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Copper-Catalyzed Hiyama Coupling of (Hetero)aryltriethoxysilanes with (Hetero)aryl Iodides

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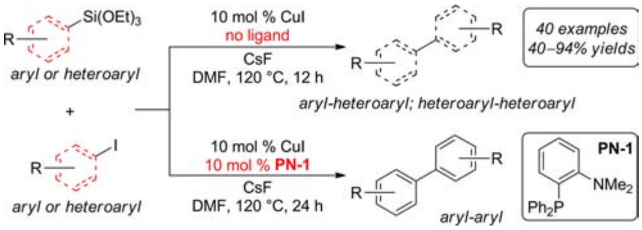
ABSTRACT



A Cu^{I}-catalyzed Hiyama coupling was achieved, which proceeds in the absence of an ancillary ligand for aryl–heteroaryl and heteroaryl–heteroaryl couplings. A P,N-ligand is required to obtain the best product yields for aryl–aryl couplings. In addition to facilitating transmetalation, CsF is also found to function as a stabilizer of the [CuAr] species, potentially generated as an intermediate after transmetalation of aryltriethoxysilanes with Cu^{I}-catalysts in the absence of ancillary ligands.

Hiyama coupling remains an indispensable synthetic tool for the construction of C–C bonds in natural products and pharmaceutical molecules.[1] This transformation offers a unique advantage over other organometallic-based cross-coupling processes owing to its exploitation of organosilicon reagents, which are advantaged due to their ease of synthesis, handling, high stability, and low toxicity.[2] The pragmatic application of the Hiyama coupling in the contexts of constructing complex molecules was further reinforced by the Denmark[1d,3] and DeShong[1e,f] groups with the use of organosilicon reagents in both the presence and absence of fluoride sources. Despite the synthetic appeals tendered by the organosilicon compounds, Hiyama coupling is typically conducted with Pd-based catalysts.

Nonetheless, remarkable reports from the Fu group on Ni-catalyzed couplings of aryltrialkoxysilanes with alkyl halides[4] have raised anticipation that the Hiyama coupling could now be conducted with non-noble metals with a high level of efficacy.[5] Moreover, the Ball group has recently demonstrated that aryl/allyltrialkoxysilanes undergo facile transmetalation with (NHC)Cu(F) (NHC = *N*-heterocyclic carbene) to generate (NHC)Cu(Ar/allyl) complexes.[6]

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(5) For examples of Cu-catalyzed Suzuki–Miyaura coupling, see: (a) Thathagar, M. B.; Beckers, J.; Rothenberg, G. *J. Am. Chem. Soc.* **2002**, *124*, 11858. (b) Li, J.-H.; Li, J.-L.; Wang, D.-P.; Pi, S.-F.; Xie, Y.-X.; Zhang, M.-B.; Hu, X.-C. *J. Org. Chem.* **2007**, *72*, 2053. (c) Li, J.-H.; Wang, D.-P. *Eur. J. Org. Chem.* **2006**, *2006*, 2063. (d) Li, J. H.; Li, J. L.; Xie, Y. X. *Synthesis* **2007**, 984. (e) Mao, J. C.; Guo, J.; Fang, F. B.; Ji, S. J. *Tetrahedron* **2008**, *64*, 3905. (f) Ye, Y. M.; Wang, B. B.; Ma, D.; Shao, L. X.; Lu, J. M. *Catal. Lett.* **2010**, *139*, 141. (g) Yang, C.-T.; Zhang, Z.-Q.; Liu, Y.-C.; Liu, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 3904. (h) Lipshutz, B. H.; Nihan, D. M.; Vinogradova, E.; Taft, B. R.; Bogkovic, Z. V. *Org. Lett.* **2008**, *10*, 4279. For examples of Cu-catalyzed Stille coupling, see: (i) Takeda, T.; Matsunaga, K.-I.; Kabasawa, Y.; Fujiwara, T. *Chem. Lett.* **1995**, *24*, 771. (j) Falck, J. R.; Bhatt, R. K.; Ye, J. *J. Am. Chem. Soc.* **1995**, *117*, 5973. (k) Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 2748. (l) Kang, S.-K.; Kim, J.-S.; Choi, S.-C. *J. Org. Chem.* **1997**, *62*, 4208. (m) Nudelman, N. S.; Carro, C. *Synlett* **1999**, 1942.

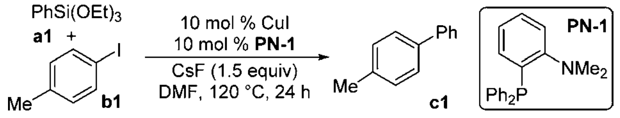
(6) (a) Herron, J. R.; Ball, Z. T. *J. Am. Chem. Soc.* **2008**, *130*, 16486. (b) Herron, J. R.; Russo, V.; Valente, E. J.; Ball, Z. T. *Chem.—Eur. J.* **2009**, *15*, 8713. (c) Russo, V.; Herron, J. R.; Ball, Z. T. *Org. Lett.* **2009**, *12*, 220.

10.1021/ol402701x

However, the resultant organocopper species were shown to be reactive only toward aldehydes, acyl halides, and allylic substrates.[6] Transmetalation of $ArSiF_3$ with (NHC)Cu(Br) in the presence of a fluoride source to generate (NHC)Cu(Ar) species was also proposed previously by the Hoveyda group[7] in the conjugate addition of $ArSiF_3$ to cyclic enones.[8] In addition, Cu-salts are known to improve the product yields in Pd-catalyzed Hiyama couplings.[9] A previous report[10] showed that $[CuOC_6F_6]$ could mediate the coupling of arylsilicon reagents with aryl iodides but with limited substrates and required a stoichiometric amount of the copper salt.[11] Herein, we report the first Cu-catalyzed Hiyama coupling of aryl- and heteroaryltriethoxysilanes with aryl- and heteroaryl iodides, a transformation that proceeds, depending upon the types of substrates, with and without requiring the addition of ligands for the best product yields. In addition, we have demonstrated a dual role for CsF, one as a fluoride source to facilitate the transmetalation of $ArSi(OEt)_3$ with CuI, and the other as a stabilizer of monomeric [CuAr] species by preventing aggregation in reactions that are conducted in the absence of a ligand.

Our investigation began with the selection of different ligands in conjunction with CuI for screening reaction conditions in an attempt to couple arylsilicon reagents with *p*-iodotoluene (Table 1). We found that the reaction of $PhSi(OEt)_3$ (**a1**) with *p*-iodotoluene (**b1**) proceeded in the presence of a bidentate ligand **PN-1** in 24 h in DMF at 120 °C to afford 4-phenyltoluene (**c1**) in good yield (60% by GC, entry 1) when CsF was utilized as a fluoride source. Other similar P,N-ligands (see Supporting Information (SI) for details) provided the product **c1** in lower yields (entry 2). To our surprise, the reaction of **a1** with *p*-iodotoluene proceeded even in the absence of **PN-1**, albeit providing the biaryl product in only 40% GC yield (entry 3). Replacing CuI with CuOtBu (purified by sublimation)[12] generated the product in 50% GC yield (entry 4). The reaction does not proceed in the absence of either the Cu-catalyst or CsF and affords the product in $< 5\%$ yield when CsF is replaced with other F^- sources (entries 5−7). Replacing **a1** with $PhSiMe_3$ yielded no product at all (entry 8). Similarly, utilizing *p*-bromo- or *p*-chlorotoluene as an aryl halide afforded only trace amounts of the product (entry 9). Use of NMP and HMPA as solvents provided the product in 30% and 40% GC yields, respectively (entries 10, 11). Other solvents such as DMSO, dioxane, toluene, or MeCN produced 4-phenyltoluene in $< 5\%$ yield (entry 12).

Table 1. Optimization of Reaction Conditions[a]



entry	modified conditions	yield (%)[b]
1	standard conditions	60 (55)[c]
2	**PN-2**−**PN-5** (see SI for details)	45−50
3	without ligand	40
4	with CuO*t*Bu (sublimed) instead of CuI	50
5	without CuI	0
6	without CsF	0
7	LiF, NaF, KF, RbF, or TBAF instead of CsF	<5
8	$PhSiMe_3$ instead of $PhSi(OEt)_3$	0
9	4-bromo- or 4-chlorotoluene instead of 4-iodotoluene	<2
10	NMP instead of DMF	30
11	HMPA instead of DMF	40
12	DMSO, dioxane, toluene, or MeCN instead of DMF	<5

[a] Reactions were run on a 0.1 mmol scale in 0.5 mL of anhydrous DMF. CuI (99.999%) and CsF (99.9%) were used in all reactions. [b] Calibrated GC yields using 2-nitrobiphenyl as a standard. [c] Number in parentheses is the isolated yield from a 1.0 mmol scale reaction. Less than 3% homocoupling products were observed. ~30% unreacted starting materials was observed based on GC.

After establishing the optimal conditions (Table 1), we examined the substrate scope of the new cross-coupling protocol. The current conditions allow the reactions to proceed for aryl−aryl, aryl−heteroaryl, and heteroaryl−heteroaryl couplings in good to excellent product yields (Tables 2, 3). The reactions conducted in the presence of the ligand **PN-1** consistently provided good yields of products for the couplings of aryltriethoxysilanes with aryl iodides (Table 2). The use of **PN-1** increased the yields of the aryl−aryl coupling products by 20−54% relative to that of the reactions conducted without the ligand (entries 3, 6, 15). Similarly, a variety of functional groups were tolerated on the aryl rings of both the aryltriethoxysilanes and the aryl iodides. Reactions proceed well with electron-deficient and -rich aryl rings on both coupling partners. Halogen, exemplified using chloride, is also tolerated on both the aryltriethoxysilanes and the aryl iodides (entries 8−10).

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(8) For the existence of similar organocopper species in the presence of organosilicon reagents, see: (a) Miki, Y.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2012**, *15*, 172. (b) Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 949. (c) Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *J. Org. Chem.* **2002**, *67*, 8450. (d) Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *Org. Lett.* **2001**, *3*, 3811. (e) Tomita, D.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 4138. (f) Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 6536. (g) Lam, P. Y. S.; Deudon, S.; Averill, K. M.; Li, R. H.; He, M. Y.; DeShong, P.; Clark, C. G. *J. Am. Chem. Soc.* **2000**, *122*, 7600. (h) Lin, B.; Liu, M.; Ye, Z.; Ding, J.; Wu, H.; Cheng, J. *Org. Biomol. Chem.* **2009**, *7*, 869.

(9) For effects of Cu-salts on reactions involving organosilicon reagents, see: (a) Denmark, S. E.; Baird, J. D. *Org. Lett.* **2004**, *6*, 3649. (b) Hanamoto, T.; Kobayashi, T.; Kondo, M. *Synlett* **2001**, *2001*, 0281. (c) Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952. (d) Nakao, Y.; Takeda, M.; Matsumoto, T.; Hiyama, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 4447.

(10) Ito, H.; Sensui, H.; Arimoto, K.; Miura, K.; Hosomi, A. *Chem. Lett.* **1997**, *26*, 639.

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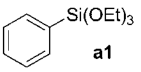
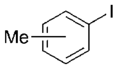
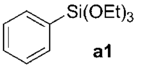
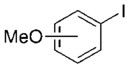
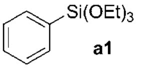
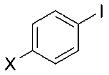
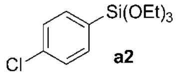
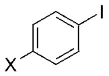
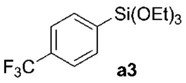
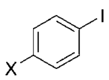
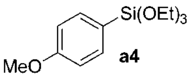
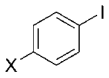
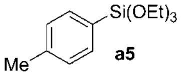
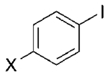
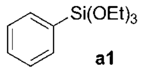
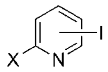
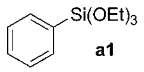
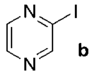
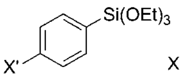
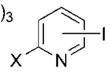
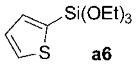
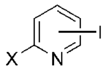
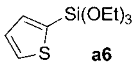
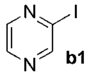
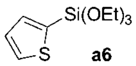
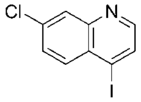
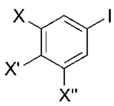
(12) Lemmen, T. H.; Goeden, G. V.; Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3680.

Table 2. Coupling of Aryltriethoxysilanes with Aryl Iodides in the Presence of **PN-1**[a]

entry	Ar−Si(OEt)$_3$	Ar−I	Ar−Ar	yield (%)[b]
1	 **a1**	 *o*-Me (**b2**)	**c3**	64
2		*m*-Me (**b3**)	**c4**	58
3		*p*-Me (**b1**)	**c1**	55 (40)
4	 **a1**	 *o*-OMe (**b4**)	**c5**	40
5		*m*-OMe (**b5**)	**c6**	41
6		*p*-OMe (**b6**)	**c7**	47 (33)
7	 **a1**	 X = CF$_3$ (**b7**)	**c8**	59
8		X = Cl (**b8**)	**c9**	48
9	 **a2**	 X = H (**b9**)	**c9**	69
10		X = Me (**b1**)	**c10**	74
11	 **a3**	 X = H (**b9**)	**c8**	64
12		X = Me (**b1**)	**c11**	40
13		X = OMe (**b6**)	**c12**	40
14	 **a4**	 X = H (**b9**)	**c7**	49
15		X = CF$_3$ (**b7**)	**c12**	51 (24)
16		X = F (**b10**)	**c13**	46
17	 **a5**	 X = H (**b9**)	**c1**	40
18		X = CF$_3$ (**b7**)	**c11**	44

[a] Reactions were run under the standard conditions from Table 1, entry 1 in 1.0 mmol scale for 24 h. [b] Isolated yields. Numbers in parentheses represent isolated yields in the absence of **PN-1**.

Table 3. Coupling of Aryl- and Heteroaryltriethoxysilanes with Aryl and Heteroaryl Iodides in the Absence of **PN-1**[a]

entry	Ar−Si(OEt)$_3$	Ar−I	Ar−Ar	yield (%)[b]
1	 **a1**	 X = H, *o*-I (**b11**)	**c14**	64
2		X = H, *m*-I (**b12**)	**c15**	42
3		X = H, *p*-I (**b13**)	**c16**	48 (41)
4		X = Cl, 4-I (**b14**)	**c17**	61 (40)
5	 **a1**	 **b15**	**c18**	53
6	 X' = OMe (**a4**); X' = Me (**a5**) X' = CF$_3$ (**a3**); X' = Cl (**a2**)	 **a4**; X = H, *o*-I (**b11**)	**c19**	59
7		**a5**; X = Cl, 4-I (**b14**)	**c20**	70 (58)
8		**a5**; X = H, *o*-I (**b11**)	**c21**	58 (50)
9		**a5**; X = H, *p*-I (**b13**)	**c22**	40
10		**a3**; X = Cl, 4-I (**b14**)	**c23**	53
11		**a2**; X = Cl, 4-I (**b14**)	**c24**	87
12	 **a6**	 X = H, *o*-I (**b11**)	**c25**	66
13		X = H, *m*-I (**b12**)	**c26**	53
14		X = H, *p*-I (**b13**)	**c27**	56
15		X = Cl, 4-I (**b14**)	**c28**	73
16	 **a6**	 **b15**	**c29**	74
17	 **a6**	 **b16**	**c30**	82
18	**a6**	 X = X'' = H, X' = CF$_3$ (**b7**)	**c31**	94
19		X = X'' = H, X' = NO$_2$ (**b17**)	**c32**	72
20		X' = H, X = X'' = CF$_3$ (**b18**)	**c33**	73
21		X' = H, X = X'' = F (**b19**)	**c34**	73
22		X = X' = H, X'' = Br (**b20**)	**c35**	77

[a] Reactions were run with the conditions from Table 1, entry 3 in 1.0 mmol scale for 12 h in the absence of **PN-1**. <3% homocoupling products observed in most cases. [b] Isolated yields. Numbers in parentheses represent isolated yields in the presence of **PN-1**.

Surprisingly, **PN-1** showed a detrimental effect on aryl−heteroaryl and hetereoaryl−heteroaryl couplings and decreased the product yields by 14−34% relative to that of the reactions performed without **PN-1** (Table 3, entries 3, 4, 7, 8). We believe that the pyridine rings of the heteroaryl iodides, which act as secondary ligands in excess, bind to CuI already ligated to the bidentate ligand **PN-1**, effectively slowing down the approach of the C−I bond of heteroaryl iodides to the Cu-catalyst for activation. The omission of **PN-1** from the reaction system, however, creates vacant sites on CuI which are only occupied by the monodentate pyridine rings in a readily reversible process. Therefore, the reactions for aryl−heteroaryl and heteroaryl−heteroaryl couplings were conducted without **PN-1**. Aryl-heteroaryl couplings tolerate a variety of functional groups and proceed well with electron-deficient and -rich aryl rings on both coupling partners. Coupling of 2-thienylsilane **a6** with electron-deficient aryl and heteroaryl iodides provided products in good to excellent yields (entries 12−22). Both aryl−heteroaryl and heteroaryl−heteroaryl couplings tolerate halides such as chloride and bromide either on both coupling partners or on the aryl iodides.

Based on our preliminary mechanistic studies and previous reports, we have proposed a catalytic cycle (Scheme 1) for the present Cu^I-catalyzed Hiyama coupling.[13] Under ligand-free conditions, iodide from the solvated CuI (**e1**, LL = solv) is displaced in the initial step by the fluoride anion from CsF to generate a solvated CuF species (**e2**, LL = solv), which then undergoes transmetalation with ArSi(OEt)$_3$ to generate a solvated monomeric [CuAr] intermediate (**e3**, LL = solv).[6a] However, a mechanistic scenario reminiscent of the Pd-catalyzed Hiyama coupling, where the ligated CuI directly undergoes transmetalation with the fluoride-activated ArSi(OEt)$_3$, also cannot be ruled out at this moment.[2] In either scenario, once the solvated monomeric [CuAr] species **e3** is generated it is expected to react with aryl halides[14] to form a cross-coupled product (Table 4, entry 1). However, when the [CuPh] complex[15] was reacted with *p*-iodotoluene under our reaction conditions, a predominant amount of the homocoupling product **d1** and only traces of the cross-coupled product **c1** were formed (entry 2). Surprisingly, when CsF was added to the reaction, a higher yield of the cross-coupled product **c1** was formed (entry 3). It is known that the isolated arylcopper species remain as aggregates, typically as tetramers, rather than as monomers.[16] Therefore, we presumed that such aggregates could possibly be unreactive toward aryl halides and that CsF disaggregates the arylcopper species, possibly by

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(13) For X-ray structure of [(**PN-1**)CuI]$_2$, see: Wesemann, L. K.; Fritz-Robert, K.; Mayer, H. A.; Wernitz, S.; Yersin, H.; Leitl, M. *PCT Int. Appl.* (2013), WO 2013014066 A1 20130131.

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Table 4. Reactions of Independently Synthesized [CuPh] Complex with *p*-Iodotoluene[a]

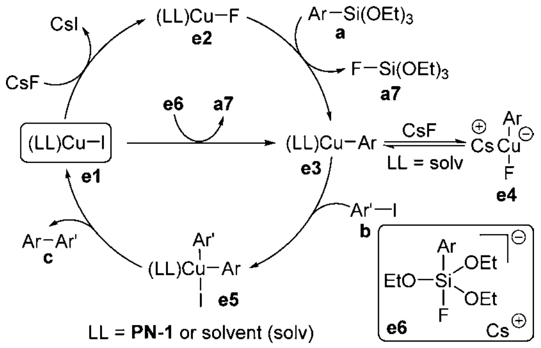
entry	additive	yield (%) (**c1**/**d1**)[b]
1	ref 14[c]	36/36[d]
2	none	3/40
3	CsF (0.15 mmol)	44/14
4	**PN-1** (0.05 mmol)	43/6

[a] Reactions were run with [CuPh] (0.05 mmol) and *p*-iodotoluene (0.10 mmol) in 0.5 mL of DMF. [b] Calibrated GC yields. Less than 3% of 4,4′-bitolyl was also formed. [c] 4-Iodoanisole was used instead of **b1** in pyridine as a solvent at 50 °C for 47 h. [d] Yields of 4-methoxybiphenyl and **d1**. 10% 4,4′-dimethoxybiphenyl was also reported.

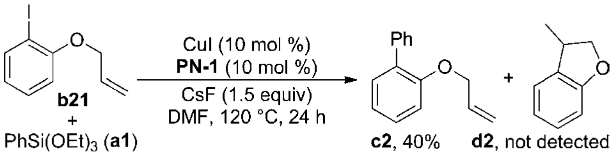
forming a monomeric cuprate complex **e4** as a resting-state species.[17] The complex **e4** could slowly equilibrate to the reactive monomeric species **e3** (LL = solv) during reaction (Scheme 1).[18] Since the reaction conducted without a ligand generates only trace amounts of homocoupling products, we believe that the reaction proceeds via a monomeric, solvated [CuAr] species **e3** and that CsF plays a second role, in addition to facilitating transmetalation, as a stabilizer for (solv)Cu(Ar) should this species begin to aggregate during reaction.[19]

In addition, [CuPh] affords a significant amount of the cross-coupled product **c1** in the presence of **PN-1** (Table 4, entry 4), suggesting that the binding of the ligand also facilitates disaggregation of polymeric [CuPh][20] and converts it to a ligated, reactive species (Scheme 1, **e3**, LL = **PN-1**).[21] A brief study of the reaction of $PhSi(OEt)_3$ with the radical probe **b21** showed that only the cross-coupled product **c2** was formed (Scheme 2).[5g,21a] The cyclized product **d2**, as expected to arise from a corresponding aryl radical, was not detected when the reaction mixture was analyzed by GC,[22] indicating that the reaction does not involve aryl radical intermediates.

Scheme 1. Proposed Catalytic Cycle



Scheme 2. Test for an Aryl Radical Intermediate



In summary, we have developed the first Cu^I-catalyzed Hiyama coupling of aryl- and heteroaryltriethoxysilanes with aryl and heteroaryl iodides, which provides the best product yields in the presence or absence of ligands for aryl–aryl, aryl–heteroaryl, and heteroaryl–heteroaryl couplings, respectively. The reaction tolerates a variety of functional groups on both coupling partners. We have also conducted preliminary mechanistic studies with a radical probe and an independently synthesized [CuPh] complex and proposed a catalytic cycle. During our studies, we unraveled a second role for CsF as a stabilizer of [CuAr] intermediates in the absence of ligands in addition to its typical role as a fluoride source to facilitate transmetalation of the organosilicon reagents with CuI.

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Supporting Information Available. Experimental procedures, characterization data, and the NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) For structures of analogous, diarylcuprates with lithium as a countercation, see: (a) Lorenzen, N. P.; Weiss, E. *Angew. Chem., Int. Ed.* **1990**, *29*, 300. (b) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337. (c) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668.

(18) Similar lithium diarylcuprates react with aryl iodides only in the presence of O_2. See: Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871.

(19) As suggested by a reviewer, we followed the ^{19}F NMR signal of CsF in DMF in the presence of [CuPh] at room temperature. A sharp singlet of CsF at δ −148.0 ppm shifted upfield to δ −222.0 ppm as a broad singlet, but the identity of the new species could not be determined unambiguously (see Supporting Information for details).

(20) For examples of ligated [CuAr] complexes, see: (a) Leoni, P.; Pesquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240. (b) Do, H. O.; Khan, R. M. K.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 15185. (c) Doshi, A.; Sundararaman, A.; Venkatasubbaiah, K.; Zakharov, L. N.; Rheingold, A. L.; Myahkostupov, M.; Piotrowiak, P.; Jäkle, F. *Organometallics* **2011**, *31*, 1546.

(21) For similar mechanistic scenarios proposed for CuI-catalyzed C-X couplings, see: (a) Tye, J. W.; Weng, Z.; Johns, A. M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 9971. (b) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4120. (c) Giri, R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 15860.

(22) The *o*-allyloxyphenyl radical generated from the radical probe **b21** is known to cyclize in DMSO at 23 °C to give the cyclized product **d2** with a k_{obs} of $9.6 \times 10^9\ s^{-1}$. See: Annunziata, A.; Galli, C.; Marinelli, M.; Pau, T. *Eur. J. Org. Chem.* **2001**, 1323.