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Catalytic Dehalogenation of Aryl Halides Mediated by a Palladium/Imidazolium Salt System

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A convenient and efficient catalytic aryl halide dehalogenation protocol has been developed using an imidazolium salt/palladium/base system. The use of the ligand precursor SIMes·HCl ((2,4,6-trimethylphenyl)dihydroimidazolium chloride) in conjunction with $Pd(dba)_2$ was found to be most effective for the dehalogenation of aryl chlorides, bromides, and polyhalogenated aromatic hydrocarbons. Strong bases having β-hydrogens both perform deprotonation of the imidazolium salt and are hydrogen sources for the dehalogenation process. The oxidative addition of the imidazolium salt to the palladium(0) precursor generating a carbene palladium hydride species may also be involved in the dehalogenation process. This oxidative-addition reaction may have fundamental implications in low-valent metal carbene mediated transformations.

Introduction

The dehalogenation of aryl halides, especially aryl chlorides, represents an important chemical transformation in organic synthesis[1] and environmental remediation.[2] Grushin and Alper[3] have used catalytic dehalogenation for the selective deuterium labeling of arenes. A potentially significant organic use of any dehalogenation methodology is in potentially directing the orientation of aromatic electrophilic substitution.[4] A large number of dehalogenating systems have been developed for the reduction of halogenated arenes. Usually these systems employ inorganic hydrides as hydrogen source and a variety of transition-metal[5−7] and lanthanide[8] centers. Few catalytic systems show the ability to efficiently dehalogenate polyhalogenated aromatic substrates. These few systems are usually based on Pd,[9] Ru,[10] Rh[11] Ni,[12,13] and Cu[14] metal salts or phosphine complexes thereof.

Nucleophilic carbenes and their hydrogenated derivatives have proven to be electron-rich donors[15] and have attracted much attention as alternatives to phosphine ligands in homogeneous catalysis. Various reactions involving carbenes as ancillary ligands have recently been reported. These include furan synthesis,[16] ruthenium-mediated olefin metathesis,[17] and hydrosilylation.[18] Palladium/carbene systems have proven a versatile tool in various C−C and C−N coupling reactions, including aryl amination,[19] Kumada,[20] Stille,[21] Suzuki−Miyaura,[22] Hiyama,[23] and polymerization reactions,[24] and other Heck-type couplings.[25]

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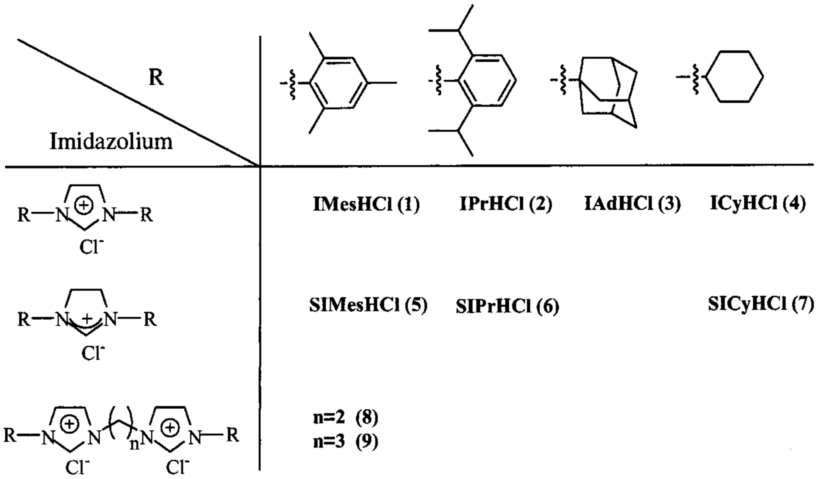
Chart 1. Imidazolium Salts

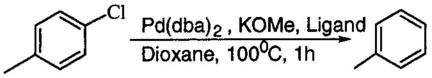


Results generated from coupling chemistry based on Pd/nucleophilic carbenes have shown that activation of C−Cl bonds in aryl chlorides can be easily achieved.[26] Solution calorimetric experiments of transition-metal-centered ligand substitution involving N-heterocyclic carbenes have shown that this class of ligands exhibits a stronger electron-donating ability and a larger steric demand than most tertiary phosphines.[17a] In view of the unique ligand properties displayed by imidazolium-based carbenes and results suggesting that aryl halide dehalogenation should be possible, a study aimed at determining the optimum system for catalytic dehalogenation of activated, nonactivated, and polyhalogenated aryl halides was undertaken.

Results and Discussion

In the course of studies aimed at finding less expensive bases for use in the N-heterocyclic carbene/palladium Suzuki−Miyaura coupling of aryl halides with arylboronic acids, we examined the efficacy of KOMe as the base. Along similar lines, Fürstner and coworkers have found that KOMe could be used with alkyl- and alkenylboronic acids in this C−C bond forming reaction.[27] Encouraged by this study, our initial experiments with KOMe and arylboronic acids showed a significant amount of aryl halide dehalogenation byproducts. Removal of the arylboronic acid from this general Suzuki−Miyaura protocol afforded a high yield of the dehalogenated arenes. On the basis of these initial experiments, we were interested in examining the generality of the dehalogenation behavior and to thereby extend the use of N-heterocyclic carbenes (and their imidazolium salt precursors) to the catalytic dehalogenation of aryl halides.

Table 1. Dehalogenation of 4-Chlorotoluene with Various Carbene Precursors[a]



entry	ligand	yield[b] (%)
1	IMes·HCl	46
2	IPr·HCl	45
3	IAd·HCl	49
4	ICy·HCl	30
5	**SIMes·HCl**	**96**
6	SIPr·HCl	56
7	SICy·HCl	2
8	**8**	10
9	**9**	2
10	$P(^tBu)_3$	15
11	PCy_3	17
12	2 SIMes·HCl	7

[a] Reaction conditions: 1.0 mmol of aryl halide, 2 mmol % of $Pd(dba)_2$, 2 mmol % of ligand, 3 mL of dioxane, 2 mmol of KOMe, 100 °C, 1 h. [b] Yields were determined by GC and are the average of two runs.

An important initial step involved in this transformation is the oxidative addition of the C−X bond of aryl halides. This step is also the first step in a number of metal-mediated C−C bond formation reactions.[19−23,25] The C−X bond activation has been shown to be favored by the presence of electron-donating ancillary ligands, such as tertiary alkylphosphines[28] and N-heterocyclic carbenes,[20−25] which render the metal center more electron-rich. The nature of the substitution pattern on the carbene ligand has been shown to have a significant effect on the catalytic activity of the metal complex. With this in mind, a survey of catalytic efficiency of different imidazolium chlorides (Chart 1) was tested on a model reaction and results are presented in Table 1.

The model reaction targeted the dehalogenation of 4-chlorotoluene in the presence of 2 equiv of KOMe. The role of KOMe was thought at this stage to be twofold: (1) it might serve as a deprotonating agent to convert the imidazolium salts into the carbene species, and (2) it could subsequently act as a hydrogen atom donor, since it possesses β-hydrogens. The saturated imidazolium salt SIMes·HCl proved to be the most effective for dehalogenation of 4-chlorotoluene, leading to a 96% yield of the dehalogenated product (Table 1, entry 5). Other 1,3-disubstituted imidazolium salts led to the formation of moderately active catalysts (Table 1,

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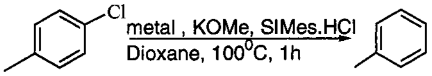
entries 1−4). The differences in activity displayed by the ligands might be attributed to the effectiveness of the base in the deprotonating step or, once the carbene is generated, to steric and electronic effects affecting the performance of the palladium species in the oxidative-addition, β-hydride-transfer or reductive-elimination steps. The donating ability of dihydroimidazolium carbenes is presumed to be higher than that displayed by unsaturated imidazolium-based carbenes.[29] On the basis of this assumption, the SICy·HCl (1,3-dicyclohexane 4,5-dihydroimidazolium chloride) ligand would be expected to perform very effectively in this system if electronic effects are solely considered, since it is a saturated carbene with alkyl substituents. However, this imidazolium salt performs poorly in the dehalogenation reaction (Table 1, entry 7). We believe this electron richness also renders the required initial deprotonation of the imidazolium salt difficult. Independent efforts aimed at generating the free carbene from KOMe have proven unsuccessful. Two bis(imidazolium) salts bearing two- or three-carbon-atom linkers between imidazolium units have been tested (Table 1, entries 8 and 9). The observed poor yields obtained may be associated with the exceptionally good σ-donating property of these chelating ligands, which confer extra stability to the metal center; a rigid “umbrella” that protects the reaction center is generated, which is catalytically undesirable. The palladium center is very electron rich and therefore an excess of ligand[30] is not required; moreover, the sterics of these chelating ligands do not allow enough space for the incoming substrate in the initial oxidative-addition step. Since an overall Pd/carbene ratio of 1:2 exists when bis-carbenes are used, a similar ratio was used in monodentate carbene systems. Results under these conditions clearly indicate the detrimental effect of excess ligand on the catalytic activity (Table 1, entries 1 and 12). A view of a catalytic cycle involving a palladium species bearing a single carbene ligand is favored.

Since the use of sterically demanding tertiary phosphines has led to significant advances in C−C bond forming reactions (see above), it was of interest to run control reactions with these ligands. The use of P^tBu_3 and PCy_3 as catalyst modifiers using the present protocol proved to be ineffective in mediating the catalytic dehalogenation (Table 1, entries 9 and 10). This observation suggests a mode of activation which might be different from simple imidazolium salt deprotonation followed by metal coordination.

Influence of the Metal Source. A number of palladium sources were tested in optimization experiments (Table 2). The complex $Pd(dba)_2$ (dba = dibenzylideneacetone) was found to be the most effective palladium precursor (Table 2, entry 1), forming an active species in situ with no induction period. Palladium(II) sources did not show significant catalytic activity (Table 2, entries 2 and 4). In these cases, palladium black was rapidly generated. Commercially available Ni(II) sources (Table 2, entries 3 and 5) did not show catalytic activity, even in the presence of strong reducing agents such as hydrazine (added to regenerate Ni(0) species to initiate the catalytic cycle). As expected, reactions run without metal catalyst resulted in no detectable reaction product (Table 2, entry 6).

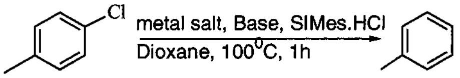
Table 2. Dehalogenation of 4-Chlorotoluene with Various Metal Salts[a]



entry	metal source	yield[b] (%)	entry	metal source	yield[b] (%)
1	$Pd(dba)_2$	96	4	$NiCl_2$	0
2	$PdCl_2(C_6H_5CN)_2$	16	5	$Ni(OAc)_2$	0
3	$Pd(OAc)_2$	2	6	no metal	0

[a] Reaction conditions: 1.0 mmol of aryl halide, 2 mmol % of metal source, 2 mmol % of SIMes·HCl, 3 mL of dioxane, 2 mmol of KOMe, 100 °C, 1 h. [b] Yields were determined by GC and are the average of two runs.

Table 3. Dehalogenation of 4-Chlorotoluene with Various Bases[a]



entry	base	yield[b] (%)	entry	base	yield[b] (%)
1	KOMe	96	7	NaOAc	0
2	NaOMe	17	8	K_3PO_4	0
3	NaOH	0	9	NaOEt	31
4	Cs_2CO_3	0	10	$KOCMe_2Et$	17
5	K_2CO_3	0	11	*sec*-BuOH/NaOH	60
6	KO^tBu	5			

[a] Reaction conditions: 1.0 mmol of aryl halide, 2 mmol % of $Pd(dba)_2$, 2 mmol % of SIMes·HCl, 3 mL of dioxane, 2 mmol of base, 100 °C, 1 h. [b] Yields were determined by GC and are the average of two runs.

In the case of $Pd(dba)_2$, reactions were carried out in the presence of metallic Hg to eliminate a possible contribution of palladium black as catalyst.[31] Reactions run with and without mercury lead to identical yields.

Influence of the Base. It appears crucial in the dehalogenation protocol to have a base possessing at least one β-hydrogen. The base, as stated above, is thought to play a dual role: it may assist the initial deprotonation of the strongly basic dihydroimidazolium salts and is an efficient source of hydrogen atoms. Previous studies have shown that alcohol/alkali-metal mixtures have a powerful reducing effect on aryl halides.[10] A control reaction on our model reaction supports these observations, as *sec*-butanol/dioxane/NaOH/$Pd(dba)_2$ mixtures lead to 60% yields of the dehalogenation product (toluene as solvent) in 1 h. Prolonged reaction time did not improve the conversion to the desired product. Changing the *sec*-butanol/NaOH mixture to KOMe leads to higher yields and shorter reaction time (Table 3, entry 1). A screening of the influence of bases on the dehalogenation of 4-chlorotoluene is presented in Table 3.

Inorganic bases such as Cs_2CO_3, K_2CO_3, K_3PO_4, and KO^tBu, useful for the Suzuki cross-coupling reaction[22] or amination reaction,[19] were not effective for the dehalogenation process. The essential factor that determines whether a base will be effective in assisting

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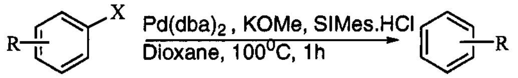
Table 4. Dehalogenation of of Arylhalides[a,b]



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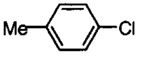
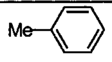
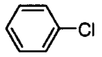
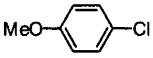
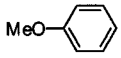
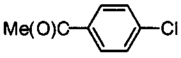
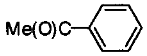
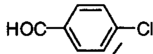
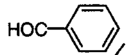
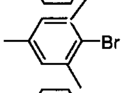
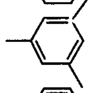
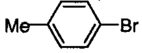
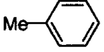
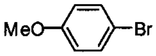
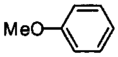
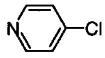
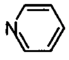
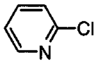
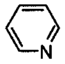
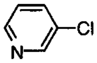
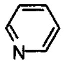
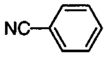
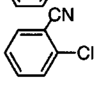
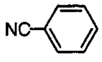
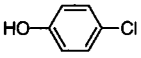
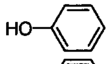
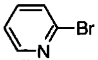
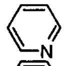
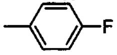
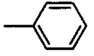
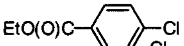
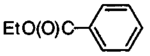
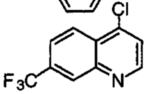
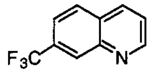
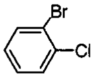
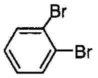
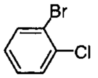
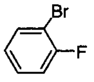
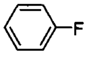
1			96
2			85
3			87
4			100[c]
5			100[c]
6			56
7			100
8			100
9			92
10			47
11			100
12			21[c]
13			100[c]
14			100
15			58
16			0
17			100
18			56

[a] Reaction conditions: 1.0 mmol of aryl halide, 2 mmol % of Pd(dba)$_2$, 2 mmol % of SiMes·HCl, 3 mL of dioxane, 2 mmol of KOMe, 100 °C, 1 h. [b] Yields were determined by GC and are the average of two runs. [c] At room temperature, 2−16 h.

Table 5. Dehalogenation of Polyhalogenated Arenes[a,b]

entry	aryl halide	product	yield (%)
1			100
2			100
3			100,79[c]
4			100
5			98

[a] Reaction conditions: 1.0 mmol of aryl halide, 2 mmol % of Pd(dba)$_2$, 2 mmol % of SiMes·HCl, 3 mL of dioxane, 2 mmol of KOMe, 100 °C, 1 h. [b] Yields were determined by GC and are the average of two runs. [c] Same as in *a* but with 1 mmol of KOMe.

the dehalogenation process appears to be the presence of, at least, one β-hydrogen. This presumably favors the formation of a palladium hydride intermediate with concurrent β-elimination of an aldehyde or ketone.[10] The large difference in metal alkoxide activity can be associated with the size of alkoxide anions (Table 3, entries 1, 9, and 10) or with solubility, as in the KOMe vs NaOMe cases (Table 3, entries 1 and 2). An early report on palladium-catalyzed dehalogenation reported the use of NaOMe as base.[32] KOMe was by far the most efficient base examined in the present study.

Dehalogenation of Aryl Halides Mediated by the Pd(dba)$_2$/SIMes·HCl/KOMe System. Once the optimum reaction conditions had been established, it was of interest to investigate the scope and limitations of the dehalogenation protocol. A survey of catalytic dehalogenation of aryl halides using SIMes·HCl as supporting ligand is provided in Table 4. Various activated and electron-rich chloroarenes are easily dehalogenated. Electron-neutral and electron-donating groups give from good to excellent yields. Hindered substrates displayed lower reaction rates, presumably due to steric congestion about the substrate leading to a slower oxidative-addition step. The substrate 2-bromomesitylene led to the dechlorination product in modest yield (Table 4, entry 6) after 1 h. A longer reaction time, 12 h, led to complete dehalogenation. Substituted pyridines perform well under the reaction conditions, with the exception of 2-chloropyridine, which affords a poor 47% yield after 1 h. This behavior is possibly due to the proximity of a coordinating nitrogen of pyridine to the metal center. At elevated temperatures, strongly activated substrates follow a different reaction pathway and side products are observed. For example, 4-chlorobenzonitrile leads to 30% of 4-methoxybenzonitrile as secondary product, as determined by GC and mass spectrometry. This fact guided us to the conclusion that nucleophilic aromatic substitution occurs at a rate that is comparable to the overall dehalogenation reaction rate at elevated temperatures. When the reaction is performed at room temperature and the amount of base is reduced to 1 equiv in order to minimize side reactions, the aromatic nucleophilic substitution is retarded for all reactions and at room temperature is negligible. Aryl bromides behave similarly to aryl chlorides. Aryl chlorides proved unreactive at room temperature, while aryl bromides can be dehalogenated but require long reaction times.

Dehalogenation of polyhalogenated aromatic substrates using 2.4 equiv of base leads to good yields (Table 5, entries 1−4). The double dechlorination of 1,4-dichlorobenzene is complete in 1 h (Table 5, entry 1). Similarly, sterically hindered 1,2-dibromobenzene was converted in 98% yield to benzene in only 1.4 h. A selectivity experiment was performed in order to determine the preference for dehalogenation. The substrate 2-bromo-1-chlorobenzene was selected for investigation using only 1 equiv of base. Chlorobenzene was obtained in 79% yield with no observed bromobenzene generated. Excess base (2.4 mmol) led to complete dehalogenation

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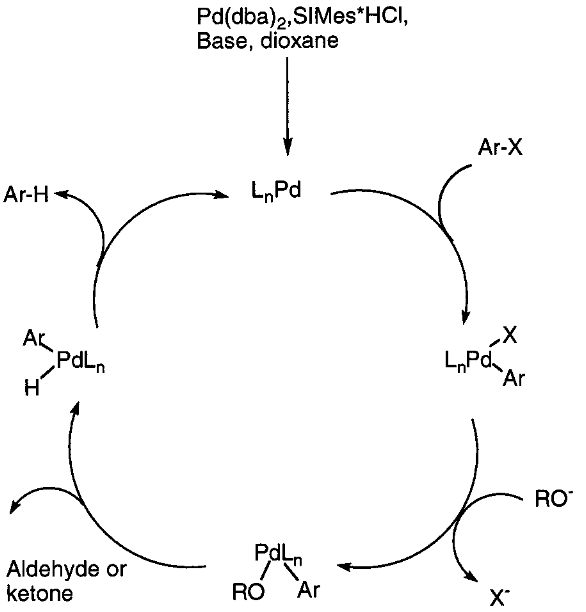
[32] Zask, A.; Helquist, P. *J. Org. Chem.* **1978**, *43*, 1619−1620.

Scheme 1. Proposed Mechanism for Dehalogenation of Aryl Halides



(Table 5, entry 2). A substrate containing multiple halides can be completely dehalogenated if excess base is used (Table 5, entry 3−4) Fluoroarenes such as 2-fluoro-1-chlorobenzene can be dehalogenated to fluorobenzene in 98% yield. Defluorination is not observed (Table 5, entry 5).

Mechanistic Considerations. A general catalytic cycle for the dehalogenation of halogenated arenes in the presence of palladium/carbene/base catalyst is presented in Scheme 1. In this catalytic cycle, the first step involves formation of the active catalyst by coordination of carbene to a Pd(0) center. The excellent σ-donor capabilities of nucleophilic carbenes favor their coordination to the metal center and displacement of more weakly bound ancillary ligands. The resulting electron-rich palladium center is able to activate the C−X bond in an oxidative-addition process.[26] The next step is methoxide anion attack at palladium and displacement of the halide, followed by elimination of formaldehyde and KX. This is then followed by a reductive-elimination step which regenerates the Pd(0) species. A similar mechanism was recently proposed for dehalogenation using a ruthenium system.[10] 2-Butanone was identified in Ru/PCy_3/2-butanol/NaOH mediated dehalogenation. We failed to identify formaldehyde, acetaldehyde, or amyl aldehyde by mass spectrometry due to the possible overlap between solvent and aldehyde products.

If the mechanism involves ligand coordination after the carbene has been generated in situ (by the base), then the negative results using the bulky tertiary phosphines become troublesome. We then tested whether an alternative activation pathway involving the imidazolium salts might be possible without involvement of the base. When a palladium(0) source, such as $Pd(dba)_2$, is reacted with an imidazolium salt, in the absence of a base, the palladium complex is rapidly converted to generate a palladium hydride, as evidenced by a characteristic proton NMR peak at −14.85 ppm.[33] We propose a formulation of this hydride as a cationic palladium(II) hydride of the type $[(IMes)Pd(H)(L)_n]Cl$, resulting from oxidative addition of the imidazolium salt to a palladium(0) complex. This complex could then act as the hydride species involved in the catalytic dehalogenation cycle. This mode of activation has not yet been reported in nucleophilic carbene chemistry and is the topic of a current investigation.

Conclusion

In summary, we investigated a palladium/imidazolium salt system that proves efficient for the dehalogenation of a large variety of aryl halides. Both aryl chlorides and bromides can be effectively dehalogenated. The catalytic system does not require an excess of the ligand and appears thermally robust. The optimum metal-to-ligand ratio is 1/1, as 1/2 ratios favor the formation of very stable, catalytically less active palladium species. A cationic palladium hydride is proposed as an important intermediate in the catalytic cycle. This species appears to be generated via an oxidative addition of the imidazolium salt. Further investigations aimed at elucidating the exact activation mode in this and related chemistry along with expanding the use of nucleophilic carbenes in catalytic systems are ongoing.

Experimental Section

General Procedure. All manipulations were carried out using standard Schlenk techniques under argon atmosphere. Solids were loaded in a MBraun drybox. Gas chromatographic analyses were performed on a Hewlett-Packard Model 6890A instrument, equipped with an AE-1 Agilent Technologies capillary column. Product identifications were made by comparison with commercially available compounds. Mass spectrometric analyses were performed using a Micromass AutoSpec. Aryl halides, arenes, and PCy_3 were purchased from Aldrich and used as received. P^tBu_3 and $Pd(dba)_2$ were purchased from Strem. Dioxane was purchased from Aldrich as anhydrous 99.5% grade and dried using solvent purification columns (MBraun system) prior to use. All imidazolium salts were synthesized according to the literature procedure.[34]

Synthesis of Dihydroimidazolium Chlorides. Anilines (mesitylamine; 0.4 mol 5.4 g, Aldrich) were reacted in methanol with glyoxal (0.2 mol, 40% aqueous solution, Aldrich) at room temperature in the presence of a few drops of formic acid. After the mixture was stirred for 3 h, the precipitated yellow product, a diazabutadiene, was filtered and washed with methanol and dried under vacuum (yield 92%). Hydrogenation of diazabutadiene (0.01 mol, 3.92 g) was performed in a MeOH/THF (40/60) mixture in the presence of $NaBH_4$ (0.1 mol, 3.78 g). After 1.5 h the solution turned white. A saturated aqueous solution of NH_4Cl was used to quench the reaction. The diamine was extracted three times with ether and washed with deionized water. Ether extracts were dried over $MgSO_4$ and evaporated under reduced pressure to afford the substituted diamine (97%, 3.6 g). One equivalent of diamine, 1.1 equiv of NH_4Cl, and 2.5 equiv of triethyl orthoformate were stirred together at 110 °C under argon flow (to drive EtOH from the

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[33] $Pd(dba)_2$ and the imidazolium salt **1** were charged in an NMR tube (in stoichiometric amounts) in C_6D_6. After this tube was heated to 100 °C for 10 min, a peak at −14.85 ppm appeared, which can be attributed to the formation of a Pd−H species. This is concomitant with the disappearance of the imidazolium proton on C2 located at 10.6 ppm in the proton NMR. The protons of cationic palladium hydrides have been reported to appear in this region ($[(P^tBu_3)_2Pd(H)(CH_3CN)_2]BF_4$ at −16.3 ppm): Sommovigo, M.; Pasquali, M. *J. Organomet. Chem.* **1991**, *418*, 119−126.

[34] (a) Arduengo, A. J., III. U.S. Patent 5 077 414, 1991. (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530−5534. (c) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. Manuscript in preparation.

reaction). After 1.5 h the reaction mixture turns to a solid. The solid was dissolved in a minimum amount of $CHCl_3$, filtered, and precipitated with ether. The ^1H NMR of the product was comparable with previously reported spectroscopic data for the desired product.[35] The desired product was obtained in >85% yield in this manner. Similar experimental methods were used for SIPr·HCl and SICy·HCl.

General Protocol for Catalytic Dehalogenation of Aryl Halides. A 40 mL scintillation vial was loaded in the drybox with $Pd(dba)_2$(0.02 mmol), SIMes·HCl (0.02 mmol), KOMe (2 mmol), 3 mL of dry dioxane, and 1 mmol of aryl halide. The reaction vessel was sealed under argon with a Teflon-lined screw cap, taken out of the glovebox, and heated at 100 °C for 1 h. After the mixture had cooled to room temperature, it was analyzed by gas chromatography.

Acknowledgment. The U.S. Department of Energy, the National Science Foundation, the Louisiana Board of Regents, and the Albemarle Corp. are gratefully acknowledged for support for this research.

OM010332S

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[35] Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, A.; Hugh, A.; Goerlich, J. R.; William, J. *Tetrahedron* **1999**, *55*, 14523−14534.