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Analyses of the Structural and Electronic Properties of NHCs with Bicyclic Architectures

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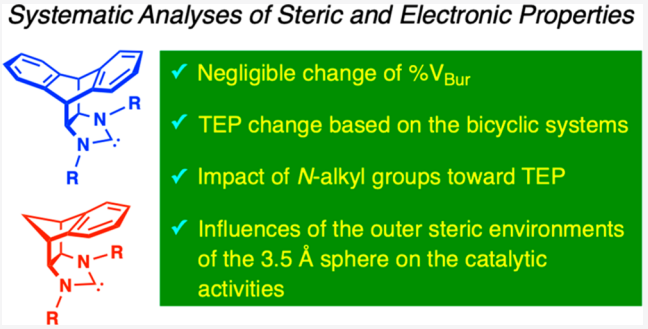
ABSTRACT: Quantification of the steric and electronic properties of ligands is an important task for the development of highly effective chemical transformations when using a metal complex as a catalyst. In this study, we used silver and iridium complexes to perform systematic analyses to quantify the steric and electronic properties of original NHCs, which we refer to as DHASI and BCPSI. In addition to two silver chloride complexes that we previously reported, two novel BCPSIiPrAgCl and BCPSICyAgCl complexes were prepared and used for XRD studies to quantify the steric properties via use of a method referred to as the percent buried volume (%V_{Bur}). We then synthesized 6 IrCl(CO)$_2$(HNC) complexes to calculate the TEP values, and the results indicated that the influences of two different core bicyclic motifs were somewhat unclear, while the influences of different N-substituents were readily apparent. Finally, the original NHCs were applied to a copper catalyzed allylic arylation of cinnamyl bromide with PhMgBr. The regioselectivity of the substitutions suggested that the steric environments existing at relatively long distances from the bound copper also exerted a considerable amount of influence over the catalytic properties.



INTRODUCTION

Steric shielding and electron donation of a ligand are important properties for making a metal complex if it is to be effective in catalyzing a specific chemical transformation. Since the fine-tuning of these factors is known to be a key factor in developing a highly useful catalytic process, a large number of ligands have been developed to widen their tuning capacity.[1] Sterically hindered ligands aptly protect active, but unstable, metals with low valence from undesired decompositions, but too much steric pressure will cause the steric repulsion of substrates, which could result in ineffective catalysis. Appropriate steric shielding is also known to accelerate the catalytic cycle, particularly the reductive elimination step. Electron donation from ligands activates the bound metals and the resultant complexes become capable of oxidative addition to relatively stable bonds such as C−F,[2] C−N,[3] and even C−H[4] bonds. Quantification of these factors has been attempted, and the most widely used examples are the Tolman cone angle[5] and the Tolman's electronic parameter (TEP).[6] Tolman cone angles are beneficial in quantifying the steric influences that phosphine ligands exert on metal complexes, and the TEP is widely used to quantify the electron donating ability of ligands.

N-heterocyclic carbenes (NHCs) are ubiquitous ligands in organometallic chemistry because of their high performance during the activation of transitional metals and for stabilizing unstable highly reactive species.[7] Although free NHCs show a relatively high level of stability, they remain air- and moisture-sensitive divalent carbons. These somewhat reactive species can easily be prepared from azolium salt precursors via deprotonation. The precursor salts are usually very stable crystalline solids, and straightforward methods to synthesize these salts have already been developed by many chemists.[8] Therefore, a number of NHCs have been synthesized and investigated to develop useful and effective catalytic processes. Due to an ease of synthesis and useful geometric features, the introduction of bulky substituents onto the nitrogen(s) of imidazolin-2-ylidenes or of imidazolidin-2-ylidenes has become the most common design (Figure 1a).[9] The bulky *N*-substituents on these representative core heterocycles effectively shield the active sites, which has resulted in the development of highly active NHC-metal catalysts. Because the structure of NHCs is not in a "cone" form, Nolan and Cavallo developed the "percent buried volume" (%V_{Bur}) as a parameter that could be used to quantify the steric properties of many types of ligands such as phosphines and NHCs.[10] Cavallo and co-workers additionally developed a steric map to evaluate the manner in which ligands wrap around bound

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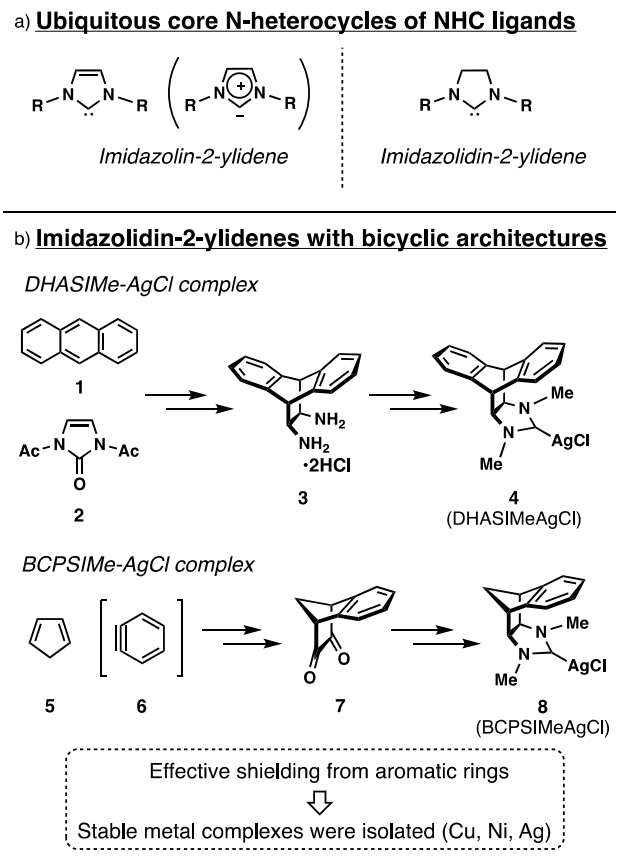


Figure 1. (a) The structures of a ubiquitous NHC core. (b) Imidazolidin-2-ylidenes with a bicyclic architecture on noncarbenic carbons.

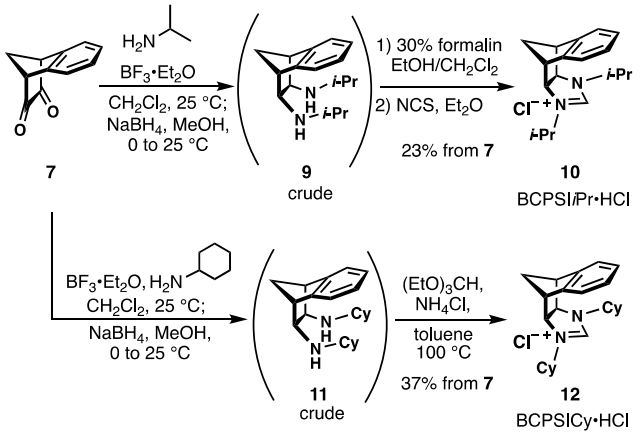
metals, which is helpful in imagining the shape of the reactive pocket.[11]

Our group has developed original NHCs that possess bicyclic architectures on the noncarbenic carbons of imidazolidin-2-ylidene, which we refer to as DHASI[12] or as BCPSI[13] (Figure 1b). These two core examples of NHC architecture showed good shielding effects when we used them as ligands to form their silver,[12,13] copper,[14] and nickel[15] complexes. Modification studies on the bicyclo[2.2.1]heptane motif of BCPSI revealed that an aromatic ring set on an active site is critical in stabilizing NHC-metal complexes. It should be emphasized that these stable complexes were formed using DHASIs equipped with alkyl groups such as methyl, isopropyl, and cyclohexyl groups or by using BCPSIMe as a ligand. Generally speaking, metal complexes using imidazolidin-2-ylidenes are unstable when the *N*-substituents are small alkyl groups, whereas DHASIMeAgCl and BCPSIMeAgCl are stable crystalline solids.[16] Herein, we report detailed analyses of DHASIs and BCPSIs in order to quantify the steric properties and electron donative abilities. We analyzed their steric properties via the structural analyses of silver complexes. To quantify the electron donative abilities of DHASIs and BCPSIs with Me, *i*-Pr, and Cy *N*-substituents, $IrCl(CO)_2(NHC)$ complexes were synthesized and used to calculate the TEP values via the Ir scale developed by Nolan and co-workers. To investigate the impact on metal catalysts, we applied ligands to a copper-catalyzed allylic arylation with PhMgBr.

RESULTS AND DISCUSSION

Syntheses of BCPSI*i*Pr and BCPSICy Precursors. In this study, we synthesized BCPSI ligands with isopropyl and cyclohexyl groups as *N*-substituents to investigate their influence compared with the use of DHASIMe,[12] DHASI*i*Pr,[14] DHASICy,[14] and BCPSIMe,[13] as reported (Scheme 1a). The

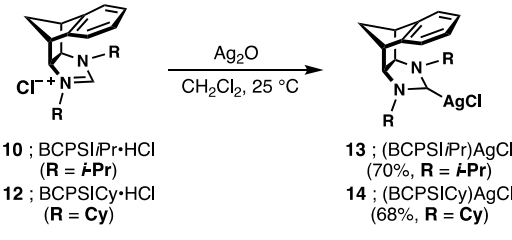
Scheme 1. Syntheses of BCPSIiPr and BCPSICy Precursors



syntheses were started with an imination of diketone **7**[13] and isopropyl amine in the presence of $BF_3{\cdot}Et_2O$, and the diimines were subsequently reduced with the use of $NaBH_4$ to afford *cis*-diamine **9** as a crude oil. The *cis*-diamine **9** was treated with formalin to form an imidazolidine ring, followed by oxidation with NCS to obtain imidazolinium chloride **10** (BCPSI*i*Pr·HCl) as a BCPSI*i*Pr precursor in a 23% yield over 4 steps. For the preparation of this BCPSI*i*Pr precursor, one step cyclization using triethyl orthoformate in the presence of ammonium chloride resulted in an inferior yield. Another NHC precursor with cyclohexyl groups was synthesized via a similar pathway through *cis*-diamine **11** obtained with the use of cyclohexylamine. The crude *cis*-diamine **11** was treated with triethyl orthoformate in the presence of NH_4Cl to afford imidazolinium chloride **12** (BCPSICy·HCl) as a BCPSICy precursor in a 37% yield from diketone **7**.

Syntheses and Structural Analyses of BCPSI*i*PrAgCl and BCPSICyAgCl Complexes. With the NHC precursors in hand, we synthesized silver complexes via treatment with Ag_2O in CH_2Cl_2 at 25 °C, which isolated BCPSI*i*PrAgCl **13** and BCPSICyAgCl **14** in 62% and 68% yields, respectively (Scheme 2). These silver complexes were stable under air on a bench in the solid state and isolated as colorless crystalline solids. Because we previously analyzed DHASIMeAgCl **4**[12] and BCPSIMeAgCl **8**[13] complexes using XRD studies, we

Scheme 2. Syntheses of BCPSIAgCl and BCPSICyAgCl Complexes



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attempted XRD studies with these novel silver complexes to observe the influences of *N*-substituents. Single crystals of these complexes were obtained via the slow diffusion of *n*-hexane in CH_2Cl_2 solutions of BCPSI*i*PrAgCl **13** or BCPSICyAgCl **14** at ambient temperature, and the ORTEP diagrams appear in Figure 2a,b. BCPSI*i*PrAgCl **13** had a symmetric structure in the solid state, and two methyl groups on the isopropyl group faced in the direction of the silver chloride. On the other hand, BCPSICyAgCl **14** was unsymmetric in the solid state, with two cyclohexyl groups that had different conformations. However, the most stable conformation in a solution state will be symmetric, as shown by the NMR spectra. Despite the fact that silver halide complexes supported by NHCs possess diverse bonding motifs,[17] all silver chloride complexes with BCPSI ligands including BCPSIMeAgCl **8** were of a monomeric linear NHC−Ag−Cl form, which is a relatively rare structure.[18] DHASIMe also gave us a DHASIMeAgCl **4** complex in the same bonding motif, suggesting that our original NHCs with bicyclic motifs on the noncarbenic carbons tend to form this linear structure in the solid state. It should be noted that this tendency is independent of *N*-substituents in contrast to the reports of varied structures that depend on *N*-substituents. We subsequently attempted to quantify the steric properties of these novel NHCs by using the SambVca 2.1 program developed by Cavallo and co-workers (Figure 2c,d).[11a] A calculation was performed using the default parameters (atomic radii; 1.17, mesh spacing; 0.10 Å), and 2.0 Å was considered as the distances for the NHC-metal bonds. The results using a 3.5 Å sphere radius are shown in Figure 2. The steric map indicated that the steric pressure from the bicyclic framework was very small in the first sphere around the metal (northern part of the steric maps). Compared with DHASIMe and BCPSIMe, the bicyclic architecture seemed to exert fewer steric effects on BCPSI*i*Pr and BCPSICy. Therefore, the $\%V_{Bur}$ for both BCPSI*i*Pr (39.0) and BCPSICy (32.9) was higher than that for BCPSIMe (29.8), which was mainly the results of bulkier *N*-substituents. The difference between BCPSI*i*Pr (39.0) and BCPSICy (32.9) was caused by the geometries of the secondary alkyl groups. As mentioned previously, the most stable structures of these complexes in solution states are symmetric, as shown in NMR spectra; therefore, the steric pressure from *N*-substituents during catalysis cannot be fully estimated using these calculations for structures in a solid state. These secondary alkyl *N*-substituents cause steric repulsion with the aromatic ring on a bicyclic architecture, and this repulsion made the dihedral angle between the aromatic ring and the NHC core *N*-heterocycles of BCPSI*i*Pr larger than that of BCPSIMe (angles *a* in Figure 2e). In a similar manner, BCPSICy had a larger dihedral angle than that of either BCPSIMe or BCPSI*i*Pr, which would have weakened the aromatic ring's influence on the silver atom. The differences in dihedral angles were apparent in calculations using a sphere radii larger than 3.5 Å, which resulted in a steric pressure in the northern portion of the steric maps of BCPSIMe (Figure S41 in the Supporting Information). Compared with imidazolin-2-ylidene ligands without a bicyclic structure (IMe, I*i*Pr, and ICy), higher levels of $\%V_{Bur}$ for DHASIs and BCPSIs were observed (Table S5 in the Supporting Information). Notably, when the longer sphere radii were considered, larger differences in $\%V_{Bur}$ were observed. These facts suggested that the steric state of the outer sphere could be heightened by the bicyclic architectures on noncarbenic carbons, which would be useful for widening the capacity when tuning the steric state of an NHC ligand.

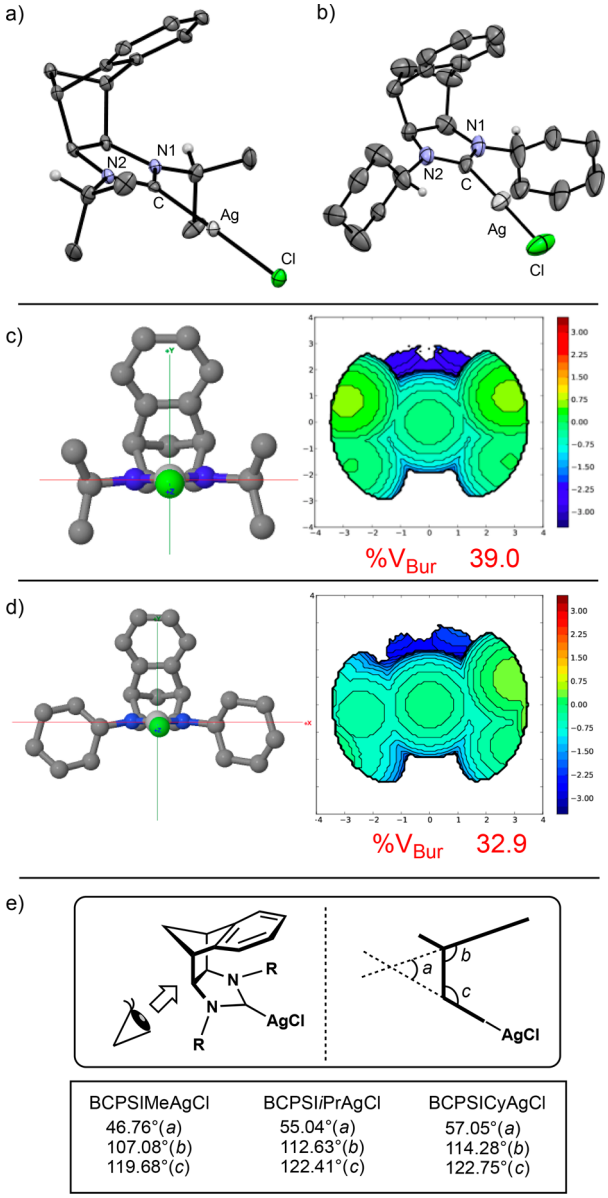

Figure 2. (a) ORTEP diagram of BCPSI*i*PrAgCl **13**. Thermal ellipsoids are shown at the 50% probability level. Most H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C−Ag, 2.086; Ag−Cl, 2.330; N1−C−N2, 109.1; and C−Ag−Cl, 179.0. (b) ORTEP diagram of BCPSICyAgCl **14**. Thermal ellipsoids are shown at the 50% probability level. Most H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C−Ag, 2.084(6); Ag−Cl, 2.320(3); N1−C−N2, 109.1(5); and C−Ag−Cl, 176.9(2). (c) Steric map and $\%V_{Bur}$ of BCPSI*i*PrAgCl (see Experimental Section for details). (d) Steric map and $\%V_{Bur}$ of BCPSICyAgCl (see Experimental Section for details). (e) Dihedral angles on silver chloride complexes of BCPSIs.

Syntheses of Ir(COD)Cl(NHC) and $IrCl(CO)_2$(NHC) Complexes with DHASIs and BCPSIs for Structural Analyses and Calculations of TEP Values. The Tolman electronic parameter (TEP) was originally developed using an IR stretch of carbonyl groups of $Ni(CO)_3L$ complexes.[6] A highly electron-donating ligand will weaken a CO triple bond attached to a metal, which reduces the ν(CO) value. This

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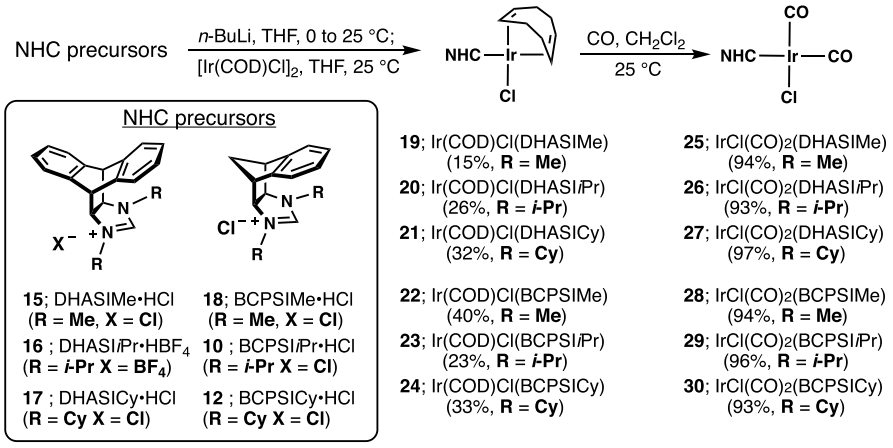
Scheme 3. Syntheses of $IrCl(CO)_2(NHC)$ Complexes with DHASIs and BCPSIs



parameter can be used not only for phosphine ligands but also for NHCs, but the high volatility and toxicity of $Ni(CO)_4$ has always been a safety drawback for this method. To avoid the handling of this hazardous material, the Rh scale and Ir scales are frequently used to quantify the electronic properties.[19] Crabtree and co-workers first systematically investigated some $IrCl(CO)_2(PR_3)$ complexes to translate the average $\nu(CO)$ value of these complexes to a TEP value based on $Ni(CO)_3L$ complexes.[20] Later, Nolan and co-workers used 9 $IrCl(CO)_2(NHC)$ complexes to extend this Ir system, and the equation they developed (eq 1; $R^2 = 0.971$) is currently used to calculate the TEP values of a wide variety of NHC ligands.[21]

$$\text{TEP} = 0.847[\nu_{av}(\text{Ir})] + 336.2\ \text{cm}^{-1} \quad (1)$$

The syntheses of $IrCl(CO)_2(NHC)$ using DHASIs and BCPSIs are summarized in Scheme 3. We treated NHC precursors with *n*-BuLi to generate free carbene in situ, and subsequently the NHC solution was transferred to a flask charged with $[Ir(COD)Cl]_2$ to afford Ir(COD)Cl(NHC) complexes **19**−**24** as yellow crystalline solids in acceptable yields. The Ir(COD)Cl(NHC) complexes **19**−**24** were then transformed to $IrCl(CO)_2(NHC)$ complexes **25**−**30** via the bubbling of CO gas into CH_2Cl_2 solutions at 25 °C, and these complexes were obtained as pale yellow solids in excellent yields.

We used Ir(COD)Cl(DHASI*i*Pr) **20** and Ir(COD)Cl(BCPSI*i*Pr) **23** for XRD analyses to perform structural investigations. With both complexes, single crystals for XRD experiments were grown via the slow diffusion of *n*-hexane into CH_2Cl_2 solutions at ambient temperature. The ORTEP diagrams are shown in Figure 3. On both complexes, the geometries of Ir were square planar, and chloride atoms existed on the other side of the aromatic rings on the bicyclic frames. The $\%V_{Bur}$ of both complexes were approximate and smaller than that of BCPSI*i*PrAgCl **13** because of the conformations of isopropyl groups (the parameters for the calculation are same as that for Figure 2). Similar to the previous analyses using DHASIMeAgCl **4** and BCPSIMeAgCl **8**,[13] the aromatic ring of the DHASI*i*Pr ligand was located further from carbene than that of the BCPSI*i*Pr ligand, which seems to be a general difference between these two similar frameworks. This means that these two similar frameworks have additional sterically tunable sites, which are aromatic rings located at different distances from the bound metals. As we show later, these differences had an unexpectedly strong influence on the catalytic activities of these copper complexes.

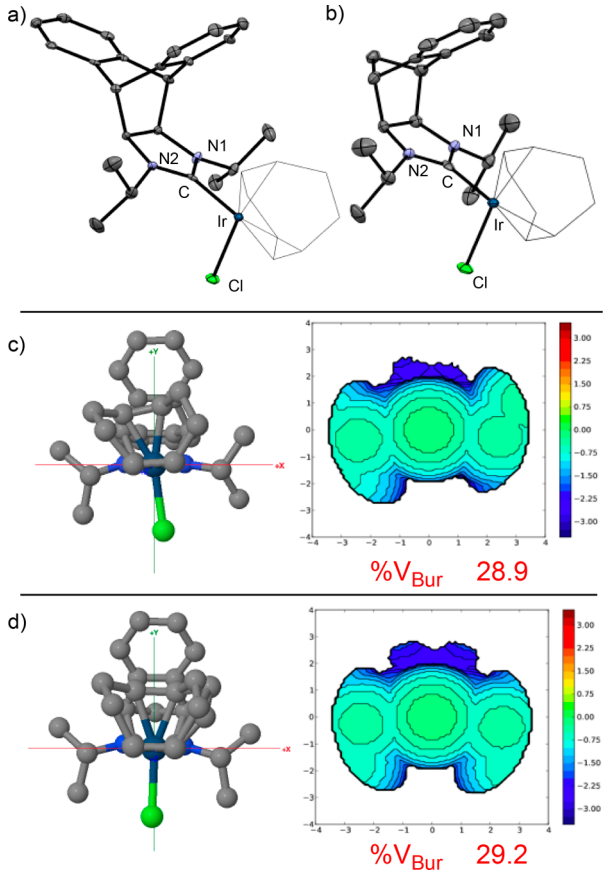


Figure 3. (a) ORTEP diagram of Ir(COD)Cl(DHASI*i*Pr) **20**. Thermal ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity. A COD ligand appears as a wireframe model. Selected bond lengths (Å) and angles (deg): C−Ir, 2.025(3); Ir−Cl, 2.375(1); N1−C−N2, 109.6(3); and C−Ir−Cl, 89.3(1). (b) ORTEP diagram of Ir(COD)Cl(BCPSI*i*Pr) **23**. Thermal ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity. A COD ligand appears as a wireframe model. Selected bond lengths (Å) and angles (deg): C−Ir, 2.017; Ir−Cl, 2.327; N1−C−N2, 109.1; and C−Ir−Cl, 92.1. (c) Steric map and $\%V_{Bur}$ of Ir(COD)Cl(DHASI*i*Pr) (see Experimental Section for details). (d) Steric map and $\%V_{Bur}$ of Ir(COD)Cl(BCPSI*i*Pr) (see Experimental Section for details).

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With the use of $IrCl(CO)_2(NHC)$ complexes **25**−**30**, the IR spectra were measured to calculate the TEP values of these NHC ligands (Table 1). Huynh previously reported extensive

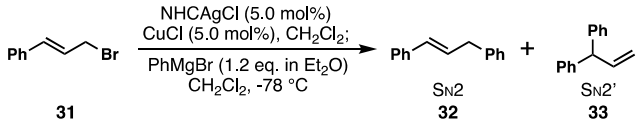
Table 1. TEP Values of DHASIs, BCPSIs, and Other Common NHCs

entry	ligand	TEP value (cm^{-1})
1	DHASIMe	2056
2	DHASI*i*Pr	2053
3	DHASICy	2051
4	BCPSIMe	2055
5	BCPSI*i*Pr	2053
6	BCPSICy	2052

studies about the relationship between TEP values and structures of NHCs, in which the limitations for the quantification of electron donative abilities based on TEP values is suggested.[19] However, the TEP value remains the most aptly studied parameter, which should help explain the relative electronic properties of NHCs, particularly NHCs with a unique core structure. In this study, we aimed to investigate the influences of bicyclic architectures, particularly the influences of aromatic rings on the different distances from the bound metals. We used CH_2Cl_2 solutions of $IrCl(CO)_2(NHC)$ complexes **25**−**30** because the solvents had a considerable amount of influence on the TEP values.[19] The results are summarized in Table 1. Unfortunately, we found no significant changes in the TEP values between NHCs with and without bicyclic architectures, although the fluctuations based on the *N*-substituents seemed influenced by the core structures.[22] However, because of the limited resolution of IR spectroscopy, the results of only these observations are not sufficiently convincing to support the theory that these slightly different degrees of the fluctuations based on *N*-alkyl groups were the result of the influences of aromatic rings.[19] In addition to other parameters for quantification of electronic properties, further studies with a series of NHCs such as a BCPSI core equipped with varied substituents on the aromatic ring might be helpful to explain the influence of π-electron of aromatic rings.

The Influences that NHCs with a Bicyclic Architecture Exert on Regioselectivity during Copper-Catalyzed Allylic Arylation with PhMgBr. We finally applied these 6 NHC ligands to a copper-catalyzed allylic arylation of cinnamyl bromide with PhMgBr to evaluate the influence of the structure on catalytic activity. Mechanistically, a bulky and electron-deficient ligand is thought to be preferable because it heightens S_N2' selectivity.[23] Our group previously found that the DHASIMeCuCl complex, which forms in situ, generates S_N2'-substituted products as its major yield (S_N2:S_N2' = 20:80), whereas IMeCuCl gave us a 1:1 mixture of S_N2 and S_N2' substituted products. BCPSIMeCuCl, which also forms in situ, generated S_N2' substituted products in a ratio (S_N2:S_N2' = 12:88) that was higher than that of DHASIMeCuCl. In addition to these previous results, we attempted the reaction with DHASI*i*Pr, DHASICy, BCPSI*i*Pr, and BCPSICy ligands, and the results are summarized in Table 2. We used silver chloride complexes as an NHC transfer reagent to form a

Table 2. Application to a Copper Catalyzed Allylic Arylation of Cinnamyl Bromide 31 with PhMgBr



entry	ligand	combined yield (%)	S_N2:S_N2'
1[12]	DHASIMe	98	20:80
2	DHASI*i*Pr	90	40:60
3	DHASICy	90	23:77
4[13]	BCPSIMe	99	12:88
5	BCPSI*i*Pr	95	7:93
6	BCPSICy	85	4:96
7	IMe	98	49:51

(NHC)CuCl complex in situ, which was directly used as a catalyst. It was somewhat surprising that the use of DHASI*i*Pr and DHASICy resulted in a selectivity for S_N2'-substituted products that was inferior to that of DHASIMe. In contrast to the results with DHASIs, BCPSI*i*Pr and BCPSICy generated the S_N2' product with selectivity that was higher than that generated by BCPSIMe. Since the TEP values were the same, the drastic differences between DHASI*i*Pr and BCPSI*i*Pr are thought to arise from the steric differences on the bicyclic structures. Although the steric properties were similar based on their $\%V_{Bur}$ and steric maps in the first sphere around the metal, these results obviously suggested that the outer steric environments of the 3.5 Å sphere (see Figures S38 and S42 and Table S5 in the Supporting Information) strongly affected the regioselectivity. At the same time, higher S_N2'-selectivity with DHASIMe and with BCPSIMe than with DHASICy cannot be explained by using $\%V_{Bur}$ values alone even if we considered the values in large spheres. One possible reason for these phenomena might be the distances between the bound copper and the aromatic ring, because we had previously observed the exceptional influence of the phenyl group.[13] The steric maps of DHASIMe and of BCPSIMe in a 5.0 Å sphere clearly showed the steric pressure of phenyl groups in the northern portions (Figures S36 and S41), which are closer to the carbenes than the phenyl group of DHASICy (Figure S40). To obtain the S_N2' product in higher selectivity with this particular substitution reaction, the closer aromatic ring on the BCPSI core and the bulky *N*-substituents were effective, which suggested the necessity to consider steric tuning on the range from the metal center in a sphere wider than 3.5 Å sphere.

CONCLUSION

In this study, we synthesized two novel NHC precursors, BCPSI*i*Pr·HCl **10** and BCPSICy·HCl **12**, and used systematic investigations to quantify the electronic and steric properties of our previously developed NHCs possessing bicyclic frameworks. The steric properties of BCPSI ligands with *N*-isopropyl and *N*-cyclohexyl groups were analyzed using silver chloride complexes. The secondary alkyl groups on nitrogen caused steric repulsion to an aromatic ring, which resulted in dihedral angles between the aromatic ring and the NHC core that were larger than those of BCPSIMeAgCl. Analyses using the SambVca 2.1 program indicated that the steric influences of

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the aromatic rings on BCPSI*i*Pr and on BCPSICy were smaller than that on BCPSIMe particularly when the sphere radii are larger than 3.5 Å, and that the secondary *N*-alkyl groups showed increased $\%V_{Bur}$ values. To quantify the electronic properties of DHASIs and BCPSIs, the 6 $IrCl(CO)_2(NHC)$ complexes were prepared and subsequently analyzed using IR spectra. The IR stretch of carbonyl showed that the TEP values of DHASIs and of BCPSIs changed depending on the *N*-alkyl groups, whereas the impact of bicyclic motifs was not so obvious. Further extensive studies are required to explain the high stabilities of metal complexes supported by DHASIs and BCPSIs. Finally, to examine the influence that our NHCs could exert on a metal catalyst, we applied 6 NHCs equipped with bicyclic frameworks to a copper-catalyzed allylic arylation of cinnamyl bromide with PhMgBr. The regioselectivity of this transformation was changed depending on the *N*-substituents as well as on the bicyclic core structure. The results obviously indicated that the outer steric environments of the 3.5 Å sphere of the bound metal affected the properties of the catalysts. Further investigations to develop catalytic transformations using the unique steric and electronic properties of DHASIs and of BCPSIs are under way in our laboratory.

EXPERIMENTAL SECTION

General Procedure and Chemicals. ***Caution!*** *Since CO gas is highly toxic and flammable, handle with extreme care.* All reactions were carried out under an argon atmosphere with freshly distilled solvents under anhydrous conditions, unless otherwise noted. Anhydrous CH_2Cl_2, DMSO, and THF were purchased and used without further distillation. Other reagents were used without further purification. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded at 600 and 151 MHz, respectively. Chemical shifts are reported in δ ppm and reference either an internal tetramethylsilane or solvent peaks. The following abbreviations are used to indicate the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; qt = quintet; sex = sextet; sept = septet dd = doublet of doublets; ddd = doublet of doublet of doublets; dddd = doublet of doublet of doublet of doublets; dt = doublet of triplets; app = apparent; m = multiplet; br = broad. Melting points were uncorrected. High-resolution mass spectra were recorded on a high resolution quadrupole time-of-flight instrument operating in an electrospray ionization (ESI) mode or on a double-focusing magnetic-sector mass analyzer operating in a fast atomic bombardment (FAB) mode. Buried volume calculations were performed using the SambVca 2.1 web application available online at https://www.molnac.unisa.it/OMtools/sambvca2.1/index.html. The crystal structures were uploaded in .xyz format. The *xz* plane was defined by the imidazolidine ring system, the *z*-axis was oriented along the *xz* projection of NHC-metal bond. All Ag, Ir, Cl, COD ligands and hydrogen atoms were excluded from the analysis. The following parameters were used for the calculations: NHC−metal bond distances, 2.0 Å; Bondi radii scaled by 1.17; and mesh spacing for numerical integration, 0.10. The results within a 3.5 Å sphere appear in Figures 2 and 3, and the results from larger spheres are shown in the Supporting Information. NHC precursors, DHASIMe·HCl,[12] DHASI*i*Pr·HBF_4,[14] DHASICy·HCl,[14] and BCPSIMe·HCl,[13] were prepared according the procedure we previously reported.

Syntheses of NHC Precursors. *BCPSIiPr·HCl* ***10***. A flask was charged with (1*R*,4*S*)-1,2,3,4-tetrahydro-1,4-methanonaphthalene-2,3-dione[13] **7** (107 mg, 0.62 mmol) and a magnetic stir bar, and the flask was evacuated and backfilled with argon (this process was repeated three times). Toluene (2.0 mL) was added to dissolve the diketone **7**. Isopropylamine (0.27 mL, 3.1 mmol) was then added to the flask at 25 °C, followed by $BF_3{\cdot}Et_2O$ (0.07 mL, 0.62 mmol). After stirring at the same temperature for 15 h, the reaction solution was diluted with EtOAc (5.0 mL), and the resulting solution was washed with sat. NH_4Cl aq. (5.0 mL × 1), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain a crude diimine. The crude residue was dissolved in MeOH (2.0 mL), and the solution was cooled in an ice bath. $NaBH_4$ (46.9 mg, 1.2 mmol) was added to the solution at 0 °C, and the mixture was stirred at 25 °C for 1 h. The reaction was then quenched with sat. NH_4Cl aq. (2.0 mL), and the mixture was extracted with EtOAc (4.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude *cis*-diamine (110 mg) as a colorless powder. The crude diamine was dissolved in CH_2Cl_2/EtOH (7/3, 3.0 mL), and 30% formalin was added to the solution at 25 °C. After stirring at the same temperature for 2 h, The reaction solution was then concentrated under reduced pressure, and the crude mixture was diluted with EtOAc (3.0 mL) and H_2O (3.0 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (4.0 mL × 3). The combined organic layers were washed with brine (5.0 mL × 1), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was dissolved in 30% EtOAc in *n*-hexane, and the solution was passed through a short pad of silica gel, which was then eluted with the 30% EtOAc in *n*-hexane. The filtrate was concentrated under reduced pressure to afford a crude imidazolidine (62.5 mg) as a colorless oil. The crude imidazolidine was dissolved in Et_2O (1.5 mL), and NCS (61.7 mg, 0.46 mmol) was added at 25 °C. After being darkened with aluminum foil, the reaction mixture was stirred at the same temperature for 23 h. The colorless precipitate was filtered and purified by a column chromatography (5% MeOH/CH_2Cl_2) on silica gel (20 mL) to afford BCPSI*i*Pr·HCl **10** (45.3 mg, 0.14 mmol, 23% from diketone **7**) as a colorless powder. mp 99−102 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 9.09 (s, 1H, NC*H*N), 7.26−7.21 (m, 4H, Ar*H*), 4.93 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 3.86 (sept, *J* = 6.6 Hz, 2H, $NCH(CH_3)_2$), 3.82 (s, 2H, C*H*), 2.09 (ddd, *J* = 10.2, 1.8, 1.8 Hz, 1H, CH_AH_B), 1.84 (ddd, *J* = 10.2, 1.8, 1.8 Hz, 1H, CH_AH_B), 1.39 (d, *J* = 6.6 Hz, 6H, $NCH(CH_3)_2$), 1.36 (d, *J* = 10.2 Hz, 6H, $NCH(CH_3)_2$) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 302 K) δ 154.7 (NCN), 141.9 (Ar), 127.6 (Ar), 123.8(Ar), 66.0 (CH), 50.8 ($CH(CH_3)_2$), 48.6 (CH), 47.3 (CH_2), 21.3 (CH_3), 20.9 (CH_3) ppm; HRMS (ESI+, TOF) *m*/*z* calcd. for $C_{18}H_{25}N_2^+$ $[M - Cl]^+$: 269.2012, found 209.2028.

BCPSICy·HCl ***12***. A flask was charged with (1*R*,4*S*)-1,2,3,4-tetrahydro-1,4-methanonaphthalene-2,3-dione[13] **7** (177 mg, 1.03 mmol) and a magnetic stir bar, and the flask was evacuated and backfilled with argon (this process was repeated three times). Cyclohexylamine (0.57 mL, 5.15 mmol) was added to the flask at 25 °C, followed by $BF_3{\cdot}Et_2O$ (0.13 mL, 1.06 mmol). After stirring at the same temperature for 15 h, the reaction solution was diluted with EtOAc (20 mL), and the resulting solution was washed with sat. NH_4Cl aq. (20 mL × 1), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to obtain a crude diimine. The crude residue was dissolved in MeOH (3.4 mL), and the solution was cooled in an ice bath. $NaBH_4$ (77.9 mg, 2.06 mmol) was added to the solution at 0 °C, and the mixture was stirred at 25 °C for 1 h. The reaction was then quenched with sat. NH_4Cl aq. (2.0 mL), and the mixture was extracted with EtOAc (4.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a crude *cis*-diamine as a colorless powder. The crude diamine was dissolved in toluene, and $(EtO)_3CH$ (0.5 mL) and NH_4Cl (66.1 mg, 1.24 mmol) were added to the resultant solution. The reaction solution was heated at 100 °C for 16 h, and then concentrated under reduced pressure. The crude residue was dissolved in CH_2Cl_2, and insoluble solid was filtered-off. *n*-Hexane was added to the filtrate to precipitate the imidazolinium chloride. The colorless solid was filtered, and dried under reduced pressure to afford BCPSICy·HCl **12** (67.6 mg, 0.38 mmol, 37% from diketone **7**) as a colorless powder. mp 125−128 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 8.86 (s, 1H, NC*H*N), 7.25−7.20 (m, 4H, Ar*H*), 4.99 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 3.82 (s, 2H, CH), 3.42 (dddd, *J* = 12.0, 12.0, 3.6, 3.6 Hz, 2H, *Cy*), 2.12 (app d, *J* = 12.0 Hz, 1H, CH_AH_B), 2.06 (ddd, *J* = 9.6, 1.8, 1.8 Hz, 1H, CH_AH_B), 1.90−1.83 (m, 4H, *Cy*), 1.73 (dddd, *J* = 12.0, 12.0, 12.0, 3.6 Hz, 2H, *Cy*), 1.68−1.63 (m, 4H, *Cy*), 1.52 (dddd, *J* = 12.0, 12.0, 12.0, 3.6 Hz, 2H, *Cy*),

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1.34−1.30 (m, 4H, *Cy*), 1.24 (ddddd, *J* = 12.0, 12.0, 12.0, 3.6, 3.6 Hz, 2H, *Cy*) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 155.0 (NCN), 141.7 (Ar), 127.5 (Ar), 123.6 (Ar), 65.6 (CH), 57.5 (*Cy*), 48.5 (CH), 47.1 (CH_2), 31.7 (*Cy*), 31.1 (*Cy*), 25.3 (*Cy*), 25.0 (*Cy*), 24.9 (*Cy*) ppm; HRMS (ESI+, TOF) *m*/*z* calcd. for $C_{24}H_{33}N_2^+$ $[M - Cl]^+$: 349.2638, found 349.2643.

Typical Procedure for the Syntheses of NHC−AgCl Complexes. A flask was charged with NHC precursor (imidazolinium chloride, 1.0 equiv), Ag_2O (2.0 equiv), molecular sieves 4 Å (100 w/w%), and a magnetic stir bar. The resultant flask was evacuated and backfilled with argon (repeated three times), and CH_2Cl_2 ([precursor] = 0.1 M) was added to the flask. The reaction mixture was darkened with aluminum foil and stirred for 24 h at 25 °C. The mixture was then filtered through a short pad of Celite, which was washed with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure to reduce the total volume of the solution to ca. 1 mL. *n*-Hexane was added to the resulting solution to precipitate the NHC−AgCl complex, which was filtered and dried under reduced pressure to afford the title complexes.

BCPSIiPrAgCl ***13***. Yield: 64 mg (0.15 mmol, 70% from 0.22 mmol of BCISI*i*Pr·HCl); mp 227−229 °C; ^1H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.18 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 7.14 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 4.66 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 3.92 (sept, *J* = 6.6 Hz, 2H, NC*H*$(CH_3)_2$), 3.64 (s, 2H, C*H*), 2.00 (app dd, *J* = 9.6, 1.2 Hz, 1H, CH_AH_B), 1.74 (ddd, *J* = 9.6, 1.2, 1.2 Hz, 1H, CH_AH_B), 1.32 (d, *J* = 6.6 Hz, 6H, NCH$(CH_3)_2$), 1.26 (d, *J* = 10.2 Hz, 6H, NCH$(CH_3)_2$) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 142.8 (Ar), 126.8 (Ar), 124.0 (Ar), 66.3 (CH), 52.6 (CH$(CH_3)_2$), 49.5 (CH), 48.5 (CH_2), 22.8 (CH_3), 22.5 (CH_3) ppm (the carbenic carbon was not observed); HRMS (ESI+, TOF) *m*/*z* calcd. for $C_{36}H_{48}N_4Ag^+$ $[L_2Ag]^+$: 643.2924, found 643.2913. Although the MS spectrum showed that *m*/*z* L_2Ag^+ was the parent peak, the structure was a L−Ag−Cl form in a solid state.

BCPSICyAgCl ***14***. Yield: 30 mg (0.06 mmol, 68% from 0.09 mmol of BCPSICy·HCl); mp 171−173 °C; ^1H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.16 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 7.13 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 4.66 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 3.64 (s, 2H, C*H*), 3.45 (dddd, *J* = 12.0, 12.0, 3.6, 3.6 Hz, 2H, *Cy*), 2.02 (app d, *J* = 12.0 Hz, 1H, CH_AH_B), 1.97 (app dd, *J* = 9.6, 0.6 Hz, 1H, CH_AH_B), 1.89−1.79 (m, 4H, *Cy*), 1.72−1.66 (m, 4H, *Cy*), 1.66−1.59 (m, 2H, *Cy*), 1.51 (dddd, *J* = 12.0, 12.0, 12.0, 3.6 Hz, 2H, *Cy*), 1.38−1.24 (m, 6H, *Cy*), 1.14 (ddddd, *J* = 12.0, 12.0, 12.0, 3.6, 3.6 Hz, 2H, *Cy*) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 142.8 (Ar), 126.6 (Ar), 123.9 (Ar), 66.6 (CH), 60.7 (*Cy*), 49.5 (CH), 48.0 (CH_2), 33.5 (*Cy*), 33.1 (*Cy*), 25.70 (*Cy*), 25.67 (*Cy*), 25.3 (*Cy*) ppm (the carbenic carbon was not observed); HRMS (ESI+, TOF) *m*/*z* calcd. for $C_{48}H_{64}N_4Ag^+$ $[L_2Ag]^+$: 803.4176, found 803.4153. Although the MS spectrum showed that *m*/*z* L_2Ag^+ was the parent peak, the structure was a L−Ag−Cl form in a solid state.

Typical Procedure for the Syntheses of [Ir (COD)Cl(NHC)] Complexes. A flask was charged with a ligand precursor (imidazolinium chloride of imidazolinium tetrafluoroborate, 1.0 equiv of Ir metal) and a magnetic stir bar, and the flask was evacuated and backfilled with argon (repeated three times). THF ([precursor] = ca. 0.2 M) was added to the flask, and the resultant mixture was cooled in an ice bath. A commercial solution of *n*-BuLi (1.54 M in *n*-hexane, 2.0 equiv of NHC precursor) was added to the mixture, and the reaction solution was stirred 15 min at 25 °C. The solution containing in situ formed NHC ligand was then transferred to another flask which was charged with $[Ir(COD)Cl]_2$ (1.0 equiv) and THF ([Ir] = 0.5 M), and the resultant solution was stirred for 4.5 h at 25 °C. The mixture was then filtered through a short pad of Celite, and the filter cake was washed with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure, and the residue was dissolved in CH_2Cl_2, and the solution was filtered through a short pad of silica gel, eluted with CH_2Cl_2. The eluted solution was concentrated under reduced pressure to ca. 1.0 mL. *n*-Hexane was added to the residual solution to precipitated the title complex as a bright yellow crystalline solid. The solid was filtered and dried under reduced pressure to afford the [Ir (COD)Cl(NHC)] complex.

[Ir(COD)Cl(DHASIMe)] ***19***. Yield: 9.2 mg (0.27 mmol, 15% from 1.79 mmol of DHASIMe·HCl); mp 234 °C (decomp) ; ^1H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.31 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.29 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.18 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.16 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 4.59 (dd, *J* = 1.2, 1.2 Hz, 2H, C*H*), 4.38 (app dd, *J* = 3.0, 3.0 Hz, 2H, *COD*), 4.20 (dd, *J* = 1.2, 1.2 Hz, 2H, C*H*), 3.36 (s, 6H, NCH_3), 2.09−2.00 (m, 2H, *COD*), 2.00−1.92 (m, 2H, *COD*), 1.90 (app dd, *J* = 3.0, 3.0 Hz, 2H, *COD*), 1.64−1.52 (m, 2H, *COD*), 1.42 (tt, *J* = 7.2, 7.2 Hz, 2H, *COD*) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 208.5 ($C_{carbene}$), 139.8 (Ar), 138.5 (Ar), 127.2 (Ar), 126.9 (Ar), 125.7 (Ar), 125.1 (Ar), 84.9 (COD), 68.5 (CH), 52.6 (COD), 46.1 (CH), 34.6 (CH_3), 33.3 (COD), 29.3 (COD) ppm; HRMS (ESI+, TOF) *m*/*z* calcd. for $C_{27}H_{30}N_2ClIrNa^+$ $[M + Na]^+$: 633.1619, found 633.1591.

[Ir(COD)Cl(DHASIiPr)] ***20***. Yield: 13.8 mg (21 μmol, 26% from 0.08 mmol of DHASI*i*Pr·HBF_4); mp 230 °C (decomp.); ^1H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.29 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.27 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.16 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.14 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 5.38 (sept, *J* = 6.6 Hz, 2H, NC*H*$(CH_3)_2$), 4.58 (s, 2H, C*H*), 4.40 (dd, *J* = 1.2, 1.2 Hz, 2H, CH), 4.33 (app dd, *J* = 3.0, 3.0 Hz, 2H, *COD*), 2.10 (app dd, *J* = 3.0, 3.0 Hz, 2H, *COD*), 2.09−2.00 (m, 2H, *COD*), 2.00−1.92 (m, 2H, *COD*), 1.62−1. 54 (m, 2H, *COD*), 1.54 (d, *J* = 6.6 Hz, 6H, NCH$(CH_3)_2$), 1.43 (tt, *J* = 7.2, 7.2 Hz, 2H, *COD*), 1.31 (d, *J* = 6.6 Hz, 6H, NCH$(CH_3)_2$) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 212.7 ($C_{carbene}$), 140.7 (Ar), 139.0 (Ar), 127.1 (Ar), 126.6 (Ar), 126.3 (Ar), 125.0 (Ar), 83.9 (COD), 64.0 (CH), 53.1 (CH), 52.6 (COD), 49.1 (CH), 33.4 (COD), 29.3 (COD), 23.4 (CH_3), 20.4 (CH_3) ppm; HRMS (ESI+, TOF) *m*/*z* calcd. for $C_{31}H_{38}N_2ClIrNa^+$ $[M + Na]^+$: 689.2245, found 689.2219.

[Ir(COD)Cl(DHASICy)] ***21***. Yield: 24.0 mg (35 μmol, 32% from 0.11 mmol of DHASICy·HCl); mp 247 °C (decomp.); ^1H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.29 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.27 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.15 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 7.13 (dd, *J* = 5.4, 3.6 Hz, 2H, Ar*H*), 4.98 (dddd, *J* = 12.0, 12.0, 1.2, 3.0, 3.0 Hz, 2H, *Cy*), 4.59 (s, 2H, C*H*), 4.40−4.35 (m, 4H, C*H*, *COD*), 2.12 (br d, *J* = 12.0 Hz, 2H, *Cy*), 2.07 (app dd, *J* = 3.0, 3.0 Hz, 2H, *COD*), 2.00−1.79 (m, 12H, *Cy*, *COD*), 1.75 (br d, *J* = 12.0 Hz, 2H, *Cy*), 1.63−1. 57 (m, 2H, *COD*), 1.53−1.38 (m, 8H, *COD*, *Cy*), 1.27−1.18 (m, 2H, *Cy*) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 212.7 ($C_{carbene}$), 140.8 (Ar), 139.1 (Ar), 127.0 (Ar), 126.6 (Ar), 126.2 (Ar), 125.0 (Ar), 83.4 (COD), 64.8 (CH), 61.2 (Cy), 52.7 (COD), 49.1 (CH), 34.7 (Cy), 33.6 (COD), 31.2 (Cy), 29.5 (COD), 27.0 (Cy), 26.1 (Cy), 26.0 (Cy) ppm; HRMS (FAB+) *m*/*z* calcd. for $C_{37}H_{46}N_2ClIrNa^+$ $[M]^+$: 746.2979, found 746.2994.

[Ir(COD)Cl(BCPSIMe)] ***22***. Yield: 40.1 mg (80 μmol,40% from 0.20 mmol of BCPSIMe·HCl); mp 234 °C (decomp.); ^1H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.21 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 7.10 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 4.45 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 4.32 (app dd, *J* = 3.0, 3.0 Hz, 2H, *COD*), 3.60 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 3.23 (s, 6H, NCH_3), 2.04−1.96 (m, 2H, *COD*), 1.95−1.88 (m, 5H, CH_AH_B, *COD*), 1.66 (ddd, *J* = 9.6, 1.2, 1.2 Hz, 1H, CH_AH_B), 1.59−1.52 (m, 2H, *COD*), 1.41−1.33 (m, 2H, *COD*) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 206.5 ($C_{carbene}$), 142.9 (Ar), 126.7 (Ar), 122.8 (Ar), 84.1 (COD), 69.9 (CH), 52.1 (COD), 47.8 (CH), 47.4 (CH_2), 35.0 (CH_3), 33.1 (COD), 29.1 (COD) ppm; HRMS (FAB+) *m*/*z* calcd. for $C_{22}H_{28}N_2ClIr^+$ $[M]^+$: 548.1570, found 548.1581.

[Ir(COD)Cl(BCPSIiPr)] ***23***. Yield: 14.5 mg (23 μmol, 23% from 0.10 mmol of BCISI*i*Pr·HCl); mp >250 °C; ^1H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.19 (dd, *J* = 5.4, 3.0 Hz, 2H, Ar*H*), 7.10 (dd, *J* = 5.4, 3.0 Hz, 2H, (Ar*H*), 5.19 (sept, *J* = 6.6 Hz, 2H, NC*H*$(CH_3)_2$), 4.62 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 4.29 (app dd, *J* = 3.0, 3.0 Hz, 2H, *COD*), 3.55 (dd, *J* = 1.8, 1.8 Hz, 2H, C*H*), 2.06−1.97 (m, 2H, *COD*), 1.96−1.88 (m, 5H, CH_AH_B, *COD*), 1.72 (ddd, *J* = 9.6, 1.2, 1.2 Hz, 1H, CH_AH_B), 1.59−1.52 (m, 2H, *COD*), 1.43−1.35 (m, 2H, *COD*), 1.39 (d, *J* = 6.6 Hz, 6H, NCH$(CH_3)_2$), 1.29 (d, *J* = 6.6 Hz, 6H, NCH$(CH_3)_2$) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 300 K) δ 210.3 ($C_{carbene}$), 143.8

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(Ar), 126.0 (Ar), 124.4 (Ar), 83.5 (COD), 64.3 (CH), 52.8 (CH), 51.9 (COD), 50.0 (CH), 48.8 (CH_2), 33.4 (COD), 29.3 (COD), 22.6 (CH_3), 20.8 (CH_3) ppm; HRMS (ESI+, TOF) m/z calcd. for $C_{26}H_{36}N_2ClIrNa^+$ $[M + Na]^+$: 627.2088, found 627.2059.

[Ir(COD)Cl(BCPSICy)] ***24***. Yield: 23.3 mg (33 μmol, 33% from 0.10 mmol of BCPSICy·HCl); mp 242 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.17 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 7.08 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 4.60 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 4.78 (dddd, J = 12.0, 12.0, 3.6, 3.6 Hz, 2H, C*H*), 4.32 (app dd, J = 3.0, 3.0 Hz, 2H, *COD*), 3.53 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 2.07−1.96 (m, 6H, *Cy*, *COD*), 1.95−1.85 (m, 7H, CH_AH$_B$, *Cy*, *COD*), 1.83−1.76 (m, 2H, *Cy*), 1.73−1.66 (m, 3H, CH$_A$$H_B$, *Cy*), 1.65−1.55 (m, 4H, *Cy*, *COD*), 1.50−1.31 (m, 8H, *Cy*, *COD*), 1.13 (dddd, J = 12.0, 12.0, 3.6, 3.6 Hz, 2H, *Cy*) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K) δ 210.2 ($C_{carbene}$), 143.9 (Ar), 125.9 (Ar), 124.5 (Ar), 83.1 (COD), 65.2 (*C*H), 60.2 (*Cy*), 52.4 (COD), 50.0, 48.6 (CH_2), 33.8, 33.6, 31.1, 29.5, 26.7, 25.92, 25.85; LRMS (ESI+, TOF) m/z calcd. for $C_{32}H_{44}N_2ClIrNa^+$ $[M + Na]^+$: 703, found 703. Anal. Calcd for $C_{32}H_{44}N_2ClIr$ (684.3850): C, 56.16; H, 6.48; N, 4.09. Found: C, 56.03, H, 6.83; N, 4.11.

Typical Procedure for the Syntheses of [IrCl(CO)$_2$(NHC)] Complexes. CO gas was bubbled through a solution of [(NHC)-Ir(COD)Cl] in CH_2Cl_2 (0.01 M) for 10 min. Ar gas was then bubbled for 5 min, and the resultant solution was concentrated under reduced pressure. The residue was washed with *n*-hexane and the insoluble solid was filtered, washed with a minimum amount of *n*-hexane, and dried under reduced pressure to afford the title complex as a pale yellow powder.

[IrCl(CO)$_2$(DHASIMe)] ***25***. Yield: 9.0 mg (16.2 μmol, 94% from 17.2 μmol of [Ir(COD)Cl(DHASIMe)] **19**); mp 190 °C (decomp) ; IR (CH_2Cl_2) ν(C═O) = 2070, 1989 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.35 (dd, J = 5.4, 3.0 Hz, 4H, Ar*H*), 7.22 (dd, J = 5.4, 3.6 Hz, 2H, Ar*H*), 7.21 (dd, J = 5.4, 3.6 Hz, 2H, Ar*H*), 4.67 (s, 2H, C*H*), 4.29 (dd, J = 1.2, 1.2 Hz, 2H, C*H*), 3.25 (s, 6H, CH_3) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K) δ 199.9 ($C_{carbene}$), 181.8 (C═O), 166.6 (C═O), 139.2 (Ar), 137.7 (Ar), 127.6 (Ar), 127.5 (Ar), 125.5 (Ar), 125.2 (Ar), 68.7 (CH), 45.8 (CH), 34.9 (CH_3) ppm; HRMS (ESI+, TOF) m/z calcd. for $C_{21}H_{18}N_2O_2ClIrNa^+$ $[M + Na]^+$: 581.0578, found 581.0560.

[IrCl(CO)$_2$(DHASIiPr)] ***26***. Yield: 8.6 mg (14.0 μmol, 93% from 15.1 μmol of [Ir(COD)Cl(DHASI*i*Pr)] **20**); mp 215−218 °C; IR (CH_2Cl_2) ν(C═O) = 2066, 1986 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.33 (dd, J = 5.4, 3.6 Hz, 2H, Ar*H*), 7.32 (dd, J = 5.4, 3.6 Hz, 2H, Ar*H*), 7.19 (dd, J = 5.4, 3.6 Hz, 2H, Ar*H*), 7.18 (dd, J = 5.4, 3.6 Hz, 2H, Ar*H*), 4.92 (sept, J = 6.6 Hz, 2H, NC*H*(CH$_3$)$_2$), 4.63 (s, 2H, C*H*), 4.49 (dd, J = 1.2, 1.2 Hz, 2H, C*H*), 1.46 (d, J = 6.6 Hz, 6H, NCH(C*H*$_3$)$_2$), 1.37 (d, J = 6.6 Hz, 6H, NCH(C*H*$_3$)$_2$) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K) δ 200.7 ($C_{carbene}$), 181.7 (C═O), 167.1 (C═O), 140.3 (Ar), 138.1 (Ar), 127.2 (Ar), 126.6 (Ar), 126.5 (Ar), 124.9 (Ar), 64.7 (CH), 52.6 (NCH(CH$_3$)$_2$), 48.4 (CH), 23.4 (CH$_3$), 19.8 (CH$_3$) ppm; HRMS (ESI+, TOF) m/z calcd. for $C_{25}H_{26}N_2O_2ClIrNa^+$ $[M + Na]^+$: 637.1204, found 637.1178.

[IrCl(CO)$_2$(DHASICy)] ***27***. Yield: 9.1 mg (13.1 μmol, 97% from 13.5 μmol of [Ir(COD)Cl(DHASI*i*Pr)] **21**); mp 232 °C (decomp.); IR (CH_2Cl_2) ν(C═O) = 2063, 1983 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.33 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 7.32 (dd, J = 5.4, 3.0 Hz, 2H,. Ar*H*), 7.18 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 7.17 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 4.66 (s, 2H, C*H*), 4.50−4.43 (m, 4H, C*H*, *Cy*), 1.90−1.65 (m, 12H, *Cy*), 1.48−1.38 (m, 4H, *Cy*), 1.29−1.22 (m, 2H, *Cy*) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K) δ 200.8 ($C_{carbene}$), 181.9 (C═O), 167.2 (C═O), 140.3 (Ar), 138.2 (Ar), 127.1 (Ar), 126.51 (Ar), 126.49 (Ar) 124.9 (Ar), 65.1 (CH), 60.9 (NC*y*), 48.4 (CH), 34.1 (*Cy*), 30.9 (*Cy*), 26.1 (*Cy*), 25.8 (*Cy*), 25.7 (*Cy*) ppm; HRMS (ESI+, TOF) m/z calcd. for $C_{31}H_{34}N_2O_2ClIrNa^+$ $[M + Na]^+$: 717.1830, found 717.1821.

[IrCl(CO)$_2$(BCPSIMe)] ***28***. Yield: 8.5 mg (17.1 μmol, 94% from 18.2 μmol of [Ir(COD)Cl(BCPSIMe)] **22**); mp 170 °C (decomp.); IR (CH_2Cl_2) ν(C═O) = 2068, 1987 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.28 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 7.18 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 4.52 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 3.72 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 3.12 (s, 6H, NCH_3), 2.03 (ddd, J = 9.6, 1.2, 1.2 Hz, 1H, CH_AH$_B$), 1.70 (ddd, J = 9.6, 1.2, 1.2 Hz, 1H, CH$_A$$H_B$) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K) δ 198.3 ($C_{carbene}$), 181.8 (C═O), 166.8 (C═O), 142.0 (Ar), 127.7 (Ar), 122.9 (Ar), 70.0 (CH), 48.1 (CH), 46.8 (CH_2), 35.5 (CH_3) ppm; HRMS (ESI+, TOF) m/z calcd. for $C_{16}H_{16}N_2O_2ClIrNa^+$ $[M + Na]^+$: 519.0422, found 519.0397.

[IrCl(CO)$_2$(BCPSIiPr)] ***29***. Yield: 10.3 mg (18.6 μmol, 96% from 19.4 μmol of [Ir(COD)Cl(BCPSI*i*Pr)] **23**); mp 168−171 °C; IR (CH_2Cl_2) ν(C═O) = 2065, 1987 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.24 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 7.14 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 4.81 (sept, J = 6.6 Hz, 2H, NC*H*(CH$_3$)$_2$), 4.70 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 3.65 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 2.02 (ddd, J = 9.6, 1.2, 1.2 Hz, 1H, CH_AH$_B$), 1.77 (ddd, J = 9.6, 1.2, 1.2 Hz, 1H, CH$_A$$H_B$), 1.35 (d, J = 6.6 Hz, 6H, NCH(CH_3)$_2$), 1.30 (d, J = 6.6 Hz, 6H, NCH(CH_3)$_2$) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K) δ 198.9 ($C_{carbene}$), 181.9 (C═O), 166.9 (C═O), 143.0 (Ar), 126.5 (Ar), 124.5 (Ar), 65.0 (CH), 52.5 (CH), 49.9 (CH), 48.9 (CH_2), 22.5 (CH_3), 20.5 (CH_3) ppm; HRMS (ESI+, TOF) m/z calcd. for $C_{20}H_{24}N_2O_2ClIrNa^+$ $[M + Na]^+$: 575.1048, found 575.1022.

[IrCl(CO)$_2$(BCPSICy)] ***30***. Yield: 8.8 mg (14.0 μmol, 93% from 15.0 μmol of [Ir(COD)Cl(BCPSICy)] **24**); mp 181−184 °C; IR (CH_2Cl_2) ν(C═O) = 2063, 1985 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ 7.21 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 7.12 (dd, J = 5.4, 3.0 Hz, 2H, Ar*H*), 4.68 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 4.36 (dddd, J = 12.0, 12.0, 3.6, 3.6 Hz, 2H, *Cy*), 3.63 (dd, J = 1.8, 1.8 Hz, 2H, C*H*), 2.02−1.95 (m, 3H, CH_AH$_B$, *Cy*), 1.93−1.84 (m, 4H, *Cy*), 1.82−1.75 (m, 2H, *Cy*), 1.74−1.65 (m, 3H, CH$_A$$H_B$, *Cy*), 1.61−1.49 (m, 4H, *Cy*), 1.43−1.29 (m, 2H, *Cy*), 1.12 (ddddd, J = 12.0, 12.0, 12.0, 3.6, 3.6 Hz, 2H) ppm; ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 300 K) δ 199.0 ($C_{carbene}$), 182.1 (C═O), 167.0 (C═O), 143.1 (Ar), 126.5 (Ar), 124.5 (Ar), 65.7 (CH), 60.5 (*Cy*), 50.0 (CH), 48.6 (CH_2), 33.2 (*Cy*), 31.2 (*Cy*), 26.0 (*Cy*), 25.6 (*Cy*), 25.5 (*Cy*) ppm; HRMS (ESI+, TOF) m/z calcd. for $C_{26}H_{32}N_2O_2ClIrNa^+$ $[M + Na]^+$: 655.1674, found 655.1673.

Typical Procedure for an Allylic Arylation. CH_2Cl_2 (0.50 mL) was added to a flask charged with CuCl (2.5 mg, 25 μmol), silver-carbene complex (25 μmol), and a magnetic stir bar at 25 °C. The resulting suspension was stirred at the same temperature for 10 min, and a solution of cinnamyl bromide (99 mg, 0.50 mmol) in CH_2Cl_2 (0.50 mL) was added to the resulting mixture, followed by cooling in a dry ice/EtOH bath. A solution of PhMgBr (0.29 mL of 3.0 M solution in Et_2O diluted with 0.25 mL of CH_2Cl_2) was added to the reaction mixture by a syringe pump over 15 min. Once the addition was complete, the resulting mixture was stirred for another 1 h at the same temperature. The reaction mixture was then diluted with Et_2O (2.0 mL) and quenched with 2 M HCl aq. (2.0 mL) at −78 °C. The resulting mixture was allowed to warm to 25 °C and extracted with Et_2O (3 × 4 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was dissolved in CH_2Cl_2, and anthracene (89 mg, 0.5 mmol) was added to the solution as an external standard to calculate the yield based on the crude ^{1}H NMR. After the removal of the solvent, the ratios of the products were calculated based on the crude ^{1}H NMR.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00564.

Copies of ^{1}H and ^{13}C NMR spectra of all new compounds and crystallographic data of complexes **13**, **14**, **20**, and **23** (PDF)

Accession Codes

CCDC 2025127−2025130 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

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Clarke, M. L.; Frew, J. J. R. Ligand Electronic Effects in Homogeneous Catalysis Using Transition Metal Complexes of Phosphine Ligands. In *Organometallic Chemistry*; The Royal Society of Chemistry, 2009; Vol. *35*, pp 19−46. (b) Gorin, D. J.; Toste, F. D. Relativistic Effects in Homogeneous Gold Catalysis. *Nature* **2007**, *446*, 395−403. (c) Helmchen, G.; Pfaltz, A. PhosphinooxazolinesA New Class of Versatile, Modular P,N-Ligands for Asymmetric Catalysis. *Acc. Chem. Res.* **2000**, *33*, 336−345. (d) Surry, D. S.; Buchwald, S. L. Dialkylbiaryl Phosphines in Pd-Catalyzed Amination: A User's Guide. *Chem. Sci.* **2011**, *2*, 27−50. (e) van der Boom, M. E.; Milstein, D. Cyclometalated Phosphine-Based Pincer Complexes: Mechanistic Insight in Catalysis, Coordination, and Bond Activation. *Chem. Rev.* **2003**, *103*, 1759−1792. (f) Chen, L.; Ren, P.; Carrow, B. P. Tri(1-Adamantyl)Phosphine: Expanding the Boundary of Electron-Releasing Character Available to Organophosphorus Compounds. *J. Am. Chem. Soc.* **2016**, *138*, 6392−6395.

(2) Ahrens, T.; Kohlmann, J.; Ahrens, M.; Braun, T. Functionalization of Fluorinated Molecules by Transition-Metal-Mediated C−F Bond Activation To Access Fluorinated Building Blocks. *Chem. Rev.* **2015**, *115*, 931−972.

(3) Wang, Q.; Su, Y.; Li, L.; Huang, H. Transition-Metal Catalysed C−N Bond Activation. *Chem. Soc. Rev.* **2016**, *45*, 1257−1272.

(4) Zhao, Q.; Meng, G.; Nolan, S. P.; Szostak, M. N-Heterocyclic Carbene Complexes in C−H Activation Reactions. *Chem. Rev.* **2020**, *120*, 1981−2048.

(5) Tolman, C. A. Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. *Chem. Rev.* **1977**, *77*, 313−348.

(6) Tolman, C. A. Electron Donor-Acceptor Properties of Phosphorus Ligands. Substituent Additivity. *J. Am. Chem. Soc.* **1970**, *92*, 2953−2956.

(7) (a) Dröge, T.; Glorius, F. The Measure of All Rings—N-Heterocyclic Carbenes. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940−6952. (b) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An Overview of N-Heterocyclic Carbenes. *Nature* **2014**, *510*, 485−496. (c) Nolan, S. P., Ed. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2001. (d) Diéz-Gonzaléz, S., Ed. *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*; The Royal Society of Chemistry: Cambridge, U.K., 2011.

(8) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V. Synthetic Routes to N-Heterocyclic Carbene Precursors. *Chem. Rev.* **2011**, *111*, 2705−2733.

(9) Izquierdo, F.; Manzini, S.; Nolan, S. P. The Use of the Sterically Demanding IPr* and Related Ligands in Catalysis. *Chem. Commun.* **2014**, *50*, 14926−14937.

(10) (a) Clavier, H.; Nolan, S. P. Percent Buried Volume for Phosphine and N-Heterocyclic Carbene Ligands: Steric Properties in Organometallic Chemistry. *Chem. Commun.* **2010**, *46*, 841−861. (b) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. A Combined Experimental and Theoretical Study Examining the Binding of N-Heterocyclic Carbenes (NHC) to the Cp*RuCl (Cp* = η^5-C_5Me_5) Moiety: Insight into Stereoelectronic Differences between Unsaturated and Saturated NHC Ligands. *Organometallics* **2003**, *22*, 4322−4326. (c) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. SambVca: A Web Application for the Calculation of the Buried Volume of N-Heterocyclic Carbene Ligands. *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759−1766.

(11) (a) Falivene, L.; Cao, Z.; Petta, A.; Serra, L.; Poater, A.; Oliva, R.; Scarano, V.; Cavallo, L. Towards the Online Computer-Aided Design of Catalytic Pockets. *Nat. Chem.* **2019**, *11*, 872−879. (b) Falivene, L.; Credendino, R.; Poater, A.; Petta, A.; Serra, L.; Oliva, R.; Scarano, V.; Cavallo, L. SambVca 2. A Web Tool for Analyzing Catalytic Pockets with Topographic Steric Maps. *Organometallics* **2016**, *35*, 2286−2293.

(12) Ando, S.; Matsunaga, H.; Ishizuka, T. Syntheses of Effectively-Shielded N-Heterocyclic Carbene Ligands. *Tetrahedron* **2013**, *69*, 1687−1693.

(13) Ando, S.; Miyata, R.; Matsunaga, H.; Ishizuka, T. Influences of Phenyl Rings on NHC Ligands with Bicyclic Architectures. *J. Org. Chem.* **2019**, *84*, 128−139.

(14) Ando, S.; Matsunaga, H.; Ishizuka, T. A Bicyclic N-Heterocyclic Carbene as a Bulky but Accessible Ligand: Application to the Copper-Catalyzed Borylations of Aryl Halides. *J. Org. Chem.* **2015**, *80*, 9671−9681.

(15) Ando, S.; Matsunaga, H.; Ishizuka, T. An N-Heterocyclic Carbene-Nickel Half-Sandwich Complex as a Precatalyst for Suzuki-Miyaura Coupling of Aryl/Heteroaryl Halides with Aryl/Heteroarylboronic Acids. *J. Org. Chem.* **2017**, *82*, 1266−1272.

(16) For example of related NHCs with a bicyclic motif, see: (a) Sampford, K. R.; Carden, J. L.; Kidner, E. B.; Berry, A.; Cavell, K. J.; Murphy, D. M.; Kariuki, B. M.; Newman, P. D. Twisting the Arm: Structural Constraints in Bicyclic Expanded-Ring N-Heterocyclic Carbenes. *Dalton Trans.* **2019**, *48*, 1850−1858. Additionally, expanded-ring NHCs, which show unique steric properties, have also been studied. For examples of investigations about the steric and electronic properties of expanded-ring NHCs, see: (b) Gómez-Suárez, A.; Nelson, D. J.; Nolan, S. P. Quantifying and Understanding the Steric Properties of N-Heterocyclic Carbenes. *Chem. Commun.* **2017**, *53*, 2650−2660. (c) Kumar, A.; Yuan, D.; Huynh, H. V. Stereoelectronic Profiling of Expanded-Ring N-Heterocyclic Carbenes. *Inorg. Chem.* **2019**, *58*, 7545−7553.

(17) (a) Lin, I. J. B.; Vasam, C. S. Preparation and Application of N-Heterocyclic Carbene Complexes of Ag(I). *Coord. Chem. Rev.* **2007**, *251*, 642−670. (b) Garrison, J. C.; Youngs, W. J. Ag(I) N-Heterocyclic Carbene Complexes: Synthesis, Structure, and Application. *Chem. Rev.* **2005**, *105*, 3978−4008.

(18) Wong, V. H. L.; White, A. J. P.; Hor, T. S. A.; Hii, K. K. M. Structure and Bonding of [(SIPr)AgX] (X = Cl, Br, I and OTf). *Chem. Commun.* **2015**, *51*, 17752−17755.

(19) Huynh, H. V. Electronic Properties of N-Heterocyclic Carbenes and Their Experimental Determination. *Chem. Rev.* **2018**, *118*, 9457−9492.

(20) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. Rhodium and Iridium Complexes of N-Heterocyclic Carbenes via

https://dx.doi.org/10.1021/acs.organomet.0c00564
Organometallics XXXX, XXX, XXX−XXX

Transmetalation: Structure and Dynamics. *Organometallics* **2003**, *22*, 1663−1667.
(21) Kelly, R. A., III; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. Determination of N-Heterocyclic Carbene (NHC) Steric and Electronic Parameters Using the [(NHC)Ir(CO)$_2$Cl] System. *Organometallics* **2008**, *27*, 202−210.
(22) TEP value of ICy was reported as 2051 cm^{-1}. See refs 18 and 21.
(23) (a) Yoshikai, N.; Nakamura, E. Mechanisms of Nucleophilic Organocopper(I) Reactions. *Chem. Rev.* **2012**, *112*, 2339−2372. (b) Selim, K. B.; Nakanishi, H.; Matsumoto, Y.; Yamamoto, Y.; Yamada, K.; Tomioka, K. Chiral N-Heterocyclic Carbene−Copper-(I)-Catalyzed Asymmetric Allylic Arylation of Aliphatic Allylic Bromides: Steric and Electronic Effects on γ-Selectivity. *J. Org. Chem.* **2011**, *76*, 1398−1408. (c) Corey, E. J.; Boaz, N. W. D-Orbital Stereoelectronic Control of the Stereochemistry of S_N2' Displacements by Organocuprate Reagents. *Tetrahedron Lett.* **1984**, *25*, 3063−3066. (d) Bäckvall, J. E.; Sellen, M.; Grant, B. Regiocontrol in Copper-Catalyzed Grignard Reactions with Allylic Substrates. *J. Am. Chem. Soc.* **1990**, *112*, 6615−6621. (e) Goering, H. L.; Singleton, V. D. Alkylation of Allylic Derivatives. 6. Regiochemistry of Alkylation of Allylic Acetates with Dialkylcuprates. *J. Org. Chem.* **1983**, *48*, 1531−1533. (f) Goering, H. L.; Singleton, V. D. The Stereochemistry of Conversion of Allylic Esters to Olefins with Lithium Dialkylcuprates. *J. Am. Chem. Soc.* **1976**, *98*, 7854−7855. (g) Goering, H. L.; Kantner, S. S. Alkylation of Allylic Derivatives. 8. Regio- and Stereochemistry of Alkylation of Allylic Carboxylates with Lithium Methylcyanocuprate. *J. Org. Chem.* **1984**, *49*, 422−426.

https://dx.doi.org/10.1021/acs.organomet.0c00564
Organometallics XXXX, XXX, XXX−XXX