ORGANOMETALLICS

Iron-Catalyzed Cross-Coupling Reactions of Arylmagnesium Reagents with Aryl Chlorides and Tosylates: Influence of Ligand Structural Parameters and Identification of a General N-Heterocyclic Carbene Ligand

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Supporting Information

ABSTRACT: A systematic evaluation of N-heterocyclic carbene ligands in the iron-catalyzed cross-coupling reactions of aryl chlorides and arylmagnesium reagents is performed. There is no clear correlation between the donor strength of the N-heterocyclic carbene and the reaction outcome. Instead, the highest yields of the desired biaryl product are obtained with sterically demanding ligands possessing large $%V_{\rm bur}$ values. Through this study, SIPrNap has been identified as an efficient and general ligand for the coupling of both aryl chlorides and tosylates.

INTRODUCTION

Palladium- and nickel-catalyzed cross-coupling reactions are widely employed in organic synthesis.¹ Recently, there have been considerable efforts toward employing iron catalysts as a replacement due to the crustal abundance, inexpensiveness, and low toxicity profile of this element.² The iron-catalyzed Kumada reaction for aryl–aryl coupling is of particular interest, since biaryls are prevalent in fine chemicals, agrochemicals, pharmaceuticals, and materials.³ However, it is difficult to control this type of coupling, as arylmagnesium reagents can undergo self-coupling rather readily under iron catalysis.⁴

In a seminal report, Nakamura et al. disclosed an iron fluoride/N-heterocyclic carbene (NHC) catalyst system for the selective cross-coupling of aryl chlorides with aryl Grignard reagents.⁵ Presumably, fluoride strongly coordinates to Fe^{II} and stabilizes the iron center against reduction by the arylmagnesium reagent, ultimately suppressing the homocoupling pathway.^{5b} We subsequently established that an iron(III) alkoxide/NHC is also highly effective for the cross-coupling reaction.⁶ Recently, we realized that a combination of $Fe(OTf)_2$ and NHC displayed a high efficiency, even surpassing that of the iron fluoride system in some cases.⁷ SIPr (1,3-bis(2,6diisopropylphenyl)imidazolidin-2-ylidene) was the best ligand among the NHCs surveyed (Scheme 1a). For the crosscouplings of C-O-based aryl electrophiles, the unsaturated NHC analogue IPr (1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) was, however, superior to SIPr (Scheme 1b).^{7,8} Interestingly, the iron triflate system seems more tolerant toward structural modifications of the NHC ligand in comparison to the iron fluoride system. Whereas FeF₃/IPr



Scheme 1. Reported Iron Catalyst Systems for the Cross-Couplings of Aryl Chlorides and Tosylates with Aryl Grignard Reagents^{5,7,8}



performed poorly in the reaction of chlorobenzene, a good yield of the biaryl product could still be obtained with $Fe(OTf)_2/IPr$ (Scheme 1a). Similar observations could be made for $FeF_3/SIPr$ vs $Fe(OTf)_2/SIPr$ in the coupling of C–O-based electrophiles (Scheme 1b). In our efforts to gain more insights into the factors governing the coupling selectivity, we have performed a systematic evaluation of a series of NHC ligands with varied steric and electronic profiles in the $Fe(OTf)_2$ -catalyzed reaction.⁹ During this investigation, we

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also discovered an efficient NHC ligand for the coupling of both aryl chlorides and tosylates. We report herein our findings.

RESULTS AND DISCUSSION

A reaction of chlorobenzene 1a with *p*-tolylmagnesium bromide 2a was studied in the presence of $Fe(OTf)_2$ and different NHCs generated in situ from the corresponding salt precursors and NaO^tBu (Table 1).

Table 1. Influence of NHCs on the Iron-Catalyzed Cross-Coupling of 1a and $2a^a$



^aThe amounts of 1a, 3a, and 3a' were determined by GC using dodecane as an internal standard. The yield of 3a' was calculated on the basis of 2a.

Notably, the counteranions of the NHC precursors affected the reaction yields considerably. The chloride salts were more effective than the corresponding tetrafluoroborate salts in all cases (e.g., L1 vs L7 or L9 vs L14). ¹H NMR measurements of 0.0025 M solutions of SIPr·HCl (L1) and SIPr·HBF₄ (L7) in CDCl₃ indeed revealed that the C2–H proton in L1 (8.27 ppm) is more downfield than that in L7 (7.67 ppm). This observation led us to question whether the counterion of NHC precursors has an influence on the acidity of the carbenic proton and, hence, the *in situ* generation of free carbenes. We thus performed the reaction of 1a and 2a in the presence of $Fe(OTf)_2/SIPr·HBF_4$ and different bases (Table 2). Notably, KO'Bu led to an improvement in the yield of 3a to 93% (entry 1).

In general, NHCs with a saturated backbone displayed a higher activity than the unsaturated counterparts (i.e., L1 vs L9,

Table 2. Effects of Bases on the Iron-Catalyzed Cross-Coupling of 1a and 2a Employing $Fe(OTf)_2/SIPr \cdot HBF_4^a$

entry	base	conversn $(\%)^a$	3a (%) ^a	3a' (%) ^{a,b}
1	KO ^t Bu	100	93	10
2	KH	100	85	5
3	NaH	85	65	13
4	KHMDS	47	10	40

^{*a*}Determined by GC using dodecane as an internal standard. ^{*b*}Determined on the basis of **2a**. L2 vs L10, L4 vs L12, and L7 vs L14). To probe the possibility of mesoionic (abnormal) carbene formation from bulky, unsaturated NHCs (e.g., IPr) through competing deprotonation of the C4/5 protons,¹⁰ we also tested the IPr^{Me}·HCl salt (L19).¹¹ However, the catalytic reaction gave a result similar to that obtained with IPr.

Since the degree of backbone unsaturation also correlates to the stereoelectronic properties of NHCs, an assessment of their donor strength and steric bulk is relevant. In this regard, it must be mentioned that the commonly used Tolman electronic parameter (TEP values) cannot discern saturated versus unsaturated NHCs.^{12a,c} Thus, the donor strength examinations were attempted by using Huynh's method,¹² whereby the influence of the NHC on the 'Pr₂-bimy (1,3-diisopropylbenzimidazolin-2-ylidene) reporter signal in *trans*-[PdBr₂(ⁱPr₂-bimy)-(NHC)] complexes is measured by ¹³C NMR spectroscopy. A greater downfield shift of the 'Pr₂-bimy carbene signal (HEP) would indicate a stronger donor.

The preparation of the complex probes is summarized in Scheme 2 and follows two methods (see the Supporting

Scheme 2. Preparation of Complex Probes for HEP and % $V_{\rm bur}$ Determination



Information for experimental details). For azolium bromides, a one-pot procedure involving silver carbene transfer with concurrent bridge cleavage of the dipalladium complex $[PdBr_2(^iPr_2-bimy)]_2$ (I) was sufficient (method A). The syntheses of the complex probes using azolium tetrafluor-oborates required method B. Here, the $NBu_4[PdBr_3(^iPr_2-bimy)]$ (II) had to be prepared first prior to mixing with the azolium BF_4 salt and Ag_2O . II was prepared by mixing dimer I with TBAB and provides a bromide anion for Ag^I precipitation, which drives the reaction.

The complex probes for ligands L1–L18 are all air-stable compounds and well soluble in CDCl₃, which facilitates handling and HEP determination. Single crystals suitable for X-ray diffraction were also obtained for most of them, and the molecular structures of two representatives are depicted in Figure 1.

The availability of solid-state molecular structures of this series of *trans*-[PdBr₂(ⁱPr₂-bimy)(NHC)] complexes allows for the determination of the respective NHC percent buried volume ($%V_{bur}$) via SambVca2 calculations for proper comparisons.¹³ Table 3 summarizes HEP and $%V_{bur}$ values for the relevant NHCs. For completeness, $%V_{bur}$ values reported in the literature are given in parentheses, where available. However, it must be noted that these were obtained using different metal systems, making a direct comparison difficult.



Figure 1. Molecular structures of *trans*- $[PdBr_2(^{i}Pr_2-bimy)(SIAd)]$ and *trans*- $[PdBr_2(^{i}Pr_2-bimy)(IPrMe)]$. Hydrogen atoms are omitted for clarity.

Table 3. Huynh's Electronic Parameter (HEP) and V_{bur} for NHC Ligands L1–L18 in *trans*-[PdBr₂(^{*i*}Pr₂-bimy)(NHC)] Complexes

entry	ligand	HEP (ppm)	$%V_{\rm bur}({ m lit.})$
L1/L7	SIPr	177.6	$-(30)^{14}$
L2	SIMes	177.6	$34.3 (27)^{14}$
L3/L8	SI ^t Bu	178.6	36.7
L4	SIAd	177.8	36.2
L5	SIPr ^t Bu	178.2	36.1
L6	SIPrPh	178.7	35.3
L9/L14	IPr	177.5	$34.4 (29)^{14}$
L10	IMes	177.2	$33.6 (26)^{14}$
L11/L15	I ^t Bu	177.6	$35.4(37)^{14}$
L12/L16	IAd	177.1	$36.0 (37)^{14}$
L13	IPrMe	178.9	29.9
L17	I ⁱ Pr	180.6	$-(27)^{15}$
L18	ICy	181.2	$31.1 (27)^{15}$

Consistent with chemical intuition, the HEP values obtained show that saturated NHCs are generally more strongly donating than their unsaturated counterparts (Table 3), which could contribute to their superior activities. However, among saturated NHCs, L3 and L4 do not perform better than the slightly weaker L1 ligand. Furthermore, unsaturated ligands such as L17 and L18 with strong donicity are very poor ligands in the iron-catalyzed reaction.

There is, however, a more pronounced trend in the influence of steric bulk on the cross-coupling performance. Saturated NHCs have larger $\%V_{bur}$ values in comparison to their unsaturated counterparts with identical wingtips due to larger N-C-N angles. Indeed, a comparison of %V_{bur} values reveals that the most sterically demanding ligands also give rise to the best catalysts (Table 3), while small differences in the electrondonating ability are less important in this type of catalysis. These bulky NHCs may provide improved steric protection for the active iron center and/or facilitate reductive elimination in a "metalate mechanism" as suggested by Nakamura et al.⁵ In agreement with this notion, we observed that the catalytic performance and selectivity are much more responsive to steric alterations. NHCs with bulky N substituents such as Dipp, ^tBu, and Ad and their mixed variations (L1/L7, L3-L5, L9, L11, and L12) in general afford a high coupling selectivity of 3a. Even the replacement of only one wingtip group with a smaller one such as Ph and Me led to very poor yields for 3a (e.g., L6 and L13).

For a better visualization of the trends observed, a plot of HEP and $%V_{bur}$ based on our Pd^{II} complex probes was prepared

(Figure 2). In this "stereoelectronic map", notable clustering of the best-performing carbenes was observed in the upper left



Figure 2. Plot of HEP versus $\% V_{\rm bur}$. Yields obtained for 3a are given in parentheses.

area, where NHCs of moderate donor strength and increased steric bulk are located.

Encouraged by these findings, we further evaluated NHCs possessing large reported V_{bur} values (Table 4). IPr* (L20)

Table 4. Influence of Bulky NHCs on the Iron-Catalyzed Cross-Coupling of 1a and 2a

Entry	NHC·HX	%V _{bur}	conv. (%) ^a	3a (%) ^a	3a' (%) ^{a,b}		
L20	Ph_Ph_ Ph_Ph_Ph_Ph_Ph_Ph_Ph_Ph_Ph_Ph_Ph_Ph_Ph_P	53.6/ 41.2 ^{16a}	48	1	65		
L21	^{npr} ^{npr} N N N N N N N N N N N N N N N N N N N	41.5/ 45.7 ^{16d}	63	22	34		
L22	SINap·HCl: $R = R' = H$	26^{17}	42	6	22		
L23	SIMeNap·HCl: R = Me, R' = H	29 ¹⁷	98	75	6		
L24	SIPrNap·HCl: $R = R' = {}^{i}Pr$	31 ¹⁷	100	>99	<1		
^{<i>a</i>} Determined by GC using dodecane as an internal standard. ^{<i>b</i>} Determined on the basis of $2a$.							

and IHept (L21), which were previously shown to be superior to IPr in Pd-catalyzed C–C and C–N cross-coupling reactions,¹⁶ only resulted in low yields of **3a**, indicating that an increase in the size of the substituents does not always translate into a gain in catalytic activity. These may be even too bulky, blocking incoming substrates. For IPr*, deprotonation at the benzylic C–H bond may occur under the highly basic conditions of the Kumada reaction, hindering the formation of the desired iron/NHC complex. Notably, a family of easily

Organometallics

accessible and stable NHC salts with *N*-naphthyl substituents developed by Dorta et al.¹⁷ displayed a steric trend similar to the *N*-phenyl NHC series in the iron-catalyzed reaction, as the yields of **3a** increased in the order SINap (**L22**, 6%), SIMeNap (**L23**, 75%), and SIPrNap (**L24**, > 99%). As reported by Dorta et al., the %*V*_{bur} value of SIPrNap is somewhat larger than that of SIPr.^{17a,18}

The promising results obtained with SIPrNap prompted us to explore the substrate scope of $Fe(OTf)_2/SIPrNap$ catalyst system. Under the optimized conditions employing 3 mol % $Fe(OTf)_2$, 3 mol % of SIPrNap, and 3 mol % of NaO^tBu, **3a** was isolated in 98% yield. These conditions were also amenable to the preparation of other biaryls (Table 5). Both electron-rich





^{*a*}Conditions: 3 mol % of Fe(OTf)₂, 3 mol % of SIPrNap·HCl, 3 mol % of NaO⁴Bu, THF, 60 °C. ^{*b*}Determined by GC.

and electron-deficient substrates, including aryl chlorides and aryl Grignard reagents, were coupled in good to excellent yields. 2-Chlorotoluene 1d reacted with 2a under the ironcatalyzed conditions, giving 3d in 87% yield whereas 2-chloro-1,3-dimethylbenzen 1e was unreactive. The ortho,ortho'disubstituted biaryl 3f was obtained in a good yield. Attempts to prepare tri-ortho-substituted biaryls resulted in only a poor yield of 3g, even at a higher catalyst loading (ca. 5 mol %).

We previously found that $Fe(OTf)_2/IPr \cdot HCl/NaO^tBu$ is a highly efficient catalyst system for the coupling of aryl tosylates and aryl magnesium reagents.⁷ For example, phenyl tosylate **4a** reacted with 4-anisylmagnesium bromide **2b** to give **3i** in 95% isolated yield. On the other hand, SIPr and other bulky unsaturated NHCs (i.e., IAd and I'Bu) gave inferior performance (Table 6). Notably, SIPrNap was also highly active in this reaction, affording **3i** in 93% yields (Table 6). Indeed, SIPrNap is comparable to IPr in the coupling of a range of aryl tosylates and Grignard reagents (Table 6).⁷ In comparison to N-phenyl NHCs (i.e., IPr and SIPr), the generality of SIPrNap as a ligand





^{*a*}Conditions: 3 mol % of Fe(OTf)₂, 9 mol % of SIPrNap·HCl, 9 mol % of NaO'Bu, THF, 60 °C. ^{*b*}Determined by GC using dodecane as an internal standard.

in the iron-catalyzed couplings of both aryl chlorides and tosylates is rather remarkable.

CONCLUSION

In conclusion, a systematic evaluation of NHC structural parameters in the Fe(OTf)₂/NHC-catalyzed cross-coupling reaction of chlorobenzene 1a and p-tolylmagnesium bromide 2a revealed a strong dependence of the reaction outcome on the bulk of N substituents, the degree of unsaturation of the NHC backbone, and the nature of the counterions of the carbene precursors. Using HEP and $%V_{burt}$ the stereoelectronic properties of the respective NHCs were evaluated. While there was no clear correlation between the reaction outcome and NHC donor strengths, a pronounced steric effect could be observed. Sterically demanding ligands possessing large $%V_{\rm bur}$ values gave rise to the highest yields of the desired biaryl product. We also discovered that SIPrNap featuring bulky Nnaphthyl substituents is a general and efficient ligand for the coupling of both aryl chlorides and tosylates with aryl Grignard reagents.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00180.

Full experimental procedures, compound characterization, and NMR spectra (PDF)

Accession Codes

CCDC 1521203–1521210 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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