 1.5 h. GC analysis of an aliquot, with calibration using authentic samples and measurements relative to dodecane as an internal standard, then revealed 94% consumption of PhCl and 64% yield of monoarylation product.

Details of X-ray Crystallographic Studies. Crystals of **12** and **13** were grown by slow diffusion of diethyl ether into a DCM solution of the compound. Crystals of **16** and **21** were grown by slow diffusion of hexanes into a DCM solution of the compound. Crystallographic data were obtained at 173(2) K, on either a Bruker PLATFORM/SMART 1000 CCD diffractometer or a Bruker D8/APEX II CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for **16** and Cu Kα radiation (λ = 1.54178 Å) for **12**, **13**, and **21**. Unit cell parameters were determined and refined on all reflections. Data reduction and correction for Lorentz−polarization were performed using Saint-plus,[31] and scaling and absorption correction were performed using the SADABS software package.[32] Structure solution by direct methods and least-squares refinement on F^2 were performed using the SHELXTL software suite.[33] Non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed in calculated positions and refined with a riding model. Multiscan absorption correction was employed in all cases. Structural figures were generated with ORTEP-3.[34] The BF_4 anion of **21** is poorly ordered, and three fluorines have been modeled as positionally disordered over two sites in a 77:23 ratio. All other atoms in all structures are well ordered. Crystallographic data are given in Table 7.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR spectra of all reported compounds, text giving NMR data, and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

Biography

Mark Stradiotto completed his Honours B.Sc. (Applied Chemistry, 1995) and Ph.D. (Organometallic Chemistry, 1999) degrees in the Department of Chemistry at McMaster University (Canada), after which he moved to the University of California at Berkeley as a Natural Sciences and Engineering Research Council of Canada Postdoctoral Fellow. In September of 2001, Mark joined the Department of Chemistry at Dalhousie University as an Assistant Professor, where he is now the Alexander McLeod Professor of Chemistry. Mark has served on the Editorial Advisory board of *Organometallics* and has received a number of awards in recognition of his excellence in teaching and research, including most recently the *Strem Chemicals Award for Pure or Applied Inorganic Chemistry*.

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